IMPACT PROPERTIES OF COATED ENGINEERING PLASTICS
IMPACT PROPERTIES OF COATED ENGINEERING PLASTICS

PROEFSCHRIFT

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Abstract  

Samenvatting  

Dankwoord  

Curriculum Vitae
List of Acronyms and Abbreviations

a = crack length
\dot{a} = crack speed
A = area
B = width of sample
B_0 = smallest width of SCAT sample
B_{\text{block}_0} = width of central block of DCAT sample
B_{\text{block},0} = smallest width of central block of SCAT sample
C = compliance
C_p = specific heat capacity
d_{\text{clamp}} = displacement of grip
E = elastic modulus (Young's modulus)
E' = storage modulus
E'' = loss modulus
E_{\text{coat}} = elastic modulus of coating
E_{\text{sub}} = elastic modulus of substrate
f = correction term in compliance function for DCAT
F = force
F_c = force at which debonding starts
F_p = force at stable crack propagation
G_c, G_{c,\text{adh}} = critical energy release rate for coating delamination
G_p = energy release rate for stable crack propagation
h = thickness of coating
h_c = critical coating thickness
H = thickness of sample
H_{\text{block}} = thickness of central block of DCAT sample
H_V = Vickers Hardness
I = moment of inertia
k = shape factor of SCAT sample
K = a constant
K_I = stress intensity factor for tensile loading
K_{la} = crack arrest toughness
K_{lc} = fracture toughness
K_{ld} = dynamic fracture toughness
L = free length of sample
L_0 = initial free length of sample
L_{\text{block}} = length of central block of DCAT sample
L_{\text{clamp}} = distance between the clamps
L_{\text{span}} = support length
m = Weibull-modulus
P = cumulative failure probability
P_{\text{deb}} = likelihood for coating delamination
P_{\text{cat}} = likelihood for catastrophic crack growth
q, q' = ductility parameter
T = temperature


\( T_{\text{min}} \) = lowest temperature at which crack arrest can occur
\( T_{\text{DB}} \) = ductile-to-brittle transition temperature
\( T_{g} \) = glass transition temperature
\( T_{m} \) = melting temperature
\( T_{\beta} \) = secondary transition temperature
\( u \) = deflection
\( U_{\text{elast}} \) = elastic energy
\( U_{\text{ext}} \) = applied external energy
\( U_{\text{plast}} \) = plastic energy
\( U_{\text{rec.elast}} \) = recoverable elastic energy
\( U_{\text{res}} \) = stored elastic energy due to residual stress
\( U_{\text{total}} \) = total applied energy (area under force/deflection curve)
\( V^{*} \) = activation volume for yielding
\( V_{0} \) = initial volume of sample
\( W \) = thickness or width of sample
\( Y \) = constant depending on geometry
\( Z \) = rate constant in Eyring equation

\( \Delta H \) = activation energy for yielding
\( \Delta H_{\text{DB}} \) = activation energy for the ductile-to-brittle transition
\( \varepsilon \) = strain
\( \dot{\varepsilon} \) = strain rate
\( \varepsilon_{f,c} \) = tensile fracture strain of the coating
\( \varepsilon_{\text{res}} \) = biaxial residual strain
\( \varepsilon_{y} \) = yield strain
\( \nu \) = Poisson ratio
\( \nu_{e} \) = entanglement density
\( \rho \) = specific density
\( \sigma \) = stress
\( \sigma_{0} \) = Weibull characteristic fracture stress
\( \sigma_{b} \) = brittle fracture stress
\( \sigma_{\text{crit}} \) = strength of prenotched sample
\( \sigma_{f} \) = fracture stress
\( \sigma_{\text{res}} \) = biaxial residual stress
\( \sigma_{s,fc} \) = stress in substrate at the moment of coating fracture
\( \sigma_{y} \) = yield stress
ABS = blend of acrylonitrile, butadiene and styrene
EPDM = elastomeric terpolymer from ethylene, propylene and dicyclopentadiene
EVA = poly(ethylene-co-vinyl acetate)
HMDI = isocyanurate trimer of hexamethylene diisocyanate
HV = adhesion promoter
IM = impact modifier
IM PA66/PPE = rubber-toughened polyamide-66/poly(phenylene ether) blend
IM PA6 = rubber-toughened polyamide-6
IM PBT/PC = rubber-toughened poly(butylene terephthalate)/polycarbonate blend
iPA = isopropyl alcohol
MF PA6 = mineral-filled polyamide-6
PA6 = polyamide-6
PA66 = polyamide-66
PC = polycarbonate
PBMA = poly(n-butyl methacrylate)
PEMA = poly(ethyl methacrylate)
PIBM = poly(isobutyl methacrylate)
PMMA = poly(methyl methacrylate)
PP = poly(propylene)
PPE = poly(phenylene ether)
PS = poly(styrene)
PSUL = polysulfone
PVC = poly(vinyl chloride)
PVF₂ = poly(vinylidene fluoride)
PUR = polyurethane
PUR-A = polyurethane coating based on polyacrylic resin
PUR-SSxx = PUR coating based on xx% polyacrylic and (100-xx)% polyester resin
RA = release agent
SAN = thermoplastic copolymer from styrene and acrylonitrile
TPE = thermoplastic elastomer
UF PA6 = unfilled polyamide-6

DCAT = double cantilever adhesion test
LEFM = linear elastic fracture mechanics
TTT = tear transition temperature
SCAT = single cantilever adhesion test
GENERAL INTRODUCTION

1.1 SURFACE EMBRITTLEMENT OF COATED PLASTICS

Over the past decades the use of engineering plastics in structural applications has increased substantially. This trend is also recognizable in the automotive industry. The total amount of plastics used in the automotive industries of Japan, Europe and North America was about 4500 million kg in 1993 [1]. On the average about 9% of the total weight of a car consisted of plastics for interior and exterior automotive applications in 1993, and this percentage is expected to grow further to about 12% in the year 2000 [2]. The growth of the amount of plastic materials used in cars is caused by the general trend to diminish the weight of the car resulting in reduced fuel consumption and exhaust gas emission. Furthermore, the impact resistance of most engineering plastics is high; during collision plastic parts can absorb a large amount of energy. Upon minor impacts plastics have the ability to deform and recover. Other advantages of plastics include ease of manufacturing complex integrated parts, high corrosion resistance and flexibility of styling at low costs [3].

About 35% of the plastics applied in cars is used for exterior body parts, e.g., bumpers, spoilers, fenders, mirror housings and door panels. Exterior plastic body parts are often provided with a coating. This is done for decorative reasons, i.e., to match colour and appearance with that of the rest of the painted car body and to hide surface irregularities, to improve the scratch and chemical resistance of the plastic, and to protect the plastic against degradation due to UV-radiation [4]. Painting of plastics also has an important drawback: it is often observed that application of a coating on a ductile plastic results in brittle fracture of the coated component upon impact loading whereas the uncoated component tested under the same conditions deforms in a ductile manner. This effect is called surface embrittlement. Figure 1.1 shows an example of surface embrittlement of a coated plastic bumper. The coated bumper was subjected to a front impact collision at a speed of 5 km/h at -20°C. Figure 1.1 shows that the coated bumper fractured in a brittle manner. It was found that the uncoated bumper tested under the same conditions deformed in a ductile manner, showing no signs of fracture at all.

The detrimental influence of coatings on the mechanical behaviour of ductile plastics can occur despite the fact that the applied coating is usually very thin compared to the thickness of the plastic. For a typical automotive part, for instance, the coating thickness is less than 2% of that of the substrate. Nevertheless, such a thin coatings can result in a 40-fold reduction of the fracture energy of ductile plastics [5]. Although brittle fracture of structural parts is nearly always undesirable, it is especially unacceptable for coated plastics used for exterior automotive parts as these parts often have to provide protection for the passengers during collisions.

It should be pointed out that the phenomenon of surface embrittlement is not restricted to coated plastics [6-18], but is also observed with degraded polymers [19-24].
It is known that the surface embrittlement effect is related to the low fracture strain of the brittle coating or degraded layer compared to the fracture strain of the uncoated ductile substrate. On loading of the coated substrate the brittle coating fractures first. On reaching the interface between the coating and the substrate, the crack from the coating may propagate through the substrate due to the high stress intensity at the tip of the crack resulting in brittle failure of the coated plastic. However, when the level of adhesion between the coating and the substrate is low, fracture of the coating may result in delamination of the coating from the substrate. It has been postulated that in such a case the surface embrittlement effect will be reduced [3,6,11,17,25]. Furthermore, it is known that in some cases the solvents used in the wet paint can also cause a deterioration of the mechanical properties of the plastic [3,4,12]. In this case the surface embrittlement is not due to the coating as such but to the changed mechanical properties of the surface of the substrate.

From the above it can be concluded that surface embrittlement of coated plastics for a given set of loading conditions and sample geometry will most likely depend on:

- the fracture behaviour of the coating
- the fracture behaviour of the substrate, including the arrest toughness
- the level of adhesion between the coating and the substrate.
1.2 AIM OF THE PRESENT STUDY

Although the phenomenon and principle of the surface embrittlement effect observed with coated ductile plastics are known, the amount of literature providing quantitative data on this subject is limited. Furthermore, quantitative models giving a complete prediction of the mechanical properties of coated plastics as a function of the properties of the coating and the substrate do not exist yet.

In the study presented in this thesis the surface embrittlement effect caused by thin coatings applied on ductile substrates was investigated in detail. The aim of this study was the development of a quantitative model describing the mechanical fracture behaviour of coated plastics on the basis of the (independently-determined) properties of the coating, the substrate and the interface, and of the loading conditions. The advantage of such a model is that it can be very worthwhile for the development of coated plastics showing no or only minor surface embrittlement.

All coatings and plastics used in this study are, or have a potential to be, used as material for exterior automotive parts. Although it is realized that a collision in practice usually results in multi-axial loading of the coated automotive part, in this investigation the coated samples were tested in uniaxial tension. As the reduction of the mechanical properties of ductile plastics due to application of a coating is particularly observed at high rates of deformation, tensile testing of the coated materials was mainly done at a high rate of strain (10^5%min^{-1}). To check the general validity of the model developed also some tests were done at low strain rate.

1.3 OUTLINE OF THIS THESIS

In this study the surface embrittlement of coated plastics was determined at various temperatures and strain rates as a function of the level of adhesion between coating and substrate, the coating thickness and the ductility of the coating. For this reason, coated plastic samples were used for which these parameters were varied systematically. To determine the influence of the level of adhesion and the coating ductility on the mechanical properties of coated plastics, it was found necessary to develop new test methods for the quantitative measurement of these properties. A very ductile, rubber-modified polyamide-66/polyphenylene ether–blend (IM PA66/PPE) was used as a model substrate.

For a description of the surface embrittlement effect it is essential to know the mechanical (fracture) behaviour of the uncoated substrate material as a function of loading conditions, such as the temperature and the rate of strain, in detail. The results of the determination of the mechanical tensile properties of IM PA66/PPE are presented in chapter 2. These tensile properties were determined over a broad range of temperatures at both high and low strain rates (10^5%min^{-1} and 10%min^{-1}, respectively). The temperature (T_{DB}) at which IM PA66/PPE undergoes a transition from brittle fracture to ductile deformation was determined at both
testing speeds. In this thesis the shift in $T_{DB}$ is often used as a measure to describe surface embrittlement.

In *chapter 3* the effect of a 40 μm, well-adhering, brittle coating on the high-speed mechanical tensile behaviour of IM PA66/PPE is described. It was observed that application of this thin coating has a large detrimental effect on the fracture behaviour of the substrate; the $T_{DB}$ of the coated substrate is shifted over approximately 75°C compared to that of the uncoated material. This deterioration of the mechanical properties of the substrate is not caused by solvent-attack. By measuring the fracture behaviour of the coating on the substrate during the high-speed tensile test, it was found that the $T_{DB}$ of the coated substrate was equal to that of the coating and it was shown that, in the critical temperature regime, the fracture behaviour of the coated substrate is determined by the ductility of the coating only.

In *chapter 4* a new test method is presented which can be used to determine the ductility of the coating itself in a quick and simple way. With this test the transition in the crack propagation behaviour of coatings is determined at low tearing speed. The temperature where the crack propagation behaviour of the coating changes from ductile tearing to brittle fracture is called the tear transition temperature TTT. It is postulated that the TTT can be used as a direct measure of the ductility of coatings. In the study described in this chapter the TTT was determined as a function of coating formulation and coating thickness.

A new test for the quantitative determination of the level of adhesion of coatings on plastics is described in *chapter 5*. This test is called the double cantilever adhesion test (DCAT) and yields a value for the critical energy release rate $G_{c,adh}$ at the onset of coating delamination. The DCAT was used a.o. to demonstrate that the method of substrate cleaning may have a large influence on the level of adhesion.

In the study described in *chapter 6* the influence of the level of adhesion and the influence of the coating thickness on the mechanical fracture behaviour of coated plastics was determined experimentally. For this purpose, IM PA66/PPE samples provided with a polyurethane coating were used for which the level of adhesion could be varied over a wide range. In the same chapter a fracture mechanics model is presented which was found to give a good description of the observed influence of coating thickness and level of adhesion on the fracture behaviour of coated plastics.

In *chapter 7* the influence of the ductility of well-adhering coatings on the fracture behaviour of various coated plastics is described. The mechanical properties of these coated plastics were determined at both high and low strain rate. It was found that for both testing speeds the $T_{DB}$ of the coated plastic could be very well predicted from the TTT of the coating. In this study the general validity of the relation between the $T_{DB}$ of the coated substrate and the TTT of the coating for well-adhering coatings was demonstrated. The (theoretical) relationship between the $T_{DB}$ of coated plastics and the TTT of the coating is also presented as a function of the level of adhesion and as a function of the arrest toughness of the substrate. It was shown that the $T_{DB}$ of coated engineering plastics can be predicted from independent measurements on substrate, coating and interface.

Chapter 5 and the Appendix have been published elsewhere [26].
1.4 REFERENCES

[16] Schlesing, W., Osterhold, M.; Kunststoffe, 82(8), 662 (1992)
MECHANICAL BEHAVIOUR OF UNCOATED PLASTICS

2.1 INTRODUCTION

Plastics, i.e., (reinforced) polymers or polymer blends, are often used as structural engineering materials. For this reason, it is important to know and understand the deformation and fracture behaviour of plastics, and the effects of temperature and strain rate there on. Like other materials, plastics can deform in a ductile or in a brittle way. The mode of deformation depends among others on temperature and strain rate as shown schematically in figure 2.1 for a typical engineering plastic. The effects of an increase of the temperature can often be compared with the effects of a decrease of the strain rate.

![Diagram of stress-strain curve](image)

Fig. 2.1 Influence of temperature and strain rate on the stress-strain curve of a typical engineering plastic. 1 = brittle fracture, 2 = onset of ductile failure, 3 = necking and cold-drawing, 4 = homogeneous deformation (quasi-viscous flow). The symbol X denotes the fracture point.

At very low temperatures, or high strain rates, most plastics show brittle behaviour. Under these conditions the material has a high stiffness (modulus) and deforms in an almost linear-elastic way up to the point of fracture. In the case of brittle fracture, the fracture strain is generally only a few percent. Assuming that all bonds between atoms or molecules have to be broken in order to cause fracture in a solid the theoretical fracture stress for most materials is roughly equal to \( E/10 \) [1], where \( E \) is Young's modulus of the material. The measured tensile fracture stress of polymers is found to be much lower than this theoretical value. As recognized by Griffith [2] the reason of this discrepancy is the presence of natural flaws in materials which act as stress-concentrators. Griffith's hypothesis forms the basis of a fracture mechanics theory that is now known as linear-elastic fracture mechanics (LEFM). According to Griffith, and the extension of this theory by Irwin [3], the brittle fracture stress...
$\sigma_b$ of a plastic containing a flaw of size $2a$ is given by:

$$\sigma_b = \frac{K_{lc}}{\sqrt{\pi a}}$$  \[1\]

where $K_{lc}$ is the critical stress-intensity factor for mode I tensile loading. $K_{lc}$ is a measure of the material's resistance to fracture and is sometimes called the fracture toughness.

If the temperature is increased, or the strain rate is decreased, the fracture behaviour of plastics changes from brittle to ductile. In the stress-strain curve ductile deformation is characterized by the occurrence of a yield point (a drop of the stress prior to fracture), see also figure 2.1. The dependence of the yield stress $\sigma_y$ of plastics on temperature $T$ and strain rate $\dot{\varepsilon}$ can often be described by the Eyring equation [5-7]:

$$\sigma_y = \frac{\Delta H}{v^*} + \frac{RT}{v^*} \ln \frac{\dot{\varepsilon}}{Z}$$  \[2\]

where $\Delta H$ is the activation energy, $v^*$ the activation volume, $R$ the gas constant and $Z$ is a rate constant. According to Eyring the deformation of plastics involves the jumps of (parts of) molecules over potential energy barriers with height $\Delta H$. The effect of the application of a stress $\sigma$ is to reduce the height of the energy barrier for a jump in the direction of the applied stress and to increase it for a jump in the opposite direction.

Ductile deformation of plastics can only occur if the mobility of (parts of) the polymer chains is high enough. Therefore, it is usually found at temperatures close to the glass transition temperature $T_g$ or above a secondary transition temperature $T_B$. In case of ductile deformation at moderate temperatures, the strain in the sample is sometimes highly localized (necking).

At temperatures well-above the glass transition polymers can deform by viscous flow. This results in very large fracture strains at low stress levels.

As stated above, plastics can undergo a change from brittle to ductile deformation if the temperature is increased. The temperature at which this transition takes place is called the ductile-to-brittle transition (DB-transition). The DB-transition is an important property for engineering plastics as it is often used as the deciding factor for their practical applicability. Below the DB-transition, where a plastic fractures in a brittle way resulting in a low fracture toughness and low energy absorption in fracture, the usefulness of the plastic will be very limited. In general it is required that the DB-transition of an engineering plastic is lower than the temperature at which it will be used.

It has been found that the DB-transition is strongly affected by both experimental conditions and material variables. This causes an important problem as even small changes in the loading conditions or modifications of the plastic can cause brittle failure of otherwise ductile plastics. In general, brittle failure of plastics is favoured by, a.o.:

- a decrease of the test temperature [8-13]
- an increase of the strain rate [8,11-13]
- the presence of sharp notches [14-17]
an increase of the sample thickness [18,19]
- a decrease of molecular weight [11,14,20,21]
- an increase of the crosslink–density [9]
- annealing [14,20,21]
- a reduction of the amount of plasticizer [9]
- reducing the amount of well–dispersed rubber particles (impact modifier) [8,11,22-25]

Although not complete this list shows the complexity of characterizing the fracture toughness of plastics.

In order to quantify the factors influencing the toughness of plastics in more detail, Vincent [9] proposed a phenomenological description of the DB–transition. Following the classical approach of Orowan [26], Vincent described the DB–transition as being caused by the competition between brittle failure mechanisms, like crazing, and ductile deformation processes, like shear yielding. He assumed that these processes are independent resulting in different temperature and strain rate dependencies of the brittle fracture stress and the yield stress. Vincent further proposed that the yield stress of plastics is much stronger affected by changes in temperature or strain rate than the brittle fracture stress. The deformation of the plastic will be determined by the mechanism that occurs at the lowest stress. As a result the DB–transition is the point where the brittle fracture stress is equal to the yield stress. This is shown schematically in figure 2.2. In the case of a homogeneous stress field, we can use the expressions for \( \sigma_b \) and \( \sigma_y \) given above (equations 1 and 2, respectively) to calculate the DB–transition.

![Graph showing the effect of temperature and strain rate on yield stress and brittle fracture stress](image)

**Fig. 2.2** Effect of temperature and strain rate on yield stress \( \sigma_y \) and brittle fracture stress \( \sigma_b \). At the DB-transition temperature \( T_{DB} \), \( \sigma_y \) is equal to \( \sigma_b \). Redrawn after Ward [4].

The approach of Vincent is a useful way to characterize the toughness of plastics. The influence of changes in test conditions or material variables can easily be analyzed in terms
of the shift of the DB-transition. The shift of the DB-transition, caused by the changes mentioned above, can often be predicted using this approach [9,27].

In this thesis the fracture behaviour of coated plastics is studied. The influence of coatings on the fracture behaviour of plastics will be described in terms of the shift of the DB-transition relative to that of the uncoated plastic. A rubber-toughened polyamide–66/polyphenylene ether-blend (=IM PA66/PPE) is used as the model substrate material in this study. This blend is used for e.g. automotive applications, such as car bumpers, spoilers and other parts of car bodies. It combines high thermal stability with improved low temperature ductility allowing on-line coating of this material. With on-line coating the plastic part is assembled first and subsequently coated along with the entire car body [28].

The IM PA66/PPE-blend with well-dispersed rubber particles has a very high toughness whereas the PA66/PPE-blend without rubber is fairly brittle [29]. As with many other brittle or notch-sensitive, rigid polymers the impact resistance of PA66/PPE can be increased by incorporation of well-dispersed rubber particles [29-31]. Although no full consensus has been reached, it is generally believed that the rubber particles are effective in increasing the toughness by initiating energy absorbing processes at numerous sites in the polymer matrix. In this way, the volume fraction of the material deforming in a ductile way is increased. For rubber-toughened thermoplastics multiple crazing and massive shear yielding are the major energy absorbing mechanisms. A detailed description of the mechanisms of rubber-toughening of polymers is beyond the scope of this thesis and can be found elsewhere [8,22–25].

The fracture behaviour of plastics is a function of both the temperature and the strain rate. A higher strain rate is qualitatively equivalent to a reduction of the temperature. This means that at temperatures close to $T_{DB}$ a transition from ductile to brittle failure can be obtained by increasing the strain rate. The mechanical properties of plastics at relatively low strain rates ($\leq 10\%\text{min}^{-1}$) can easily be determined in uniaxial tensile tests using electromechanical or hydraulic testing equipment. In the case of testing at high strain rates, i.e., impact testing, several different techniques are available. These tests can be divided into three basic categories [32,33]:

- Puncture tests (Falling dart, etc.)
- Impact flexure tests (Charpy, Izod, etc.)
- High-speed tensile tests.

A detailed description of impact testing can be found elsewhere [33,34]. For the impact measurements described in this thesis an instrumented, servo-hydraulic, high-speed tensile tester is used. High-speed tensile testing has the same advantages as standard low speed stress–strain measurements [35-37], that is (a) the tensile test is a relatively simple, uniaxial test resulting in a homogeneous stress state in the sample, (b) the strain rate in a tensile test is constant and (c) with high-speed tensile testing, "true" material properties, like Young's modulus, yield stress, and fracture stress, strain and energy are determined in a direct way. These material properties can be used in fracture mechanics calculations or finite element analysis.
Both puncture and flexure impact testing are multi-axial. In these tests the strain is distributed inhomogeneously over the sample and the strain (rate) experienced by the sample is a complex function of deflection, test speed and geometry.

While the main body of this thesis is devoted to the effects of coating parameters on the shift of the ductile-to-brittle transition, this chapter describes the mechanical properties of the substrate material in more detail to provide a good frame of reference and to introduce some techniques required in this work.

2.2 EXPERIMENTAL

2.2.1 Materials

The rubber-modified polyamide-66/polyphenylene ether–blend (IM PA66/PPE), known commercially as Noryl® GTX 940, was kindly donated by General Electric Plastics. The PA66/PPE ratio of this blend is approximately 50/50. A PA66/PPE copolymer is used as a compatibilizer in order to obtain small droplets of PPE dispersed in the PA66 matrix. The impact modifier is preferentially present in the PPE–phase. Noryl® GTX 940 was obtained as sheet material (170 * 170 * 3 mm³). The sheets were injection moulded using a film gate. Dogbone-shaped tensile specimens, according to DIN 53 455 (specimen number 3), were stamped from these sheets using a cutting tool placed in a hydraulic press. The length-axis of the samples was parallel to the direction of injection moulding. In order to facilitate the cutting process cutting was done at elevated temperature (75°C). All specimens were dried at 110°C under vacuum for 20 hours prior to testing.

To put the behaviour of IM PA66/PPE in perspective the mechanical properties of three other engineering plastics were determined too:

- unfilled polyamide–6 (= UF PA6, Akulon® K222D, DSM Plastics)
- mineral filled polyamide–6 (= MF PA6, PA–6 filled with 30% talc, Akulon® K223–HM6, DSM Plastics)
- polyamide–6 toughened with 25 vol-% impact modifier (= IM PA6, Akulon® K223–HM6, DSM Plastics)

Dogbone-shaped tensile specimens (according to DIN 53 455, specimen number 3) of these materials were made by injection moulding after standard drying procedures. These samples were tested dry as–moulded.

2.2.2 High-speed tensile tester

The high-speed tensile tests were done on a servo–hydraulic material tester (Schenck VHS 25/20). With this machine both tensile and puncture testing can be done at constant test speeds up to 20 m/s. Figure 2.3 gives a schematic diagram of the set-up used for high-speed tensile testing.
During the test the force is measured using a piezo-electric force transducer (20 kN, resolution: 0.01 N, natural frequency ±45 kHz, Kistler type 9061A). The displacement of the piston is measured with a linear variable displacement transducer (LVDT, resolution 0.05 mm and maximum stroke 300 mm). As shown in figure 2.3, a pick-up unit is used to allow the piston to reach the desired test speed before loading the sample. A rubber damping ring is used to reduce vibration between the pick-up unit and the piston. All moving parts (like the pick-up unit and the grips) are made of titanium in order to diminish inertia effects. A transient recorder (ADAM TC 210–4, Maurer) with a maximum sampling frequency of 2 MHz is used for the analog data acquisition of up to four channels. The recorded data are evaluated using a Tandon AT personal computer. For each recorded data point the engineering stress, elongation and energy are calculated. The engineering stress is defined as the measured force divided by initial cross-section of the sample and the energy as the area under the stress-strain curve.

The software program can also be used for digital filtering [38] of the data if harmonic oscillations are present on the recorded data. This noise is sometimes present when tests are done at very high speed. It is due to oscillation of the components attached to the force transducer at their natural frequency ("ringing").

2.2.3 Modifications used for high-speed tensile testing

During high-speed tensile testing the displacement of the piston is measured using a LVDT. Due to the loose contact between piston and lower clamp the sample starts to oscillate at the onset of the actual loading, see above. These dynamic effects make measuremet of the true displacement of the lower clamp necessary, especially in the initial stage of the impact test [39,40]. In order to solve this problem we designed and constructed a non-contacting optical displacement recording system which determines the displacement of the lower clamp very
accurately, see also figure 2.3. For this purpose, a laser beam is guided through a flexible optical cable attached to the lower clamp. The laser beam is focused on a linear optical detector (resolution 20 μm, maximum stroke 20 mm). The displacement of the lower clamp is determined from the position of the laser spot on this detector.

The high-rate impact tests described in this chapter were done at temperatures ranging from -80°C to +60°C. As no suitable temperature chamber was commercially available for this tester, a small temperature chamber was designed to allow high-speed tensile testing at both low and high temperatures, see figure 2.4. The dimensions of the chamber are chosen in such a way that the lower clamp almost seals the chamber at the bottom side. In this way the optical displacement recording system can also be used for tests at temperatures other than room temperature. During a test the lower clamp is pulled out of the chamber.

![Diagram](image)

Fig. 2.4 Experimental set-up used for high-speed tensile testing at temperatures other than room temperature.

A nitrogen flow is used to control the temperature in the oven. For this purpose, the nitrogen is first cooled by passing it through a heat exchanger plunged in liquid nitrogen. Before entering the temperature chamber the nitrogen flow passes a heating element. The temperature in the chamber is measured with a thermo-couple. A temperature controller (Eurotherm, type 822) is used to adjust the output of the power supply (SM 6020, Delta Elektronika) to the heating element. Temperature control is within 1°C of the set value. The piezo-electric force transducer and the pick-up unit are kept at room temperature with a separate flow of pressurized air (not shown in figure 2.4).

2.2.4 High-speed tensile testing procedure

During the high-speed tensile test the displacement of the lower grip $d_{clamp}$ is measured.
These displacement values can be converted into the effective engineering strain (defined as the increase of sample gauge length divided by the initial gauge length) experienced by the parallel section of the sample. For this calculation the values for the distance between the clamps \( L_{\text{clamp}} \), the shape of the sample and the yield strain \( \varepsilon_y \) of the material are also used. Using simple finite element calculations we have determined the following relations for the engineering strain of tensile samples according to DIN 53 455 (specimen number 3, gauge length is 60 mm) and a \( L_{\text{clamp}} \)-value of 120 mm as used in this study. It can be well-described by:

\[
\text{Below the yield point: } \text{strain} (%) = \frac{d_{\text{clamp}}(\text{mm})}{1.04} \quad [3a]
\]

\[
\text{Above the yield point: } \text{strain} (%) = \frac{d_{\text{clamp}}(\text{mm})}{0.6} - 0.73 * \varepsilon_y(\%) \quad [3b]
\]

The validity of the equations given above was confirmed in a separate study using an electro-optical non-contacting extensometer (Zimmer camera, type 200X-20). This extensometer determines the strain of the sample by measuring the relative displacement of two targets on the sample. As this type of extensometer cannot be used in combination with our temperature chamber, the optical displacement recording system described above was used to determine the displacement of the lower clamp.

In this thesis we will preferentially use elongation instead of engineering strain. If needed engineering strain values can be calculated using the equations given above.

Due to their low thermal conductivity, it takes a long time for a polymer sample to uniformly obtain the temperature of its surroundings. For this reason, we have used a separate temperature chamber (temperature range: \(-70^\circ\text{C}/+180^\circ\text{C}\), Grasso, type GTTS 27.70) to precondition the samples if tests were done at temperatures other than room temperature. Before testing all samples were stored at the test temperature in this temperature chamber for a minimum period of one hour. The samples are then placed in the temperature chamber of the tensile tester for at least 10 minutes before testing. This period is sufficient for the samples to attain the test temperature [8].

All high-speed tensile tests described in this chapter are done at a test speed of 1 m/s resulting in a (final) strain rate of approximately \(10^2\%\text{min}^{-1} (= 17 \text{ s}^{-1})\). A minimum of six samples was tested at each temperature. The results of samples where fracture undoubtedly initiated at a black pit, i.e., an impurity or degradation product, were ignored (see discussion below).

### 2.2.5 Tensile testing at low test speeds.

Low-rate tensile testing was done on a Zwick 1474 tensile testing machine at a test speed of 6 mm/min (\(= 10\%\text{min}^{-1} = 0.0017 \text{ s}^{-1}\)). The displacement of the cross-head was measured using an incremental extensometer (Heidenhain MT101K, resolution: 0.5 \( \mu \text{m} \)). A
temperature chamber (Brabender type TEE52) was used for testing at low temperatures. The actual temperature was measured using a Cr–Al thermo–couple (Comark type 6110) positioned close to the mounted sample.

### 2.2.6 Dynamic Mechanical Thermal Analysis (DMTA)

Dynamic mechanical thermal analysis can be used to determine the change of modulus (stiffness) of materials as a function of temperature and loading rate (frequency). DMTA is very useful for determining transitions in materials, like $T_g$ and $T_m$. The reader is referred to the literature for more details on this subject, see for instance [41,42].

Dynamic mechanical measurements were carried out using a Rheometrics RDA700 mechanical spectrometer. Torsional moduli were measured on rectangular sample bars ($3 \times 10 \times 60 \text{ mm}^3$) at a frequency of 1 Hz and a heating rate of 3°C/min.

### 2.3 RESULTS AND DISCUSSION

The main objective of this chapter is to report the results of a study of the effects of temperature and strain rate on the mechanical behaviour of IM PA66/PPE. As described in the introduction this material combines high stiffness and high toughness with a high thermal stability. The high thermal stability of IM PA66/PPE, compared to IM PA66, is due to the high glass transition temperature $T_g$ of PPE. Figure 2.5 shows the torsional (storage) modulus and $\tan\delta$ of IM PA66/PPE as a function of temperature.

![Fig. 2.5 Torsional modulus and tan\(\delta\) of IM PA66/PPE (dried under vacuum at 110°C) as a function of temperature, measured at a frequency of 1 Hz and a heating rate of 3°C/min.](image)

The $T_g$ of the PPE phase is found at 215°C and the $T_g$ of the PA66 phase at 77°C. The $T_g$ is defined as the temperature where the $\tan\delta$ curve reaches a maximum. These values compare well with the values reported in the literature of 70°C for PA66 [43] and 209°C for PPE [44].
The $T_g$ of the impact modifier is determined at $-58^\circ$C. At a temperature of about $250^\circ$C the PA66–phase starts to melt.

The mechanical properties of IM PA66/PPE were determined using tensile testing at both low (10% min$^{-1}$) and high (10$^5$% min$^{-1}$) strain rates. Typical temperature- and strain rate dependencies of the stress–elongation behaviour of IM PA66/PPE are shown in figure 2.6.

![Stress–elongation–curves of IM PA66/PPE measured at a strain rate of 10$^5$% min$^{-1}$ at $-60^\circ$C (curve 1), $-40^\circ$C (curve 2), $-20^\circ$C (curve 3) and $20^\circ$C (curve 4). Curve 5 is measured at a strain rate of 10% min$^{-1}$ at 20$^\circ$C.](image)

At a strain rate of 10$^5$% min$^{-1}$, IM PA66/PPE fractures in a brittle way at $-60^\circ$C. At a temperature of $-40^\circ$C or higher the deformation behaviour of this material is ductile at this strain rate. Under these conditions the stress–elongation curves exhibit a yield point (a maximum in the stress–elongation curve before the fracture point). Above the yield point the material deforms by cold–drawing before it finally fractures. Comparison of curves 4 and 5 of figure 2.6 shows that the yield stress of IM PA66/PPE does indeed decrease on lowering of the strain rate.

The results of more extensive tensile tests carried out at both high and low strain rates are presented in figure 2.7 where the measured yield stress (defined as the maximum engineering stress in the stress–elongation curve) is given for a wide range of temperatures. At temperatures just below the $T_g$ of PA66 the yield stress of IM PA66/PPE increases almost linearly with decreasing temperature. At temperatures below $-50^\circ$C (10% min$^{-1}$) or $-30^\circ$C (10$^5$% min$^{-1}$) the yield stress increases more rapidly with decreasing temperature. This change in slope of the yield stress as a function of temperature was also reported by others [6,13]. It is most probably caused by an increased stiffness of IM PA66/PPE as the temperature approaches the $T_g$ of the impact modifier. On lowering the loading rate the $T_g$ of polymers decreases. This explains the observed effect of the strain rate on the temperature at which the change in the slope of yield stress occurs.
A linear increase of the yield stress with decreasing temperature is frequently observed for plastics. Equation 2 was used to fit the yield stress data for temperatures just below the $T_g$ of PA66. In figure 2.7 the yield stress calculated using the Eyring equation is represented by the lines. For this calculation we have assumed $\Delta H$, $v^*$ and $Z$ to be independent of temperature and strain rate. From the data in figure 2.7 the following values were determined: $\Delta H = 235$ kJ/mol, $v^* = 2.65$ nm$^3$, $Z = 5.3 \times 10^{23}$ s$^{-1}$. The calculated value of $\Delta H$ compares well with the value reported for PA6 (240 kJ/mol, [45]). From this figure it is clear that the Eyring equation can describe the dependence of the yield stress on temperature and strain rate fairly well.

The fracture energy and the elongation at break of IM PA66/PPE as a function of the temperature are plotted in figure 2.8 and figure 2.9, respectively. The values of the fracture energy and the elongation at break were determined at two different rates of strain. At a strain rate of 10% min$^{-1}$ the fracture energy decreases slightly with decreasing temperature, but even at very low temperatures (−80°C) the fracture energy of IM PA66/PPE is at a high level. If the temperature is decreased below −80°C the fracture energy decreases very rapidly. At −100°C the IM PA66/PPE samples fractures before the yield point is reached. At this temperature the fracture behaviour of IM PA66/PPE is fully brittle. The sharp decrease in the fracture energy is caused by the transition from ductile deformation to brittle fracture. At a strain rate of 10$^5$% min$^{-1}$ the fracture energy of IM PA66/PPE is practically constant over a very broad range of temperatures. For this very high strain rate the fracture energy remains at a high level until a temperature of −40°C. A sharp decrease of the fracture energy is observed if the temperature is decreased below −40°C at this strain rate. It is attended by an abrupt decrease of the elongation at break. At −60°C the mechanical behaviour of IM PA66/PPE is completely brittle. These results confirm the high impact resistance of IM PA66/PPE.
Fig. 2.8 Fracture energy of IM PA66/PPE as a function of temperature measured at a strain rate of 10% min⁻¹ (○) and 10⁵% min⁻¹ (□).

Fig. 2.9 Elongation at break of IM PA66/PPE as a function of temperature measured at a strain rate of 10% min⁻¹ (○) and 10⁵% min⁻¹ (□).

As observed by visual inspection samples tested in the fully ductile regime show extended stress-whitening over the complete gauge length of the sample. In the fully brittle regime the samples hardly show any stress-whitening. Samples tested at temperatures close to the transition temperature only show stress-whitening close to the fracture surface.

If the ductile-to brittle transition temperature $T_{DB}$ is defined as the highest temperature where all samples fail in a brittle way, it is clear from figure 2.8 that $T_{DB}$ is approximately -100°C for IM PA66/PPE tested at a strain rate of 10% min⁻¹. In table 2.1 this $T_{DB}$-value of IM PA66/PPE is compared with the $T_{DB}$-values of various other polymers determined at similar strain rates.
Table 2.1  Ductile-to-brittle transition temperatures $T_{DB}$ of various polymers determined at low strain rate (in the order of $10^\text{0.01}$ min$^{-1}$).

<table>
<thead>
<tr>
<th>Polymer</th>
<th>$T_{DB}$ (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>IM PA66/PPE</td>
<td>-100</td>
</tr>
<tr>
<td>PS</td>
<td>90 [46]</td>
</tr>
<tr>
<td>PMMA</td>
<td>45 [46]</td>
</tr>
<tr>
<td>SAN</td>
<td>45 [47]</td>
</tr>
<tr>
<td>PEMA</td>
<td>23 [46]</td>
</tr>
<tr>
<td>PVC</td>
<td>10 [46]</td>
</tr>
<tr>
<td>PBMA</td>
<td>-25 [46]</td>
</tr>
<tr>
<td>PSUL</td>
<td>-100 [47]</td>
</tr>
<tr>
<td>PC</td>
<td>-200 [48]</td>
</tr>
</tbody>
</table>

If the strain rate is increased to $10^\text{5.01}$ min$^{-1}$, the $T_{DB}$ of IM PA66/PPE increases to approximately $-60$°C. Although the number of data is very limited we can use an Arrhenius-equation to obtain the apparent activation energy $\Delta H^{DB}$ for the ductile-to-brittle transition:

$$\dot{\varepsilon} = K \exp \left[ \frac{-\Delta H^{DB}}{RT} \right]$$  \[4\]

where $\dot{\varepsilon}$ is strain rate, $K$ is a constant, $R$ is the gas constant and $T$ is the absolute temperature. The $\Delta H^{DB}$-value calculated for IM PA66/PPE is 70 kJ/mol. Gaggar [11] has reported a $\Delta H^{DB}$-value of 60 kJ/mol for impact-modified PVC independent of the amount of impact modifier used.

Comparison of the fracture data at $10^\text{0.01}$ min$^{-1}$ and $10^\text{5.01}$ min$^{-1}$ indicate that an increase of strain rate is not fully equivalent to a decrease of the temperature. If, for instance, the curve of the fracture energy against temperature, measured at $10^\text{0.01}$ min$^{-1}$, is shifted over 40°C (being the difference in $T_{DB}$) to higher temperatures a different curve compared to the curve measured at $10^\text{5.01}$ min$^{-1}$ is obtained. At temperatures close to $T_{DB}$ comparable values of the fracture energy are determined for the two strain rates used. At higher temperatures the fracture energy measured at low strain rate is found to increase, whereas it is almost constant at high strain rate. This difference can be explained by the change from isothermal to adiabatic testing conditions caused by the increased test speed. During plastic deformation of ductile plastics a large fraction of the energy taken up by the specimen is converted into heat. At low strain rates this heat will be conducted away to the surroundings. At high strain rates the heat generated during plastic deformation cannot be conducted away rapidly enough, causing a local temperature rise in the sample. This increase in local temperature can cause strain-softening and may lead to a significant reduction in the fracture energy.
This is called the isothermal–adiabatic transition. Due to the low thermal conductivity of plastics this transition is found at relatively low strain rates. As the generated heat is due to plastic deformation of the sample, no increase of temperature occurs below the yield point\(^1\). For this reason, the isothermal–adiabatic transition does not influence the yield stress and consequently does not change the ductile-to-brittle transition.

According to the calculations of Bin Ahmad [49] we can assume that at a strain rate of 10\(^\%\)\(\min^{-1}\) the deformation of IM PA66/PPE is isothermal, while at a strain rate of 10\(^5\)\(\%\)\(\min^{-1}\) it will be almost fully adiabatic. Under adiabatic testing conditions and assuming that the plastic energy \(U_{\text{plast}}\) is completely converted into heat, we can calculate the average temperature rise \(\Delta T\) from:

\[
\Delta T = \frac{U_{\text{plast}}}{C_p \rho \ V_0}
\]

where \(C_p\) is the specific heat capacity (estimated value for IM PA66/PPE is 1.4 J/g/K [50]), \(\rho\) is specific density (1.1 g/cm\(^3\) for IM PA66/PPE [51]) and \(V_0\) is the volume of the sample.

For samples tested at a strain rate of 10\(^5\)\(\%\)\(\min^{-1}\) at 20°C the maximum value of \(\Delta T\) was calculated to be 10°C (just before fracture). In practice ductile deformation is often localized. For this reason, the heat will also be generated non-uniformly in the sample and the actual (local) temperature rise can be much higher than calculated above.

In this study it was found that the scatter in the experimental fracture data is much higher than the scatter in the experimental yield and modulus data. This can easily be understood as the fracture behaviour of (unnotched) plastics is strongly influenced by the presence of numerous pre-existing defects, like flaws and cracks, in the material. The natural variation in the size of these defects cause the crack initiation process to be a statistical event. For this reason, fracture in plastics cannot be fully described by a single value for the fracture stress or strain.

In order to study the variability of the fracture data of IM PA66/PPE in more detail we determined the variation in the high-rate mechanical tensile properties of IM PA66/PPE. For this purpose 50 samples were tested at a test speed of 1 m/s (10\(^5\)\(\%\)\(\min^{-1}\)) at room temperature. The average values, the standard deviations and the variation coefficients for the fracture stress, the elongation at break and the fracture energy are given in table 2.2.

The variation of the fracture stress of brittle materials can often be described by a two-parameter Weibull distribution function [52,53]. The Weibull model [54] assumes that fracture of a sample is due to failure of the most serious pre-existing defect. For a given sample length the cumulative failure probability function \(P\), i.e., \(P\) is the probability that a sample has fractured at a stress equal to or lower than \(\sigma\), can be described by an empirical

\(^1\) More precisely, there is even a small decrease of temperature at low strains. This reversible thermo-elastic temperature effect of Hookean solids was described in 1857 by Joule [61].
Table 2.2  Fracture properties of IM 6A60/PPE measured in tension at a strain rate of $10^6\%\text{min}^{-1}$ at 20°C.

<table>
<thead>
<tr>
<th></th>
<th>Fracture stress (MPa)</th>
<th>Elongation at break (mm)</th>
<th>Fracture energy (J)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Average value</td>
<td>57.3</td>
<td>19.0</td>
<td>30.1</td>
</tr>
<tr>
<td>Standard deviation</td>
<td>1.5</td>
<td>4.9</td>
<td>8.3</td>
</tr>
<tr>
<td>Variation coefficient</td>
<td>2.6%</td>
<td>25.8%</td>
<td>27.6%</td>
</tr>
</tbody>
</table>

distribution function introduced by Weibull [54]:

$$P = 1 - \exp \left[-\left(\frac{\sigma}{\sigma_0}\right)^m\right]$$  \[6\]

where $\sigma_0$ is the Weibull characteristic fracture stress (roughly equal to the average strength [55]) and $m$ is the Weibull shape parameter (Weibull-modulus).

The variability in strength is described by the Weibull modulus. Rearranging equation 6 yields:

$$\ln(-\ln(1-P)) = m * \ln(\sigma) - m * \ln(\sigma_0)$$  \[7\]

In practice we can approximate the cumulative failure probability $P_i$ at a stress $\sigma$ by [55–59]:

$$P_i = \frac{i-0.5}{N}$$  \[8\]

where $i$ is the number of samples that have fractured at or below a stress $\sigma$ and $N$ is the total number of experiments.

The total number of experiments used in this study ($N=50$) is sufficient to obtain reliable values of the Weibull parameters [52,55,59,60].

It should be pointed out that the Weibull distribution, although often used for describing the distribution of strength values, is a general statistical distribution function. It has also been used to describe non-mechanical properties, like the length distribution of adult males born in Britain [54]. The Weibull equation is used here to describe the variation in fracture stress, fracture strain and fracture energy values.

In particular in the case of materials with approximately ideal elastic–plastic behaviour (such
as IM PA66/PPE) a better impression of the material’s variability is obtained by analyzing the variation of elongation at break and/or fracture energy data. For this purpose an equation similar to equation 7 is used, but now the fracture stress is replaced by either the elongation at break or by the fracture energy:

$$\ln(-\ln(1-P)) = m \ast \ln(X) - m \ast \ln(X_0)$$  \[9\]

where X is the elongation at break (or fracture energy), X₀ is the Weibull characteristic elongation at break (or fracture energy) and m is the Weibull shape parameter (Weibull–modulus).

The distribution of the measured fracture stress, the elongation at break and the fracture energy of IM PA66/PPE are given as a Weibull–plot in figure 2.10, figure 2.11 and figure 2.12, respectively.

![Fracture stress for 4 engineering plastics measured at 20°C at a strain rate of 10⁵%min⁻¹. The data are given as a Weibull–plot according to equation 7. MF PA6 = mineral filled PA6, UF PA6 = unfilled PA6, IM PA6 = rubber-toughened PA6, IM PA66/PPE = rubber-toughened PA66/PPE.](image)

As a comparison, the variation of the fracture data of three other engineering plastics were also determined. The fracture behaviour of these materials differs from very brittle (MF PA6) to extremely tough (IM PA6). Of each material 50 samples were tested under the same conditions as described for IM PA66/PPE. The fracture data of these materials is also given in these figures. It is clear that the fracture data of all four materials can be well–described by the two parameter Weibull equation.

In table 2.3 the calculated Weibull parameters (the Weibull modulus and the Weibull characteristic value) describing the data of the fracture stress, the elongation at break and the
Fig. 2.11  *Elongation at break for 4 engineering plastics measured at 20°C at a strain rate of 10^5% min^-1. The data are given as a Weibull-plot according to equation 9. See legend of figure 2.10 for an explanation of the abbreviations used.*

Fig. 2.12  *Fracture energy for 4 engineering plastics measured at 20°C at a strain rate of 10^5% min^-1. The data are given as a Weibull-plot according to equation 9. See legend of figure 2.10 for an explanation of the abbreviations used.*

Fracture energy are given. MF PA6 and UF PA6 are brittle (low values of ε_0 and U_0) and IM PA66/PPE and IM PA6 are ductile (high values of ε_0 and U_0) when tested under these conditions. The measured variability of the elongation at break of IM PA66/PPE and MF PA6 is high (low value of m), whereas it is low for UF PA6 and IM PA6 (high value of m). These results clearly show that no simple correlation exists between ductility and amount of scatter.
of the fracture data. Most probably the value of m will be influenced by the presence and size of defects in the material. From figure 2.11 it can be seen that the variation in the elongation at break of IM PA66/PPE is high compared to those of the other materials. Visual inspection of the fracture surfaces of IM PA66/PPE shows that fracture of these samples is frequently initiated at black inclusions ("black pits") in the material. Most probably these black pits consist of degraded polymer material caused by the high processing temperature of IM PA66/PPE [51]. In general, a lower fracture strain level correlated with a large size of the black pit.

The effect of temperature and strain rate on the value of m will be limited, although we can expect m to be lower at temperatures close to T<sub>DB</sub>.

Table 2.3. The Weibull-moduli m and characteristic values for the data of the fracture stress, the elongation at break and the fracture energy for four engineering plastics determined in tension at a strain rate of 10<sup>5</sup> % min<sup>−1</sup> at 20°C.

<table>
<thead>
<tr>
<th>Material</th>
<th>Fracture stress</th>
<th>Elongation at break</th>
<th>Fracture energy&lt;sup&gt;‡&lt;/sup&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>m</td>
<td>σ&lt;sub&gt;0&lt;/sub&gt; (MPa)</td>
<td>m</td>
</tr>
<tr>
<td>MF PA6</td>
<td>19.4</td>
<td>104.0</td>
<td>6.2</td>
</tr>
<tr>
<td>UF PA6</td>
<td>95.5</td>
<td>112.9</td>
<td>13.7</td>
</tr>
<tr>
<td>IM PA6</td>
<td>82.8</td>
<td>43.4</td>
<td>18.0</td>
</tr>
<tr>
<td>IM PA66/PPE</td>
<td>43.4</td>
<td>57.9</td>
<td>4.7</td>
</tr>
</tbody>
</table>

‡ All fracture energy data were normalized to the volume of the parallel section of the IM PA66/PPE samples.

2.4 CONCLUSIONS

The tensile stress–strain behaviour of IM PA66/PPE was studied over a broad range of temperatures at both low (10% min<sup>−1</sup>) and high (10<sup>5</sup> % min<sup>−1</sup>) strain rates. At a strain rate of 10<sup>5</sup> % min<sup>−1</sup> the fracture energy of IM PA66/PPE was found to be nearly independent of temperature between +60°C and –40°C, showing the high impact resistance of this material. On further lowering of the test temperature IM PA66/PPE undergoes a transition from ductile failure to brittle fracture. At this high strain rate the ductile-to-brittle transition temperature of IM PA66/PPE was determined to be approximately –60°C. On lowering of the strain rate to 10% min<sup>−1</sup> the ductile-to-brittle transition temperature decreases to –100°C.

It was found that the variability of both the elongation at break and of the fracture energy of IM PA66/PPE, determined at high strain rate, can be adequately described by a modified two-parameter Weibull distribution function. A comparison of the Weibull-plots of IM PA66/PPE and three other engineering plastics shows that the scatter in the fracture energy and in the elongation at break of IM PA66/PPE is high compared to those of the other
materials. The high scatter is attributed to pre-existing defects due to polymer degradation at the high processing temperature. However, with 6 samples per testing condition the ductile-to-brittle transition temperature can be determined with an accuracy of ± 5°C.

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3.1 INTRODUCTION

In the automotive industry plastics are rapidly replacing metals in many applications, such as car-bumpers, spoilers, body panels and mirror housings. The use of plastics instead of metals has some important advantages, e.g. weight reduction (fuel savings), reduction of energy consumption during fabrication, flexibility in design, corrosion resistance and ease of manufacturing complex structural parts. Most plastics used for exterior automotive parts are painted. This is done for a variety of reasons, e.g. colour and appearance matching with the rest of the coated car body, hiding flow lines and other irregularities in the surface of the plastic, improvement of the scratch and weather resistance and protection of the plastic against UV-degradation and solvents (petrol, etc). The painting of plastic components is either done by on-line painting or by off-line painting [1-3]. On-line painting means that plastic parts are assembled on the car body before they are painted along with the steel body in the coating application line. With off-line painting the plastic part is coated in a separate painting process and is subsequently assembled on the coated body of the car. On-line painting allows optimum colour matching and reduces the application costs. As the curing temperatures of coatings used for steel parts are high (typically above 140°C) only plastics with a very high thermal stability are suitable for on-line coating.

Beside the above mentioned advantages, there are also some well-known disadvantages when plastic parts are coated. Some plastics are sensitive to a wide range of solvents commonly used in the paint formulation. Exposure of the plastic to these solvents can cause surface-etching or, in more severe cases, it can lead to premature mechanical failure of the plastic part in service (solvent-attack) [4-7]. Another problem with coating of plastics is the low heat resistance of most thermoplastics, restricting the temperature at which curing of the coating can take place. The coating of plastics is further hampered by the variability in the level of adhesion due to internal and external mould releasing agents used in the fabrication of the plastic part [8].

Probably the most serious problem with coated plastics is the dramatic change in the mechanical properties, and in particular the drastic reduction in the impact strength, that is often observed if plastic parts are painted [2,5-7,9-19]. This phenomenon is sometimes called surface embrittlement. It may cause brittle failure of coated plastics under conditions under which the uncoated plastic would deform in a ductile manner.

In 1962 Carhart et al [15] reported the reduction of the mechanical fracture properties of high impact polystyrene (HIPS) sheets used for refrigerator door liners after coating the sheets with a high gloss clear-coating. The elongation at break was found to decrease from 40% for the uncoated HIPS to 10% for the coated material. Falling dart impact properties of the HIPS sheets were also influenced by the use of the coating. The change in impact
properties was found to depend on the position of the coated side with respect to the dart impact side. With front impact testing (where the dart hits the coated side) a 3-fold decrease in the impact energy was found, with reverse impact (where the dart hits the uncoated side of a coated sheet) even a 40-fold decrease in the impact energy was observed! A similar decrease in the mechanical fracture properties was found after laminating the HIPS sheets with a biaxially oriented polystyrene film. In this case the thickness of the polystyrene film was 25 μm, only one hundredth of the thickness of the HIPS sheet.

Maier and Laible [2] studied the puncture impact behaviour of coated plastics in the temperature region between -20°C and 0°C at a test speed of 4.5 m/s. For an uncoated flexible PBTP-blend ductile fracture was observed at -20°C. The fracture behaviour of this material was found to be brittle after the application of a conventional automotive coating, even at 0°C.

Schönfelder et al. [6,13] studied the influence of various polyurethane coatings on the mechanical impact properties of ABS. For all coatings studied he found a decrease in the impact energy of ABS if the samples were tested in reverse impact. The negative influence of the polyurethane coating increased with decreasing flexibility of the coating. In some cases the use of a highly flexible primer layer was found to slightly reduce the surface embrittlement caused by the brittle topcoat.

Schlesing and Osterhold [14] used high-speed puncture testing to determine the brittle-to-ductile transition temperature $T_{DB}$ of coated plastics relative to that of the uncoated material. For two different types of EPDM-modified PP they found a shift of the $T_{DB}$ of about 10°C if a highly flexible coating was used. If the substrates were provided with a semi-flexible coating a shift of the $T_{DB}$ of about 30°C was found.

It is now general knowledge that surface embrittlement is caused by the lower fracture strain of the brittle surface layer compared to the fracture strain of the ductile substrate. If the coated substrate deforms the brittle layer fractures first. If the crack from the brittle layer reaches the interface it may propagate through the substrate due to the high stress intensity at the crack tip, causing premature failure of the coated part. In other words, the crack from the coating acts as a notch when it reaches the interface between the coating and the substrate. This is shown schematically in figure 3.1. Please note that the thickness of the brittle layer is usually only a small fraction of the total thickness. For a typical coated plastic component for instance, the ratio between the thickness of the coating and the thickness of the substrate is about 1:50.

From the above it can be concluded that the surface embrittlement effect can be reduced by increasing the fracture strain of the coating. Obviously, if the fracture strain of the coating is equal to or higher than the fracture strain of the substrate no change in the mechanical behaviour of the plastic is found. In the ideal case the ductile-to-brittle transition temperatures of the coating is either below the temperature at which the coated material is used, or below the ductile-to-brittle transition temperature of the substrate.
The crack from the coating reaches the interface:

![Diagram of coating and substrate with a crack reaching the interface](image)

and acts as a notch:

![Diagram of substrate with a notch](image)

Fig 3.1 *Schematic representation of a coated plastic with a crack in the coating layer. If the crack reaches the interface with the substrate it can be compared to a notch with a length equal to the coating thickness.*

In contrast to the ideal coating described above, standard automotive topcoat systems for metal parts exhibit a very low fracture strain of only a few percent [3]. The use of these coatings on plastic parts generally leads to an enormous reduction in the impact properties of the coated part. For the reasons mentioned previously it seems desirable to increase the fracture strain of automotive coatings for plastic parts. A high elongation at break can be achieved if coatings are used with a low glass transition temperature and a low cross-link density. However, there are serious drawbacks to lowering the glass transition temperature and the cross-link density of automotive coatings, such as the low solvent and weather resistance and the prolonged drying time of these coatings [2,12,13]. In practice, automotive coatings must also have a sufficiently high level of polishability [20]. The surface appearance of the coating after curing is sometimes poor due to craters, dust particles etc. These bad spots are repaired two hours after the painting process by gentle sanding and subsequent polishing of the bad spot. Good polishability demands a sufficiently high hardness of the coating (even shortly after curing) and thus requires a sufficiently high glass transition temperature of the coating. It is clear that polishability and high fracture toughness (at low temperatures) are conflicting requirements for coatings for plastics.

It should be mentioned here that surface embrittlement does not always occur if a brittle coating is present on a ductile substrate. If delamination of the coating takes place after fracture of the coating, the fracture behaviour of the substrate is not influenced by the coating. Although this fact was recognized and reported by some authors as a possible route to reduce the effects of surface embrittlement [2,6,7,18,21] to our knowledge no quantitative data are reported in the literature regarding the influence of the level of adhesion on the fracture behaviour of coated plastics.

From the above it is clear that the fracture behaviour of a coated plastic is influenced by both the fracture behaviour of the coating and by the level of adhesion of the coating on the substrate. In this thesis the effect of both properties on the impact properties of coated plastics will be studied in detail.
It is also interesting to note that surface embrittlement is not only observed with coated plastics but also with ductile plastics after (outdoor) weathering. With weathered plastics the brittle layer consists of a surface layer embrittled by e.g. UV-degradation [22-29]. The similarity between surface embrittlement found with coated plastics and that found with plastics after weathering was shown by some authors who successfully reproduced the effects of outdoor weathering by laminating thin sheets of a brittle polymer onto the surface of (unaged) ductile plastics [26,27,30].

In this thesis the fracture behaviour of plastics provided with a coating is studied in detail. A rubber-toughened polyamide-66/poly(phenylene ether)-blend (=IM PA66/PPE) is used as a model substrate material. This material is often used in automotive applications and combines high stiffness with high impact toughness even at low temperatures. Due to its high thermal stability it is well-suited for on-line painting. The mechanical tensile properties of the uncoated material at high and low strain rate were presented in the previous chapter.

In this study the influence of a polyurethane coating on the high rate mechanical tensile properties of IM PA66/PPE is determined. Polyurethane (PUR) coatings are widely used as clearcoats in the automotive, the car refinish and the aerospace fields. The properties of PUR coatings, such as their mechanical properties, durability and chemical resistance, are excellent [31,32]. PUR coatings are formed by the reaction of hydroxyl groups with isocyanate groups. The reaction scheme of the urethane formation is shown schematically in figure 3.2, reaction A. Besides the urethane formation the isocyanate group can be hydrolysed leading to the formation of urea groups, see reaction B in figure 3.2. The latter reaction is generally known as moisture-hardening. It can affect the degree of urethane formation at low curing temperatures [33]. Consequently, relative humidity has a significant influence on the chemical structure of the coating film cured at room temperature. At high curing temperatures reaction B hardly occurs [32].

![Urethane formation and Urea formation](image_url)

**Fig 3.2** Reaction scheme for the urethane formation and the urea formation, reaction A and B, respectively. The chemical structure of the cross-linker (isocyanurate trimer of HMDI) used in these experiments is also shown in the figure.
3.2 THEORY

In this section a model will be presented which can be used to predict the fracture behaviour of coated plastics. This model describes the influence of the mechanical properties of the coating and the mechanical properties of the substrate on the fracture behaviour of the coated plastic. It also provides a way to describe the influence of the adhesion level of the coating on these fracture properties. The discussion is based on a ductile plastic provided with a brittle (automotive) coating. As discussed before the behaviour of weathered samples and the behaviour of ductile samples laminated with a brittle sheet are essentially identical to the behaviour of coated samples. Consequently, the model presented is in principle applicable to all cases of surface embrittlement. In the model it is assumed that the coating is more brittle than the substrate, that is, fracture of the coating occurs before fracture of the substrate. It is further assumed that the coated sample is loaded in uniaxial tension.

If the crack in the brittle coating layer reaches the interface it can either:

- cause debonding of the coating from the substrate.
- be arrested at the interface or in the ductile substrate.
- propagate through the substrate (causing catastrophic failure of the substrate).

Which of the above situations will occur for a given coated substrate can be predicted using the simplified linear-elastic fracture mechanics models described below.

3.2.1 Delamination

The situation in which the crack from the coating causes delamination as it reaches the interface is schematically shown in figure 3.3.

![Diagram](image)

Fig 3.3 Schematic representation of the situation where the crack from the coating causes debonding of the coating layer from the substrate.

In general, a stressed coating can delaminate from the substrate if the stored, recoverable elastic energy in the coating layer is greater than the energy required for debonding [34-36]. The total amount of energy needed to debond a coating from a substrate per unit of area is
the energy release rate $G_{c, \text{adh}}$. It follows that the coating will debond if:

$$G_{c, \text{adh}} \leq U_{\text{rec, elast}} \ h$$  \hspace{1cm} [1]

where $U_{\text{rec, elast}}$ is the recoverable elastic energy per unit volume stored in the coating and $h$ is the thickness of the coating layer. For a linear-elastic material deformed in a uniaxial tension test $U_{\text{rec, elast}}$ is equal to $\frac{1}{2} E \varepsilon^2$, with $E$ is the elastic modulus of the material and $\varepsilon$ is the strain. In our model the coating will delaminate from the substrate as the crack from the coating reaches the interface if:

$$G_{c, \text{adh}} \leq \frac{1}{2} E_{\text{coat}} \varepsilon_{f,c}^2 \ h$$  \hspace{1cm} [2]

where $E_{\text{coat}}$ is the elastic modulus and $\varepsilon_{f,c}$ is the tensile fracture strain of the coating.

It is well-known that residual stresses in coatings can also contribute to delamination of the coating. An important origin of residual stress is the difference in thermal expansion between coating and substrate resulting in a thermal stress after cooling down from the curing temperature. Residual stresses can also arise due to coating shrinkage caused by solvent evaporation after solidification of the coating. Because the coating layer is thin it is generally in a plane-stress state. Therefore, residual stresses will cause a biaxial tensile stress state in the plane of the coating layer. The internal elastic energy in the coating due to residual stresses generally increases linearly with thickness of the coating. The recoverable elastic energy in the coating layer due to a biaxial residual stress $\sigma_{\text{res}}$ is equal to [34-38]:

$$U_{\text{res}} = \frac{\sigma_{\text{res}}^2 (1-\nu)}{E_{\text{coat}}} = \frac{E_{\text{coat}} \varepsilon_{\text{res}}^2}{(1-\nu)}$$  \hspace{1cm} [3]

where $\nu$ is Poisson ratio and $\varepsilon_{\text{res}}$ is the biaxial residual strain. At a certain thickness of the coating the internal energy may even be sufficient to cause spontaneous delamination of the coating [34,35,37,38]. If the stored elastic energy due to the residual stress in the coating is significant the condition for delamination is given by:

$$G_{c, \text{adh}} \leq \frac{1}{2} E_{\text{coat}} \varepsilon_{f,c}^2 \ h + U_{\text{res}} \ h$$  \hspace{1cm} [4]

As shown by equation 4 the probability of delamination increases with increasing fracture strain of the coating and with increasing level of internal stress in the coating. At the same level of adhesion thick coatings will delaminate more easily than thin coatings.

3.2.2 Crack arrest

If the level of adhesion is sufficiently high delamination of the coating will not take place. The crack in the coating can then either be arrested at the interface or in the ductile substrate, or it can propagate through the substrate material. The latter case results in catastrophic failure of the coated plastic. The conditions for arrest of the crack from the brittle coating in the substrate material were extensively studied by Broutman and co-
workers [21,20,39-42]. In their model it was assumed that the crack from the brittle layer reaching the interface with the substrate can be compared to a notch in the substrate of a length equal to the brittle layer thickness. This is shown schematically in figure 3.1.

The conditions under which a notch in a material will start to grow can be calculated using linear-elastic fracture mechanics (LEFM). According to LEFM a notch in a material will start to grow if the value of the stress intensity factor at the tip of the notch is higher than a critical value. For linear-elastic conditions the stress intensity factor at the crack tip $K_I$ of a sample with a sharp notch loaded in uniaxial tension (mode I) is given by:

$$K_I = Y \sigma \sqrt{h}$$

where $Y$ is a constant depending on the geometry of the sample, $\sigma$ is the applied stress and $h$ is the length of the notch. For single edged notched specimen the value of $Y$ can be calculated from [43,44]:

$$Y = 1.99 - 0.41 \left( \frac{h}{W} \right) + 18.70 \left( \frac{h}{W} \right)^2 - 38.48 \left( \frac{h}{W} \right)^3 + 53.85 \left( \frac{h}{W} \right)^4$$

where $W$ is the thickness or width of the sample.

The critical stress intensity factor $K_{lc}$ of a material determines the strength $\sigma_{crit}$ of a prenotched sample:

$$\sigma_{crit} = \frac{K_{lc}}{Y \sqrt{h}}$$

The critical stress intensity factor is a material dependent parameter and is called the fracture toughness of the material. Equation 7 can be used to describe the influence of the length of the notch on the fracture behaviour of a material containing a surface notch. For low values of $h$ equation 7 predicts a very high value of the strength of the material and equation 7 is obviously not valid under these conditions. For samples with small notches the strength of the material is given by the net-section yield stress:

$$\sigma_{crit} = \sigma_y \left(1 - \frac{h}{W}\right)$$

where $\sigma_y$ is the yield stress of the material.

In figure 3.4 the strength of a material is given as a function of the length of the notch according to equations 7 and equation 8. From this figure it can be seen that there exists a critical value of the notch length $h^*$. For values of the notch length smaller than $h^*$ the strength of the material can be calculated from the net-section yield criterium (equation 8), otherwise it can be calculated from the LEFM fracture criterium (equation 7). The value of $h^*$ depends on the material and the sample geometry. Under the condition that $W$ is much
larger than \( h^* \) the value of \( h^* \) can be approximated by:

\[
 h^* = \left( \frac{K_{lc}}{Y \sigma_y} \right)^2 [9]
\]

Using equation 9 the calculated value of \( h^* \) is 36 \( \mu m \) for the example shown in figure 3.4.

![Graph showing fracture stress vs. length of notch](image)

**Fig 3.4** The fracture stress of a material as a function of the length of the notch calculated from the net-section yielding criterion (equation 8) and calculated from the stress intensity factor (equation 7). For the calculations the following values were used: \( K_{lc} = 0.9 \text{ MPa m}^{1/2} \), \( \sigma_y = 75 \text{ MPa} \) and \( W = 2.9 \text{ mm} \).

It should be mentioned here that the use of the energy release rate as a failure criterion, as used in equation 1, is comparable to the use of the stress intensity as a failure criterion. For mode I loading under linear-elastic conditions a simple relation between the stress intensity factor \( K_I \) and the energy release rate \( G_I \) exists:

\[
 G_I = \frac{K_I^2}{E} \quad \text{for plane stress} [10]
\]

\[
 G_I = \frac{K_I^2}{E} (1 - v^2) \quad \text{for plane strain} [11]
\]

From an experimental point of view the use of \( K_I \) instead of \( G_I \) for polymers has the advantage that for the former knowledge of the (rate and temperature-dependent) value of the elastic modulus \( E \) is not needed.

The concepts of linear-elastic fracture mechanics can also be used to calculate the conditions under which the crack from the coating will be arrested at the interface or in the substrate.
In this case fracture behaviour is described with the crack arrest toughness $K_{Ia}$ of the substrate. The fracture toughness $K_{lc}$ is defined as the value of the stress intensity factor for crack initiation. Analogously, $K_{Ia}$ is the stress intensity factor for the termination (arrest) of a propagating crack [45-49]. $K_{lc}$ and $K_{Ia}$ are both material properties depending on the temperature at the crack tip [50]. The values of $K_{lc}$ and $K_{Ia}$ are only valid under quasi-static crack growth conditions. We can think of $K_{lc}$ and $K_{Ia}$ as the value of $K_I$ just before the initiation of crack growth and the value of $K_I$ just after crack arrest, respectively. $K_{lc}$ is approximately equal to $K_{Ia}$ for brittle materials but for ductile materials $K_{lc}$ is significantly higher than $K_{Ia}$ [51]. Literature data of $K_{lc}$ and $K_{Ia}$ for several plastics are compared in figure 3.5.

![Graph](image)

Fig 3.5  Comparison between literature data of $K_{Ia}$ and $K_{lc}$ for various materials. Materials: $1=ps$, $2=PMMA$, $3,11=pc$, $4=nylon$, $5=polycetal$, $6-9$: various epoxies, $10=polyester$. References: $1-5=[41]$, $6=[52]$, $7=[53]$, $8=[54]$, $9-10=[55]$, $11=[56]$.

Rolland and Broutman [41] and Young [54] measured $K_{lc}$ and $K_{Ia}$ as a function of temperature for polycarbonate and an epoxy resin, respectively. They both found that the value of $K_{lc}$ is much more temperature-sensitive than $K_{Ia}$. The value of $K_{Ia}$ is independent of the length, shape and sharpness of the starting notch. The value of $K_{lc}$ is independent of notch length, but the actual sharpness of the prenotch can have a significant effect on the measured value of $K_{lc}$.

Using the LEFM concept we can easily derive an expression in terms of the $K_{Ia}$-value of the substrate describing the conditions under which the crack from the brittle coating will be arrested. Assuming that the fracture strain of the coating is smaller than the yield strain of the substrate, the stress in the substrate at the moment of coating fracture is equal to $E_{sub}\varepsilon_{fc}$, where $E_{sub}$ is the modulus of the substrate and $\varepsilon_{fc}$ is the fracture strain of the
coating. In that case the condition for crack arrest is:

\[
\frac{(K_{la})_{sub}}{E_{sub}} \geq \varepsilon_{fc} Y \sqrt{h}
\]  \[12\]

where \((K_{la})_{sub}\) is the arrest toughness of the substrate material. Equation 12 is only valid if the thickness of the coating is larger than \(h^*\).

As shown by equation 12 there is a critical value of the crack arrest toughness of the substrate. For values of the crack arrest toughness above this critical value the crack is arrested, for values of the crack arrest toughness below this critical value catastrophic failure of the substrate is found. This critical value of the arrest toughness depends on the modulus of the substrate, the fracture strain of the coating and the thickness of the coating. Equation 12 shows that the probability of crack arrest increases with decreasing fracture strain of the coating and with decreasing thickness of the coating. A decreasing surface embrittlement effect with decreasing thickness of the brittle layer has indeed been found experimentally [14,17,26,39,40,42]. If the crack is arrested, either due to a low fracture strain of the coating or due to a low thickness of the coating, the stress in the ductile substrate can continue to increase with increasing elongation of the sample. The coated sample will finally fail by re-initiation of the arrested crack as the corresponding stress intensity factor increases or by a newly created crack for which the condition given by equation 12 is no longer satisfied due to the higher stress in the ductile material. For this reason a significant loss of the mechanical fracture properties of the substrate can be expected even if the (first) crack from the coating is arrested.

As can be further noted from equation 12 the chance of crack arrest also increases with increasing toughness of the ductile substrate (higher value of \(K_{la}\)) or decreasing modulus of the substrate material. Unfortunately, plastics with a high toughness/modulus ratio can often not be used as material for coated plastics as they are frequently inferior in other key properties, such as melt viscosity, load carrying-capacity, solvent resistance, heat distortion temperature and level of adhesion between coating and substrate [7].

A possible solution to this problem is the use of a thin layer with a high crack arrest toughness between the brittle outer layer and the substrate. The thin layer can arrest the coating crack while avoiding the disadvantages associated with the use of highly flexible substrates. There is indeed experimental evidence that the use of very flexible primer layers can diminish the surface embrittlement effect of brittle topcoats under certain conditions [2,9]. As explained above it is, however, not likely that crack arrest in the primer layer will lead to a very large reduction of the surface embrittlement effect.

Using equation 12 the conditions for crack arrest in coated plastics can be calculated from the value of \(K_{la}\) of the substrate. It was mentioned above that the values of \(K_{la}\) and \(K_{lc}\) are valid under quasi-static conditions only. When the crack growth rate or the loading rate becomes high, like under impact conditions, dynamic effects may become significant and consequently the quasi-static approach is no longer completely valid. Under these conditions the instantaneous value of the stress intensity factor for the running crack should be used.
This instantaneous value is called the dynamic fracture toughness $K_{id}$. The value of $K_{id}$ is a temperature-dependent function of the crack speed $\dot{a}$. In figure 3.6 an example of the dependence of $K_{id}$ on crack speed is given for an thermoset epoxy [50]. The value of $K_{id}$ is often well-described by the empirical equation [50]:

$$K_{id} = \frac{K_{la}}{1 - \left( \frac{\dot{a}}{\dot{a}_L} \right)^m}$$  \[13\]

where $\dot{a}$ is the speed of the propagating crack, $\dot{a}_L$ is the limiting value of the crack speed equal to a fraction of the shear wave velocity in the material [50,57,58] and $m$ is a temperature-dependent material constant. As shown by equation 13 the value of $K_{la}$ can be considered as the minimum value of $K_{id}$.

![Graph showing the relationship between $K_{id}$ and crack speed](image)

*Fig 3.6 Literature data of dynamic stress intensity factor $K_{id}$ as a function of crack speed for a thermoset epoxy, redrawn after Kanninen and Popelar [50].*

Rolland and Broutman [21,20,40,41] used the dynamic fracture mechanics approach to propose the following criterion for crack growth across the interface:

$$(K_{la})_{sub} \geq [(K_{id})_{coat}]_{interface}$$  \[14\]

where $[(K_{id})_{coat}]_{interface}$ is the value of the dynamic stress intensity factor of the crack in the brittle coating layer as it reaches the interface. Note that equation 14 and equation 12 are similar under quasi-static conditions. As shown by equation 14 there is a critical value of the stress intensity factor of the running crack as it reaches the interface. For values of the stress intensity factor below this critical value the crack is arrested, for values of the stress intensity factor above this critical value catastrophic failure of the substrate is found. The critical value depends on the actual arrest toughness of the ductile material. As shown by equation 13 the value of the dynamic stress intensity factor is directly related
to crack speed. This led Rolland and Broutman to the conclusion that for a given combination of a brittle layer and a ductile substrate there is a critical propagation speed of the crack, as it reaches the interface, above which the crack is not arrested and surface embrittlement takes place. This idea is shown schematically in figure 3.7 where the value of $K_{Id}$ is given as a function of crack speed for a ductile substrate and two brittle coatings. The toughness of coating-2 is higher than the toughness of coating-1. If the value of $K_{Id}$ of the crack from the coating is higher than the minimum value of $K_{Id}$ of the substrate (equal to $K_{Ia}$ of the substrate) catastrophic failure takes place. From this figure it can be seen that crack arrest takes place if the crack speed falls below a certain critical value. This critical value is $\dot{a}_{crit}^{-1}$ for coating-1 and $\dot{a}_{crit}^{-2}$ for coating-2. The critical crack speed decreases with increasing toughness of the coating and with decreasing $K_{Ia}$ of the substrate.

Fig 3.7 Schematic representation of the value of $K_{Id}$ as a function of crack speed for a tough substrate and for two brittle coatings. If the value of $K_{Id}$ for the coating crack is higher than the arrest toughness $K_{Ia}$ of the substrate crack arrest will not occur. Redrawn after Rolland and Broutman [20,21,40].

It is obvious that the condition for crack arrest as proposed by Rolland and Broutman (equation 14) is more generally valid compared to the quasi-static LEFM condition (equation 12). However, as indicated by Kanninen and Popelar [50], the simpler quasi-static fracture mechanics treatment suffices for most situations. With coated plastics the thickness of the brittle layer is generally very thin (about 40 $\mu$m) and it is not very likely that the crack speed will be significant when the crack reaches the interface. Broutman and Rolland [30,40] have determined the crack speed in a brittle and in a ductile epoxy coating as a function of thickness of the coating layer. They measured an almost linear increase of crack speed with coating thickness. For the same coating thickness they found that the crack speed in the more flexible coating was higher. This is caused by the higher amount of stored elastic energy in this coating. Extrapolation of their results to a thickness of 40 $\mu$m yields a crack speed of 20 m/s for the brittle coating and a crack speed of 28 m/s for the flexible coating. These crack speeds are low compared to $\dot{a}_L$ and a significant increase of $K_{Id}$ cannot be
expected as is also indicated by the data shown in figure 3.6. These results indicate that the use of static values of the stress intensity factor for cracks in thin coatings is justified. In this study we will therefore use the quasi-static approach to describe the condition under which the crack will be arrested.

The validity of the above model will be checked in this thesis. In the experiments reported hereafter in this chapter the level of adhesion of the PUR coating on IM PA66/PPE is very high and no debonding of the coating from the substrate was observed. The results of these tests were used to check the validity of the crack arresting model presented above. For this reason, a new method for determining the fracture strain of the coating during the high-speed tensile test was used. The influence of the level of adhesion on the fracture behaviour of coated plastics will be studied in detail in chapter 6 of this thesis.

3.3 EXPERIMENTAL

3.3.1 Materials

A rubber-modified polyamide-66/polyphenylene ether-blend (IM PA66/PPE) is used as a model substrate material in this study. This blend, known commercially as Noryl® GTX 940, was kindly provided by General Electric Plastics as sheet material (170 x 170 x 3 mm³). The PA66/PPE ratio of this blend is approximately 50/50. A PA66/PPE-copolymer is used as a compatibilizer. The impact-modifier is preferentially found in the PPE-phase. The (mechanical) properties of this material are described in detail in chapter 2.

The polyurethane clearcoat (PUR-A) was prepared using a polyol acrylate resin (Setalux® 1152xx51, Akzo Coatings) as binder material. Setalux® 1152xx51 contains primary hydroxyl groups. The molecular weight (M_w) of this binder is 9000 g/mol and the equivalent weight (= weight of binder containing one mole of reactive hydroxy groups) is 390 g. The binder is cross-linked with the isocyanurate trimer of hexamethylene diisocyanate (HMDI, see figure 3.2). The molar ratio of hydroxyl groups and isocyanate groups was chosen 1:1. All coating components were filtered using a pressure filter (Millipore, 5.0 μm) before use.

3.3.2 Application, curing and dynamic mechanical behaviour of PUR-A

The PUR-A clearcoat was applied by spincoating using an Erichsen spincoater (model 334/2) to obtain coating films of uniform thickness. With spincoating the thickness of the coating is mainly determined by spin speed and the viscosity of the wet coating solution [59]. Uniformity of coating thickness was better than 1 μm. The concentration of solid materials in the PUR-A wet paint was 57 w-%. The coatings
were cured at 100°C. The thickness of the coatings was determined on free standing coating films using magnetic induction with a Fischer Deltascope. Free films were obtained by spincoating on polypropylene (PP) substrates. The level of adhesion of the coating on PP is very low and the cured coating can easily be removed.

Due to their high curing rate at room temperature the cross-link density of PUR coatings can continue to increase if unreacted isocyanate groups are still present in the coating after curing at high temperature. The cross-link density has a significant effect on the mechanical properties of coatings and, consequently, the mechanical properties of incompletely cured PUR coatings may change in time. For this reason, the curing behaviour of the PUR-A clearcoat was investigated in detail to determine the minimum curing time required to produce a fully reacted coating with reproducible (mechanical) properties. This was done by measuring the dynamic mechanical tensile behaviour of free films of the clearcoat after curing for various times. For these experiments a modified Rheovibron (Toyo Baldwin, type DDV-II-C) was used at a frequency of 11 Hz with a dynamic strain of 0.03% and a heating rate of 2.3°C/min. The width and length of the films were 3 mm and 30 mm, respectively. The thickness of the fully cured coating was approximately 34 µm. The curing temperature was kept constant at 100°C in these experiments. In figure 3.8 the measured \( T_g \) and the value of the rubber modulus measured at 120°C are given for the PUR-A clearcoat as a function of curing time at 100°C.

![Graph showing Glass transition temperature and rubber modulus as a function of curing time at 100°C for the PUR-A clearcoat. The rubber modulus was measured at 120°C.](image)

**Fig 3.8**  Glass transition temperature and rubber modulus as a function of curing time at 100°C for the PUR-A clearcoat. The rubber modulus was measured at 120°C.

The \( T_g \) is defined as the temperature where the maximum of the tanδ curve was found. From this figure it is clear that the \( T_g \) and the rubber modulus at 120°C of the PUR-A coating increase even at long curing times. In practice, exposure to very long heating times should be avoided to minimize degradation of both the coating and the substrate. In the experiments described hereafter curing conditions for the PUR-A clearcoat were fixed at 7 hours at 100°C.
3.3.3 Preparation of painted samples

Prior to the painting process all IM PA66/PPE sheets were dried at 110°C under vacuum for 20 hours and subsequently cleaned by immersion of the sheets in a hot alkaline solution (2M NaOH, 85°C), rinsing with demineralised water and finally by wiping the sheets with isopropyl alcohol. The PUR-A clearcoat was applied to the cleaned IM PA66/PPE sheets by spincoating at a spin speed of 280 rpm resulting in a thickness of the coating of approximately 40 μm. The coated IM PA66/PPE sheets were cured at 100°C for 7 hours.

Dogbone-shaped tensile specimens according to DIN 53 455 (specimen number 3, gauge length is 60 mm) were stamped from the coated sheets using a cutting tool placed in a hydraulic press. The length-axis of the samples was chosen parallel to the direction of injection moulding. The stamping was done at an elevated temperature (75°C) to facilitate the cutting process.

3.3.4 High-speed tensile testing

The high-speed tensile tests were done using a servo-hydraulic material tester (Schenck VHS 25/20). A transient recorder (ADAM TC 210-4, Maurer) with a maximum sampling frequency of 2 MHz was used for the analog data acquisition of the force and displacement signals during the high-speed test. A small temperature chamber was used for the experiments done at temperatures other than room temperature. For these experiments the samples were preconditioned at the test temperature in a separate temperature chamber (temperature range: -70°C/+180°C, Grasso, type GTTS 27.70) for a minimum period of one hour. The samples were then placed in the temperature chamber of the tensile tester for at least 10 minutes before testing. Further details on high-speed tensile testing and the testing procedure used can be found in paragraphs 2.2.2, 2.2.3 and 2.2.4 of this thesis.

All high-speed tensile tests are done at a test speed of 1 m/s resulting in a strain rate of approximately 10^5%min^{-1} (= 17 s^{-1}). A minimum of four samples was tested at each temperature.

3.3.5 Determination of the coating fracture strain during tensile testing.

The model presented in paragraph 3.2 is based on the assumption that coating embrittlement is due to coating failure preceding the fracture of the total sample. To measure the fracture strain of the coating independently of that of the total sample the following technique was developed. During high speed tensile testing fracture of the coating layer on the IM PA66/PPE substrate was determined with the aid of a very thin conductive graphite layer on top of the PUR-A coating. The layer of graphite (Graphit 33, Kontakt Chemie) on the coated side of the test sample was obtained by spraying. A removable adhesive mask was used to obtain the shape of the graphite layer as shown on the bottom half of figure 3.9. The electrical resistance of the graphite layer during a high-speed tensile test was measured using the set-up as shown on the top half of figure 3.9.
The graphite layer was placed in series with a resistor ($R_{\text{serial}} = 500 \, \text{k} \Omega$). Electrical contact with the sample was made via the insulated clamps of the high-speed tensile tester. A power supply (Delta Elektronica, E030-1) was used to apply a voltage of 10 volt ($=V_{\text{tot}}$) to the circuit. The voltage $V_{\text{det}}$ was measured over the serial resistor using the ADAM transient recorder. A probe (10x, 50 MHz) was used as the input impedance of the transient recorder (1 M$\Omega$) is too low for these measurements [60]. The electrical resistance of the graphite layer $R_{\text{graphite}}$ was calculated using:

$$R_{\text{graphite}} = R_{\text{serial}} \left( \frac{V_{\text{tot}}}{V_{\text{det}}} - 1 \right)$$

If a crack initiates in the coating layer this will cause fracture of the very thin, well-adhering graphite layer. Consequently, fracture of the coating layer was observed as a steep increase in the measured resistance of the graphite layer and in this way the fracture point of the coating can easily be determined. Evidently, only the point at which the first crack in the coating layer appears can be detected in this way.

The graphite used is on the basis of a polymer binder and is very ductile even at low temperatures. This was confirmed by an experiment where the graphite was applied on a very ductile, uncoated plastic. This sample was tested in a high-speed tensile test at $-80^\circ \text{C}$ and it was found that the graphite layer deforms fully ductile even under these conditions.
3.4 RESULTS AND DISCUSSION

To illustrate the detrimental effects that brittle coatings can have on the fracture behaviour of a ductile substrate material, figure 3.10a shows fractured samples of uncoated IM PA66/PPE (upper sample) and IM PA66/PPE with a 40 μm PUR-A clearcoat (bottom sample). Both samples were subjected to a high-speed tensile test at 15°C with a strain rate of $10^5 \% \text{min}^{-1}$.

Fig 3.10 (a) Fractured samples of uncoated IM PA66/PPE (top) and IM PA66/PPE provided with a 40 μm PUR-A coating (bottom). The samples were tested in tension at a strain rate of $10^5 \% \text{min}^{-1}$ at 15°C. (b) Fracture surface of a coated IM PA66/PPE sample tested under the same conditions. The coating layer is on top of the sample.

The appearance of these samples is very different. The uncoated sample shows stress whitening over a large part of the parallel section and plastic deformation has clearly taken
place in the sample. The coated sample does not show any stress-whitening and the amount of permanent plastic strain is very limited for this sample. It should be stressed that no signs of debonding were observed anywhere on the deformed coated samples. This indicates that the combination of the cleaning procedure and the coating composition used in this study leads to good adhesion of the coating. The level of adhesion of this coating will be quantified in chapter 5.

The fracture surface of a PUR-A coated IM PA66/PPE sample is shown in figure 3.10b. This sample was tested under the same conditions as the samples shown in figure 3.10a. Figure 3.10b shows that fracture in this sample started at the coated side (top of the figure). From this fracture surface it is clear that the corresponding crack started to grow in the substrate uniformly over the complete width of the sample. This resulted in a planar wave front. Observe that the propagation of cracks resembles the wave patterns that can be seen in flowing water. The fracture surfaces of uncoated samples, tested under the same conditions, reveal that fracture starts in the bulk of the material.

The corresponding stress-elongation curves of these two samples are shown in figure 3.11.

![Stress-Elongation Curve](image)

**Fig 3.11**  Tensile stress-elongation curves of uncoated IM PA66/PPE and PUR-A coated IM PA66/PPE determined at a strain rate of $10^3\%\text{min}^{-1}$ at 15°C (same samples as in figure 3.10a).

The load-elongation curves of both samples in the elastic region, i.e., at low strains, are identical. This is to be expected as the coating thickness is small (40 μm) in relation with the sample thickness (2900 μm). Also the yield strains of both samples are comparable. The main difference in the stress-strain curves is the fracture strain. The elongation at break of the uncoated sample was 22 mm which corresponds to a ductile behaviour. In contrast the elongation at break of the coated sample is only 5.4 mm which indicates a very brittle behaviour. The large difference in fracture strain results in a large difference in energy at break of 38 J for the uncoated sample and 7 J for the coated sample. The fracture stress is hardly influenced by the presence of the coating.
The detrimental effect of the coating on the fracture behaviour of the substrate can be attributed either to solvent attack or to the presence of the coating. To determine the sensitivity of IM PA66/PPE to solvent attack the surface of uncoated sheets of IM PA66/PPE was exposed for a period of 7 hours at 100°C to the same mixture of organic solvents as used in the PUR-A wet paint. A thick sponge covering the surface of the IM PA66/PPE sheets was used to slow down the evaporation of the solvents. After the solvent-exposure the mechanical properties of the sheets were determined in high-speed tensile tests at $10^5 \text{min}^{-1}$ at various temperatures. The results of these measurements are shown in figure 3.12.

![Figure 3.12](image)

**Fig 3.12** Fracture energy (top) and elongation at break (bottom) as a function of temperature measured at a strain rate of $10^5 \text{%min}^{-1}$ of unexposed IM PA66/PPE (○) and of IM PA66/PPE after solvent-exposure (●).

In this figure the fracture energy and the elongation at break of the exposed samples are given as a function of temperature. As a comparison the fracture data determined for
unexposed samples of IM PA66/PPE are also given. Although the procedure used leads to an
exposure of the substrate material to the solvents far in excess of that encountered in
practice, the data in this figure clearly show that solvent-attack does not have a significant
effect on the high-speed mechanical properties of IM PA66/PPE. For this reason this material
is well-suited as a model substrate material to study the influence of the mechanical
behaviour of coatings on the surface embrittlement of coated plastics. Furthermore, as the
reduction of the mechanical fracture properties of coated IM PA66/PPE is not caused by
solvent-attack, we may conclude that the observed surface embrittlement effect is solely due
to the mechanical fracture behaviour of the PUR-A coating.
The influence of the PUR-A coating on the high-speed tensile properties of IM PA66/PPE was
studied as a function of temperature at a strain rate of 10^5% min^{-1}. The results are shown in
figure 3.13 which also contains the data for uncoated samples. The data of this figure show
that the fracture behaviour of IM PA66/PPE is dramatically changed by the PUR-A coating
over a wide range of temperatures. At temperatures below 15°C the fracture behaviour of
the coated IM PA66/PPE samples is completely brittle. Above 15°C the fracture energy of
coaed IM PA66/PPE increases rapidly with temperature. At 40°C the fracture energy of
coaed IM PA66/PPE is only slightly lower than that of uncoaed IM PA66/PPE.

Fig 3.13 Fracture energy as a function of temperature measured at a strain rate of 10^5% min^{-1} of
uncoated IM PA66/PPE (○) and of IM PA66/PPE with a 40 μm PUR-A coating (△).

Defining the ductile-to-brittle transition temperature T_{DB} as the temperature at which all
samples fail brittle, the T_{DB} of PUR-A coated IM PA66/PPE is 15°C. The T_{DB} of the coated
samples is about 75°C lower than the T_{DB} of uncoated IM PA66/PPE. This shift in T_{DB} is large
but not unrealistic in comparison to the results reported in literature. Bucknall [27] found a
similar shift of T_{DB} if ABS was laminated with a layer of SAN. These samples consisted of a
5.75 mm thick sheet of ductile ABS laminated with a 0.5 mm thick SAN-layer and were tested
in a notched Izod impact configuration. Several authors [2,12,14] have reported a shift of
T_{DB} over 20°C or more for ductile substrates with automotive coatings in high-speed
puncture testing.
Examination of the data of figure 3.13 shows that the coating only leads to embrittlement over a well-defined temperature interval. At low temperatures, i.e., below the $T_{DB}$ of the uncoated substrate material, the substrate fails in a brittle manner anyway and the additional reduction in fracture energy due to the presence of the coating is negligible. Furthermore, at high temperatures the coated samples fail in a ductile manner. It will be shown below that this ductile behaviour takes place if the test temperature is above the $T_{DB}$ of the coating material. The resulting embrittlement factor, i.e., the ratio of the fracture energy of the coated material and the fracture energy of the uncoated material, is shown in figure 3.14 as a function of temperature. In the literature and the commercial practice the embrittlement is often measured at only one temperature. From figure 3.14 it is clear that no effect on the mechanical fracture properties due to application of the coating will be found if the chosen testing temperature is well-above the $T_{DB}$ of the coated material. However, this observation does not exclude that surface embrittlement can occur at lower temperatures.

\[ \frac{U_t^{\text{coated}}}{U_t^{\text{uncoated}}} \]

**Fig 3.14** Schematic representation of the temperature-dependence of the ratio between the fracture energy of the coated substrate ($U_t^{\text{coated}}$) and the fracture energy of the uncoated substrate ($U_t^{\text{uncoated}}$).

To check the validity of the fracture mechanics model described before we have determined the fracture strain of the PUR–A coating on the substrate during high speed tensile testing. This was done by measuring the electrical resistance of a thin graphite layer on top of the coating (see paragraph 3.3.5 for more details). In figure 3.15 the stress-elongation curve and resistance-elongation curve are shown for a PUR–A coated IM PA66/PPE sample measured during a tensile test at a strain rate of $10^3 \text{% min}^{-1}$ at $0^\circ \text{C}$. The measured resistance-elongation curve shows a sharp increase of the electrical resistance of the graphite layer at an elongation of about 5.7 mm. This point denotes the fracture point of the coating layer. As can be seen from the stress-elongation curve fracture of the coated sample follows almost immediately after fracture of the coating layer in this experiment. This observation clearly shows that crack arrest did not take place in this sample.
In figure 3.16 the results of a similar experiment are shown for coated IM PA66/PPE tested in a high-speed tensile test at 20°C. The coating layer fractures at an elongation of approximately 7.5 mm whereas the elongation at break of the coated substrate is about 10.3 mm. Clearly, fracture of the coating layer does not cause instantaneous fracture of the whole sample and we may conclude that the crack from the PUR–A coating is arrested in this experiment. The elongation at break of uncoated IM PA66/PPE tested under the same conditions is approximately 19.5 mm. Evidently, crack-arrest is not sufficient to eliminate the surface embrittlement effect in this case.
From the curves shown in figure 3.15 and 3.16 it can be seen that at low levels of elongation the resistance of the graphite layer increases almost linearly with elongation of the sample. This is caused by the stretching and subsequent thinning of the graphite layer leading to an increase of the electrical resistance. The graphite layer acts as a primitive strain gauge in these experiments.

The results of the measurements of the elongation at break of the coating on the substrate as a function of temperature are summarized in figure 3.17. The values of the elongation at break of the coated samples and those of the uncoated samples are also given in this figure. The temperature dependence of the fracture strain of the coating and of the coated substrate are very similar. The $T_{DB}$ of the coating layer is 15°C, the same $T_{DB}$-value as found for the coated substrate. At low temperatures the fracture points of the coating and of the coated substrate coincide. Crack arrest does not take place in any of the samples tested in this temperature region. At 0°C a very small difference in the elongation at break of the coating and of the coated substrate is determined in one of the tested samples. At higher temperatures crack arrest is often observed and the difference in fracture strain of the coating and that of the coated plastic increases with temperature. As mentioned before the influence of arrest of the crack from the PUR A coating on the final fracture strain of the coated sample is very limited for all tested samples. Figure 3.17 shows conclusively that for these samples the fracture behaviour of the coated substrate is dominated by the fracture behaviour of the coating.

![Elongation at break (min) vs. temperature (°C)](image)

**Fig 3.17**  
Elongation at break as a function of temperature measured at a strain rate of $10^6$ %min$^{-1}$ of uncoated IM PA66/PPE (○), coated IM PA66/PPE (□) and the PUR-A coating on the substrate (■).

From the graphite resistance measurement the fracture point of the coating layer is easily determined for every tested coated sample. From this measured fracture point we can determine the stress in the substrate at the onset of coating fracture. If we assume that the time, needed for the initiated crack to reach the interface between coating and substrate, is
short in comparison with the time-scale of the experiment we can use this stress value to calculate the value of the stress intensity factor $K_I$ for this crack reaching the interface between the coating and the substrate using equation 5. For this calculation the notch length is assumed to be equal to the coating thickness. The calculation of $K_I$ using equation 5 is only valid under linear-elastic conditions. We will assume that the behaviour of a sample can be considered linear-elastic below the yield point of the substrate material. For this reason, the value of $K_I$ can only be calculated for those experiments in which the fracture strain of the coating is smaller than the yield strain of IM PA66/PPE.

The calculated values of $K_I$ for the high-speed tensile experiments on PUR-A coated IM PA66/PPE within this linear-elastic limit are shown in figure 3.18 as a function of temperature. In this figure the solid symbols denote experiments in which crack arrest occurred. If the fracture points of the coating and the coated substrate were equal the experiment is represented by an open symbol.

![Graph showing stress intensity factor as a function of temperature.]

**Fig 3.18** Value of the stress intensity factor of the crack from the coating reaching the interface calculated for individual tests as a function of temperature. The tensile experiments were done at a strain rate of $10^3 \text{%min}^{-1}$.

Figure 3.18 shows that crack arrest is only found in the coated samples which fail at low values of $K_I$. If the value of $K_I$ is higher than roughly 0.9 MPa m$^{1/2}$ crack arrest is never observed in the tested samples. This observation is consistent with the fracture mechanics model presented in paragraph 3.1.2 (equation 12) and we may conclude that the stress intensity factor for crack arrest of IM PA66/PPE is about 0.9 MPa m$^{1/2}$ at 0°C. The yield stress of uncoated IM PA66/PPE at 0°C is 75 MPa. In figure 3.4 the same values of the yield stress and the stress intensity factor were used. From this figure we can see that the stress intensity approach is indeed valid for the coating thickness used here.
3.5 CONCLUSIONS

The influence of a 40 μm PUR-A clearcoat on the high-speed mechanical tensile behaviour of IM PA66/PPE was studied. The presence of the coating has an enormous influence on the fracture behaviour of the substrate. In the experiments described in this chapter the fracture behaviour of the coated plastic is dominated by the fracture behaviour of the coating. The ductile-to-brittle transition temperature of the coated substrate is shifted over approximately 75°C compared to that of the uncoated material. In the temperature range between the $T_{DB}$ of the coated substrate and the $T_{DB}$ of the substrate material the fracture energy is about a factor 5 lower than the fracture energy of the uncoated substrate. This deterioration of the mechanical properties is not caused by solvent-attack but is directly related to the fracture behaviour of the coating on the substrate. The elongation at break of the coating on the substrate was determined during the high-speed tensile test by measuring the electrical resistance of a thin graphite layer on top of the coating. The crack from the coating is arrested if the value of the stress intensity factor of the crack reaching the interface between the coating and the substrate is lower than the arrest toughness of the substrate. The occurrence of crack arrest has a limited beneficial effect on the fracture behaviour of the coated plastic.

The large influence of the fracture behaviour of the coating on the fracture behaviour of the coated plastic is confirmed by the observation that the ductile-to-brittle transition temperatures of the coated plastic and the coating are equal. In order to predict the temperature range over which the fracture behaviour of coated plastics changes due to the presence of a coating, it is necessary to know the ductile-to-brittle transition temperature of the coating. In chapter 4 of this thesis a new test will be presented that measures the fracture mode transition temperature of coatings.

For the cleaning conditions used a high level of adhesion of the PUR-A coating on IM PA66/PPE was obtained and no delamination was observed in these experiments. The test developed to measure the level of adhesion of coatings on plastics quantitatively is described in chapter 5.

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mechanical behaviour of coated plastics

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THE TROUSER TEAR TEST, 
A SIMPLE TEST TO DETERMINE COATING DUCTILITY

4.1 INTRODUCTION

In use, coatings are subjected to various types of mechanical stress. The particular type, or types, of stress depend on the actual conditions of use. The different types of stress involved may require different, or sometimes even conflicting forms of mechanical behaviour of the coating. For example, automotive coatings used for exterior plastic body parts must have a sufficiently high level of polishability and stone-chipping resistance, no more than a minor (negative) effect on the high level of impact resistance of the plastic, and a high level of gloss and scratch resistance. Good polishability of automotive coatings is needed because the surface appearance of the coating after curing is sometimes poor due to craters, dust particles etc. These bad spots are repaired two hours after the painting process by slightly sanding and subsequently polishing. For this reason polishability demands a sufficiently high surface hardness of the coating shortly after curing. As the temperature of the coating increases slightly during polishing the hardness of the coating must be sufficient even at elevated temperatures. On the other hand, stone-chipping and impact resistance of the coated plastic require a high toughness of the fully cured coating at low and high temperatures. Obviously, polishability and toughness are conflicting requirements for coatings for plastics. Therefore, commercial automotive coatings need to have a finely tuned set of physical (and chemical) properties.

In this thesis we are mainly concerned with the mechanical properties of coatings. Due to their visco-elastic nature the mechanical properties of polymers, and thus of coatings, vary with temperature and deformation rate. This was discussed in detail in chapter 2. If the temperature is changed the mechanical behaviour of polymers can change from ductile deformation to brittle fracture. The temperature above which a material deforms ductile and below which it fractures in a brittle manner is called the ductile-to-brittle transition temperature $T_{DB}$. If a material has a low $T_{DB}$ it deforms ductile even at low temperatures. Therefore a material with a low $T_{DB}$ may be considered more ductile compared to a material with a high $T_{DB}$, even though the material with the higher $T_{DB}$ may have an equal or even higher fracture strain (or fracture toughness) at higher temperatures. In this study the ductility of a coating is assumed to be directly related to its $T_{DB}$. We will classify a material with a low $T_{DB}$ more ductile compared to a material with a high $T_{DB}$, although we have to be aware that the fracture properties of the former material may only be superior in the temperature range between the $T_{DB}$'s of these two materials.

It is further important to notice that the $T_{DB}$ of a polymer not only depends on composition but also on the rate of loading. In general an increase in loading rate results in an increase in the $T_{DB}$ of a material. By applying the time-temperature superposition principle the results obtained at a certain loading rate can be used to predict the behaviour of the material at
other loading rates. The mechanical fracture behaviour of materials under specified testing conditions is often sufficiently described by the corresponding value of $T_{DB}$. Actual knowledge of, e.g. the fracture strain or fracture energy, is only of minor importance.

If the temperature a material encounters during use ($T_{use}$) is higher than the $T_{DB}$ of the material, it will not fail in a brittle manner. Note that in this case we refer to the $T_{DB}$ corresponding to the actual loading conditions experienced by the sample. In general the $T_{DB}$ of a material is found below the glass transition temperature $T_g$. Above $T_g$ the modulus of a polymer is very low, unless the material is highly cross-linked or highly crystalline. Consequently, for a polymer to have a sufficiently high hardness it is often necessary that $T_{use}$ is well below $T_g$. For these reasons, the difference between $T_g$ and $T_{DB}$ is an important material parameter as it determines the temperature range where a material can be used (in the ideal case: $T_{DB} < T_{use} < T_g$). In this respect it seems appropriate to state that the difference between $T_g$ and $T_{DB}$ gives an indication of the intrinsic ductility of a polymer. The intrinsic ductility of a polymer is high if this temperature gap is wide. Wu [1] defined a ductility parameter $q$ based on the difference between $T_{DB}$ and $T_g$:

$$q = 1 - \frac{T_{DB}}{T_g}$$  \[1\]

In this equation $T_g$ and $T_{DB}$ are absolute temperatures. For very brittle materials $q$ is equal to zero ($T_{DB} = T_g$), while for extremely tough materials $q$ is 1 ($T_{DB} = 0$ K).

Determination of the $T_{DB}$ of coatings can be done by measuring the stress-strain behaviour of the coating as a function of temperature. These measurements are generally done in uniaxial tension by stretching a rectangular (or sometimes dogbone-shaped) sample of a free standing coating film at a uniform rate and simultaneously measuring the force on the specimen. These tests have the advantage that they result in knowledge of the temperature-dependence of true material properties, like the yield stress and the stress, strain and energy at break. Unfortunately, these tests also have some important drawbacks. During preparation of the coating specimens small flaws are easily introduced at the cutting edges. Fracture of the tensile coating specimen is often initiated at these small flaws [2,3]. Scatter in the results of stress-strain measurements of coatings also originates from scratches at the surface of the sample causing premature failure of the sample. Slippage, or even fracture, of the sample in the tensile grips is another cause of experimental scatter in these tests. Variation in the thickness of the coating hampers the uniformity and determination of the true (local) elongation of the material. Due to these difficulties a large number of tensile experiments is needed at each testing condition to obtain reliable values of the mechanical fracture properties.

Some of the disadvantages mentioned above can be solved by testing the coating well-bonded on a suitable carrier sheet. Ladstädter and co-workers [4,6] have applied coatings on thin sheets of (etched) PTFE and corrected the results afterwards for the known mechanical behaviour of the carrier. In this way they were able to determine the mechanical behaviour of various coatings as a function of addition of pigment, temperature, relative humidity and
strain rate (up to strain rates as high as $10^5\%\text{min}^{-1}$). Others [7,8] increased the reproducibility of tensile testing by using pre-notched samples of free films and applied the concepts of linear-elastic fracture mechanics for the quantitative evaluation of the results. Other conventional methods to determine the level of coating flexibility include the Mandrell test [9] and other bending tests [10], the Erichsen indentation film test and falling weight tests [11].

It is clear that the development and use of meaningful, reproducible tests for measuring mechanical properties of coatings is essential for the development of materials with improved properties. These tests can help to increase the basic knowledge about the parameters influencing the mechanical (fracture) properties of coatings. As explained in chapter 2 the fracture behaviour of materials depends on many variables, e.g., experimental conditions and material parameters. Experimental conditions include rate of deformation, temperature, notches, sample geometry and mode of loading. Material properties that can influence the toughness of materials are molecular weight, cross-link density, chain flexibility, crystallinity, phase morphology etc. Over the years people have tried to explain the fracture behaviour of materials in terms of dynamic mechanical properties and the possible correlation between the ductile-to-brittle transition temperature and transitions in molecular mobility has been studied extensively [12-14]. Before we will discuss the results of the research on this subject, a brief explanation of (measuring) dynamic mechanical properties of polymers will be given.

The dynamic mechanical properties of materials can easily be determined as a function of temperature and deformation rate using DMTA (dynamic mechanical thermal analysis). With DMTA a sample of the material is subjected to a small oscillating sinusoidal strain and the resulting stress is measured, see figure 4.1.

Fig. 4.1  Schematic view of the sinusoidal stress and strain curves in a DMTA experiment with $e_{\text{max}}$ is the amplitude of the applied strain, $\sigma_{\text{max}}$ is the amplitude of the measured stress and $\delta$ is the phase angle.
In this way the elastic storage modulus $E'$, the loss modulus $E''$ and the loss tangent $\tan\delta$ are determined. Here it is assumed that the sample is loaded in tension in the DMTA experiment which is the common case for dynamic mechanical testing of coatings. The value of $\tan\delta$ is a direct indication of the degree of visco-elasticity of the material. For an ideal elastic material $\tan\delta$ is equal to zero revealing that all the energy stored in the material during loading is recovered on unloading. For an ideal Newtonian liquid $\tan\delta$ becomes infinitely high as all applied energy is lost.

The strain level used in DMTA-tests is very low, much lower than the yield strain. For this reason, this test is non-destructive and the measurements can be repeated at various temperatures using the same sample. In this way, the values of $E'$, $E''$ and $\tan\delta$ can easily be determined as a function of temperature. By changing the frequency the influence of deformation rate on the dynamic mechanical behaviour of polymers can be determined. In the glass transition temperature range the value of $\tan\delta$ reaches a maximum and the peak temperature is often used to define $T_g$. This transition is called the $\alpha$-transition. At temperatures below $T_g$ other maxima of $\tan\delta$ are sometimes found, the so-called secondary transitions. When arranged in order of appearance on a decreasing temperature scale the secondary transitions are subsequently denoted $\beta$-transition, $\gamma$-transition etc.

Dynamic mechanical testing can also be used to determine the entanglement (or cross-link) density of polymers. The entanglement density $\nu_e$ can be calculated from the value of the tensile storage modulus $E'$ at a temperature well-above $T_g$ using the rubber elasticity theory [15,16]:

$$\nu_e = \frac{E'}{3RT}$$  \hspace{1cm} \text{(2)}$$

where $R$ is the gas constant and $T$ is the absolute temperature at which the rubber modulus $E'$ was measured. For uncross-linked, amorphous polymers the entanglement density varies between approximately 0.02 mmol/cm$^3$ and 0.85 mmol/cm$^3$ [15,17-19]. For cross-linked coatings the entanglement density is about 1-10 mmol/cm$^3$ [16].

Dynamical mechanical measurements give an indication of the flexibility of (parts of) the molecules and the degree of viscous losses in the material. This has led to the idea that the ductile-to-brittle transition would coincide with the (main) mechanical relaxation transition, the $T_g$. For some materials, like polystyrene, the $T_g$ and the $T_{DB}$ are found to be indeed almost equal, but for most engineering plastics the $T_{DB}$ is found below the $T_g$. It was then suggested that, if mechanical transitions are present below $T_g$, the $T_{DB}$ of a material could be related to these secondary transitions. For some polymers a clear correlation between $T_{DB}$ and $T_g$ was found experimentally, but again various exceptions to this rule were also observed. Heijboer [20] for instance found a perfect correlation between $T_{DB}$ and the secondary transition for POM. For some other polymers, however, he found a distinct secondary transition below $T_g$ but no corresponding increase in the fracture energy. Also some polymers were found to be ductile at very low temperatures although they did not show pronounced mechanical transitions below $T_g$. These experiments lead Heijboer to the conclusion that a correlation between secondary transitions and transitions in the fracture
energy of polymers can only exist if the secondary transition is caused by movement in the back-bone of the polymer, although the temperature of the secondary transition and the $T_{DB}$ may differ considerably. Furthermore, polymers with low damping may be ductile and may even show a ductile-to-brittle transition. Vincent [21-23] came to a similar conclusion after testing various engineering plastics and stated that [21] "no general correlation between $T_{DB}$ and secondary transitions exists, although there seems to be a correlation in some cases".

As the dynamic mechanical properties of polymers are measured at very small strains, whereas the transitions in the fracture behaviour are determined at high strains, it is not very likely that a general correlation between $T_{DB}$ and mechanical transitions exists. The shear yielding behaviour, the crazing behaviour and the entanglement density of the material only have a small influence on the dynamic mechanical transitions, but these properties may have a significant effect on the fracture behaviour. Furthermore, the transitions in fracture behaviour of polymers are affected by various experimental parameters, like the presence of flaws and the thickness of the sample, which do not influence the dynamic mechanical behaviour of the material.

Using the concepts of fracture mechanics the influence of e.g. flaws and material thickness can be understood. Unfortunately, they do not directly provide the material scientists with routes to synthesize materials with improved mechanical performance. For obvious reasons, a lot of research in the past decades has been focused on finding a correlation between molecular structure and mechanical properties, like toughness and creep, of polymeric materials.

The correlation between the entanglement density and the ductility parameter $q$ for uncross-linked polymers has been extensively described by Wu [15,17,24,25]. Wu has tried to correlate the value of the ductile-to-brittle transition temperature of various polymers with molecular parameters, like the chain structure and the entanglement density$^1$. Wu uses the characteristic ratio $C\infty$ as a measure of the stiffness of polymer chains. The characteristic ratio is defined as:

$$C\infty = \lim_{n \to \infty} \left[ \frac{R_0^2}{n l^2} \right]$$

[3]

where $R_0^2$ is the mean-square end-to-end distance of an unperturbed chain, $n$ is the number of effective statistical chain units, and $l^2$ is the mean-square length of such a statistical unit. The entanglement density $\nu_e$ of a polymer is directly related to the rigidity of the chains (and thus to $C\infty$):

$$\nu_e = \frac{\rho_a}{3 M_e C\infty^2}$$

[4]

$^1$ Unfortunately, Wu supposes that the $T_{DB}$ of polymers is always equal to $T_B$. As described earlier this assumption is not always true.
where \( \rho_a \) is the amorphous density and \( M_v \) is the average weight per statistical chain unit. The values of \( \nu_e \) and \( C_{\infty} \) can be determined experimentally or can be calculated from the chemical structure of the polymer [17]. Wu has postulated that the ratio between \( T_{DB} \) and \( T_g \) for polymers is a function of the rigidity of the chain. For various polymers he found that this ratio could be described by [25]:

\[
\frac{T_{DB}}{T_g} = 0.135 + 0.082C_{\infty}
\]  \[5\]

As the ratio \( \rho_a/M_v \) is almost equal for most polymers [17], equation 5 predicts that the ductility parameter \( q \) increases with increasing entanglement density. However, for materials with an intermediate to high entanglement density it is often suggested that the ductility of these materials will decrease with increasing cross-link density. A decrease in fracture energy with increasing entanglement density has been found experimentally for cross-linked epoxies, for instance by Fischer et al. [26] and by Batzer et al. [27].

In this study we will compare the toughness of coatings with various material parameters, like the \( T_g \), the \( T_{\beta} \) and the entanglement (or cross-link) density. The toughness of these coatings was determined using a newly developed test, the trouser tear test, which is discussed below. Some of the tested coatings will also be used in the impact studies described in subsequent chapters.

### 4.2 TROUSER TEAR TEST

Crack propagation in (pre-notched) materials strongly depends on temperature. Above \( T_{DB} \) the crack in the material usually propagates in a stable, ductile manner with plastic zones around the crack. Below \( T_{DB} \) the propagation of the crack generally becomes unstable (brittle) and the plastic zones almost completely disappear. Determination of the crack propagation behaviour in materials as a function of temperature can thus be used to measure \( T_{DB} \). As shown in figure 4.2 there are three fundamental modes in which a crack can be loaded. Arbitrary loading conditions can be regarded as a superposition of these 3 modes.

![Modes of loading of a crack in a material](image)

**Fig. 4.2** Modes of loading of a crack in a material. Mode-I is the tensile mode. Mode-II is the in-plane shear (sliding) mode. Mode-III is the anti-plane shear (tearing) mode.
The tensile mode (mode-I) is the most important one as it is the predominant stress situation in many practical cases and usually the one resulting in failure of the sample. In thin materials, like coatings, mode-II is unlikely to take place.

For thin, flexible materials both mode-I and mode-III type loading have been used to study crack propagation. Rivlin and Thomas and their co-workers [28-32] have extensively studied crack propagation in flexible polymeric sheets, especially rubbers. They have used various shapes of prenotched samples to determine the value of the tearing energy, defined as the amount of energy for unit crack growth per unit thickness of the material. This definition can be considered as a modification of Griffith's failure criterion for brittle solids.

One of the tests that they have used successfully is the trouser leg tear test. In figure 4.3a the shape of the sample used in this test is shown. With this test a cut is made in the sample and the two "legs" formed in this way are clamped in the grips of a standard tensile tester and the sample is subjected to tear. Under the condition that the thickness of the sheet is small and the length of the legs are long compared to the width of the specimen, the stress distribution at the tip of the crack is complex, but independent of the length of the tear [28]. The rate of stable crack propagation in this test only depends on the rate of separation of the grips and is independent of, for example, the crack length. The trouser leg tear test has been used successfully to determine the value of the tear energy as a function of temperature and crack speed for rubbers [30,31] and other polymers [33-35].

![Image of trouser leg tear test sample](image)

Fig. 4.3 Shape of the sample used in the trouser leg tear test (a), and shape of the sample of the trouser tear test used in this study in the undeformed (b) and the deformed state (c).

The advantage of the trouser leg tear test is that the stress concentration at the crack tip does not increase as the crack grows (assuming fixed grips), making this test well-suited to study stable crack propagation in materials. If a material is tested in simple tension, an increase in crack length easily leads to an increase in the stress concentration at the crack tip and this will often lead to catastrophic failure. Other advantages of the trouser leg tear test include the simple geometry and ease of clamping of the sample. Furthermore, crack growth in the trouser leg tear test will lead to a crack with a natural sharpness, independent of the sharpness of the artificial pre-cut.
The main goal of this study is the determination of the \( T_{DB} \) of coatings. For reasons mentioned above we therefore have to determine the crack propagation behaviour of the material at various temperatures. As coatings are very thin (typically 40 \( \mu \text{m} \)) they attain the surrounding temperature almost immediately, see also the discussion below. This has an enormous advantage as it allows change of the temperature \textit{during} the crack propagation test. In this way the influence of temperature on the crack propagation behaviour can be studied instantaneously in one single specimen and the temperature at which the crack propagation behaviour changes can easily be recorded. We have used this idea to determine the transition in the crack propagation behaviour in free films of coatings. For this purpose a modified trouser leg tear test was used. This modified version of the test will be called the trouser tear test to distinguish it from the trouser leg tear test. With this test two parallel pre-cuts are made in the sample. The undeformed and the deformed shape of the sample used in this test are shown in figure 4.3b and 4.3c, respectively. The advantage of the geometry used in this version of the trouser tear test is the obtained symmetrical, uniform loading of the specimen.

Figure 4.4 shows schematically the crack path that can be observed in a trouser tear test sample after subjecting it to tearing at steadily decreasing temperature (starting well-above the crack propagation transition temperature). At high temperatures the crack propagates steadily in the direction of the tearing force resulting in a smooth crack path. On lowering of the temperature the crack propagation behaviour can suddenly change. At a certain temperature the crack abruptly starts to propagate in a brittle, uncontrolled manner in a direction almost perpendicular to the direction of the applied force. Consequently, the change in the crack propagation behaviour may be regarded as a transition from stable, mode-III tearing to unstable, mode-I crack propagation. For this reason the temperature at which the crack propagation behaviour suddenly changes is strictly spoken not a "true" ductile-to-brittle transition temperature. We will call this temperature the tear transition temperature TTT to distinguish it from \( T_{DB} \).

**Temperature decreases during tearing**

![Diagram](image)

**Fig. 4.4** Schematic view of the crack path in the sample after subjecting it to a trouser tear test at a steadily decreasing temperature.
As will be shown later the TTT is very well-suited to characterize the ductility of coatings. Besides the advantages already mentioned for the trouser leg tear test, this modified test has the advantage that the measurement of the force and the elongation is not required. Especially the accurate measurement of the (small) forces observed in the trouser tear test as a function of temperature is often a difficult task. The trouser tear test can be used to determine the ductility of coatings in a relatively simple and fast way. An additional advantage of this test is that the results are neither influenced by the substrate nor by the level of adhesion between the coating and the substrate.

4.3 EXPERIMENTAL

4.3.1 Materials

To study the influence of coating flexibility on the mechanical tear behaviour, polyurethane coatings based on a polyacrylic resin and a polyester resin were used. The polyacrylic resin (Setalux® 1152xx51, Akzo Coatings) contains primary hydroxyl groups and has a high T_g. The polyester resin (Setal® 168, Akzo Coatings) is an aliphatic/ aromatic resin containing hydroxyl groups and has a low T_g. These resins are miscible over the complete range of compositions and phase separation was never observed. These coatings are named PUR−SSxx coatings, where xx denotes the percentage of the polyacrylic resin in the coating. The resins were mixed in the desired compositions and subsequently cross-linked with the biuret of hexamethylene diisocyanate (Desmodur® N75, Bayer). Curing conditions were kept constant at 4 hours at 100°C. A small amount of dibutyltin dilaurate (0.03 w/w-% based on solid weight of isocyanate cross-linker) was used to catalyze the reaction.

The influence of the thickness of the coating on the tear behaviour was investigated for coating PUR−A. This PUR−A coating is a polyurethane clearcoat with Setalux® 1152xx51 (Akzo Coatings) as the resin material. The resin was cross−linked with the isocyanurate trimer of hexamethylene diisocyanate (Desmodur® N3390, Bayer) at a curing temperature of 100°C for 7 hours. The PUR−A coating was also used in chapter 3.

For all coatings the molar ratio of hydroxyl groups and isocyanate groups was chosen 1:1. All coating components were filtered using a pressure filter (Millipore, 5.0 μm) before use.

4.3.2 Spincoating of coatings

In this study free films of the coatings were obtained by spincoating on cleaned PP-sheets using an Erichsen spincoater, model 334/2. With spincoating the substrate plate is placed on the rotor of the spincoater and an excess amount of wet paint is poured on the middle of the substrate. As the substrate is rotated most of the wet paint is spun off and a very uniform film of paint is obtained. The thickness of the coating is mainly determined by rotating speed and the viscosity of the wet coating solution [36]. In this study the typical thickness of
the coating was 40 \( \mu m \). The thickness of the cured coating was determined using magnetic induction with a Fischer Deltascope.

In one series the thickness of the PUR-A coating was varied by spincoating at various rotating speeds. In figure 4.5 the thickness of the cured PUR-A coating is given as a function of the rotating speed. The concentration of solid materials in the wet paint was kept constant at 57 w-% and the coatings were cured at 100°C for 7 hours. From figure 4.5 it can be seen that the thickness of the coating can easily be controlled by the rotating speed. The variation of the thickness of this coating spincoated over a large area \((170 \times 170 \text{ mm}^2)\) was determined to be very low (standard deviation less than 0.5 \( \mu m \)).

![Graph showing thickness of coating as a function of rotating speed.](image)

Fig 4.5  Thickness of PUR-A coating as function of rotating speed used for spincoating.

4.3.3 DMTA-measurements

Dynamic mechanical measurements (DMTA) were done as described previously in paragraph 3.3.2 using a modified Rheovibron (Toyo Baldwin, type DDV-II-C). The glass transition temperature \( T_g \) and the secondary transition temperature \( T_\beta \) are defined as the temperature where the maximum of the corresponding \( \tan \delta \) peak is found. The entanglement density \( \nu_e \) of the coatings was calculated from the rubber modulus \( E' \) measured at 150°C using equation 2.

4.3.4 Trouser Tear Test

Rectangular samples \((12 \times 30 \text{ mm})\) with two starting notches were stamped from free standing coating films using a special cutting tool placed in a hydraulic press. The distance between the starting notches was 4 mm and the initial length of the notches was 7 mm. Ten samples were made in one cutting sequence.

The experimental set-up used for the trouser tear test measurements is shown schematically
in figure 4.6. The samples were torn using a miniature tensile tester (Minimat, Polymer Laboratories) equipped with a temperature chamber. The temperature in the chamber was controlled by a flow of nitrogen obtained by placing a heating element in a liquid nitrogen vessel (Messer Griesheim, Medivent VT65). The temperature of the evaporated nitrogen was adjusted with the help of a second heating element connected to a temperature controller (Shimaden, SR24). The temperature in the chamber was measured with a thermo-couple and could be varied between $-150^\circ C$ and $+50^\circ C$. Temperature control was within 1°C of the set value. At low temperatures an additional external flow of dry nitrogen gas was used to prevent ice deposition on the outer side of the viewing window of the tensile tester.

![Diagram of experimental set-up](image)

**Fig. 4.6**  *Experimental set-up used for the trouser tear measurements.*

Tearing of the sample was done in mode-III by clamping the two outer legs of the sample in one grip and the middle leg of the sample in the other grip. The distance between the grips was increased at a speed of 0.5 mm/min or 1.0 mm/min. During the tear test the failure mode of the sample was determined through visual inspection using a macroscope (Wild, M420) with a typical magnification of 30x. The macroscope was equipped with a video camera. A second video camera was used to record the actual temperature in the temperature chamber. The images of the two cameras were mixed and recorded on video tape.

Tearing of the sample was started at a temperature where deformation of the sample took place in a ductile manner. During the test the temperature was decreased at a rate of approximately 5°C/min. On lowering the temperature the failure mode of the sample changes from stable, ductile tearing (mode-III) to rapid, brittle fracture (mode-I). The lowest temperature at which ductile tearing is found is called the tear transition temperature TTT. A minimum of five samples was tested for each material. The standard deviation in the determined value of TTT was typically less than 3°C.
4.3.5 Micro-hardness measurements

The surface hardness of the coatings was measured with a micro-indentation hardness tester (Fischer, Fischerscope H100) using a pyramid-shaped indenter. With this test the applied load on the indenter is increased stepwise and the resulting indentation is measured (typically about 20 steps). Using a pyramid-shaped indenter with a top-angle of 136°, the Vickers hardness \( H_V \) in the linear-elastic range of the coating can be calculated from the slope of the measured indentation depth \( u \) against the applied load \( F \) [37]:

\[
H_V = \frac{F}{26.43 \cdot u^2}
\]  

[6]

The applied force was adjusted in such a way that the maximum indentation depth was below 10% of the coating thickness. In this manner hardness values independent of the plastic substrate are obtained. All measurements were done at 23°C/50% RH on coatings applied on plastic sheets. A minimum of three measurements was done on each coating.

4.4 RESULTS AND DISCUSSION

In this study we have used the trouser tear test to determine the ductility of various clear coatings. The validity of this test is discussed in paragraph 4.4.1. The results of the determination of the tear transition temperature for various clear coatings are presented in paragraph 4.4.2. In one series of coatings the composition, and thus the \( T_g \) and the flexibility, of the coating was varied systematically. The measured TTT’s are compared with the values of the \( T_g \), the \( T_\beta \) and the entanglement density of the coatings. In paragraph 4.4.3 the influence of the thickness of the coating on the tear transition temperature is studied.

4.4.1 Validation of the trouser tear test

In paragraph 4.2 it was assumed that, due to the low thickness of coatings, the coating free film will attain the surrounding temperature almost immediately. For this reason, the temperature can be varied during the trouser tear test and the change in crack propagation behaviour with the change of the temperature can be studied with a single sample. The validity of this assumption was checked by calculating the temperature in a polymeric sheet as a function of time after a change of temperature at the boundaries of the sheet. The temperature of the sheet can be calculated by solving the equation of heat conduction:

\[
\frac{\partial T}{\partial t} = \frac{\lambda}{\rho c_p} \frac{\partial^2 T}{\partial x^2}
\]  

[7]

where \( t \) is the time, \( \lambda \) is the thermal conductivity, \( \rho \) is the density, \( c_p \) is the specific heat capacity and \( x \) is along the normal of the layer. For the coating sheet in the trouser tear test we assume that at \( t=0 \) the temperature at the boundaries \( (x=0 \text{ and } x=h) \) is equal to \( T_{\text{oven}} \).
and the (uniform) temperature of the sheet is \( T_0 \). The temperature \( T_x \) as a function of time at any depth \( x \) in the sheet is given by [38]:

\[
\frac{T_x - T_{oven}}{T_0 - T_{oven}} = 4 \frac{1}{\pi} \sum_{n=0}^{\infty} \frac{1}{2n+1} \cdot \exp \left( \frac{-t}{\tau_n} \right) \cdot \sin\left( (2n+1) \pi \frac{x}{h} \right)
\]

with \( \tau_n = \frac{\rho c_p h^2}{\lambda (2n+1)^2 \pi^2} \)

In figure 4.7 the calculated temperature at the mid-plane is given as a function of time for two polyurethane sheets (h=100 \( \mu \text{m} \) and h=40 \( \mu \text{m} \), respectively) and a polycarbonate sheet (h=100 \( \mu \text{m} \)).

![Graph showing temperature as a function of time for different materials](image)

**Fig. 4.7** Calculated temperature \( T \) in the middle of two polyurethane sheets (100 \( \mu \text{m} \) and 40 \( \mu \text{m} \), respectively) and a polycarbonate sheet (100 \( \mu \text{m} \)). The temperature was calculated using equation 8. Values for \( \lambda \), \( \rho \) and \( c_p \) for the polymers were taken from van Krevelen [50].

Although in practice the finite heat transfer rate at the film boundaries may slow down the relaxation of the film temperature somewhat, it is clear that even the thick polymeric sheets attain the surrounding temperature well within 100 ms. Taking into account the typical thickness of coatings of about 40 \( \mu \text{m} \) and a cooling rate of 5\(^\circ\text{C}/\text{min} \) used in the trouser tear test we can conclude that it is indeed justified to assume temperature equilibrium in the coating film. This assumption was further checked by determining the tear transition temperature of some coatings as a function of cooling rate. Within experimental error no influence of the cooling rate on the tear transition temperature of these coatings was observed. The highest cooling rate used in these experiments was 10\(^\circ\text{C}/\text{min} \). In standard trouser tear test we have used a cooling rate of approximately 5\(^\circ\text{C}/\text{min} \).
The validity of the trouser tear test to determine the crack propagation transition of coatings has also been studied by doing some cyclic trouser tear experiments. In these experiments the temperature is varied depending on the actual mode of crack propagation. If the crack in the sample grows in a stable, ductile manner the testing temperature is decreased. If the crack propagation behaviour changes to an unstable, brittle mode the temperature is increased. It was found that in this way the crack propagation behaviour in the sample subsequently changes from ductile to brittle to ductile etc. In a typical experiment the first brittle failure was found at -45°C. On increasing the temperature ductile crack propagation was observed at -40°C in this sample. As the temperature was lowered brittle fracture was again found at -43°C. Increasing the temperature again changed the crack propagation behaviour to ductile at -40°C and this experiment was terminated at -44°C where the sample fractured in a (catastrophic) brittle way. This example indicates that the sample indeed obtains the surrounding temperature very quickly. It further shows that the crack propagation transition in coatings is (remarkably) reversible. In the trouser tear tests presented below the test temperature was decreased continuously and the lowest temperature at which ductile crack propagation was observed was taken as the tear transition temperature. The reproducibility of the determination of TTT is very good, in most cases the standard deviation of TTT is less than 3°C.

4.4.2 Effect of coating composition on $T_g$, micro-hardness and TTT

For one series of polyurethane coatings the glass transition temperature, the surface hardness and the tear transition temperature were measured as a function of the ratio between the hard resin and the soft resin on which the coating was based. In figure 4.8 the glass transition temperature of these PUR–SS coatings is shown as a function of composition.

![Glass transition temperature of the PUR–SS coatings as a function of the amount of polyacrylic resin. The solid line was calculated using equation 9. The $\Delta C_p$-value of PUR–SS0 and PUR–SS100 is 0.40 J/g/K and 0.39 J/g/K, respectively (determined with DSC at a heating rate of 20°C/min).](image)
For these coatings the $T_g$ increases linearly with the amount of polyacrylic resin. It varies between 100°C for the coating based on the pure polyacrylic resin (coating PUR–SS100) and 30°C for the coating based on the pure polyester resin (coating PUR–SS0). A linear dependence of $T_g$ with concentration of one of the components has also been found for some blends of miscible polymers, like PVF$_2$–PMMA [39] and PVC–EVA [40] and miscible rubbers [41].

The effect of composition on the $T_g$ of miscible blends can often be well-described by the Couchman-equation [42,43]:

$$\ln T_{gm} = \frac{X \Delta C_{p,1} \ln T_{g,1} + (1-X) \Delta C_{p,2} \ln T_{g,2}}{X \Delta C_{p,1} + (1-X) \Delta C_{p,2}}$$

where $T_{gm}$ is the $T_g$ of the miscible blend, the indices 1 and 2 refer to the pure components, $X$ is the weight fraction of component 1 in the blend and $\Delta C_{p,i}$ is the jump in the specific heat at $T_g$. In figure 4.8 the $T_g$ calculated using the above equation is shown as a solid line. The agreement between the calculated and the experimental values of the $T_g$ of these blends is very good.

In figure 4.9 the micro-indentation hardness of the PUR–SS coatings is given as a function of the amount of the polyacrylic resin. The hardness of these coatings was measured at 23°C. As expected the hardness of the coating increases with increasing amount of the hard polyacrylic resin. Above a concentration of roughly 50% of the polyacrylic resin the hardness is almost constant. In this concentration range the $T_g$ of the polyurethane coating is high and a hardness value characteristic for polymer glasses is measured. Note that, due to the slow loading rate used in the hardness tests, the $T_g$ of the coating shifts to lower temperatures compared to the $T_g$ values measured with DMTA.

![Graph](image)

Fig. 4.9 Micro-indentation surface hardness of the PUR–SS coatings as a function of the amount of polyacrylic resin.
The tear transition temperature TTT of the PUR-SS coatings is shown in figure 4.10 as a function of the amount of polyacrylic resin for a coating thickness of 40 μm. From figure 4.10 it can be seen that the TTT decreases with the amount of the polyester resin in the coating. As a lower value of the TTT indicates a higher ductility of a material, the results of these tests clearly show that the ductility increases significantly with the amount of the soft, flexible polyester resin in the coating. For the PUR-SS0 coating a very low TTT of about −140°C is measured. Although both for the T_g and the TTT a linear dependence on composition was observed, the maximum temperature shifts in T_g and TTT with composition are rather different: 65°C and 130°C, respectively. The difference between T_g and TTT is 110°C for the PUR-SS100 coating and 175°C for the PUR-SS0 coating.

![Fig. 4.10 Tear transition temperature of the PUR-SS coatings as a function of the amount of polyacrylic resin.](image)

In figure 4.11 the tear transition temperature is given as a function of T_g for various clear coating systems including the PUR-SS coatings described above. The thickness of all coatings was kept constant at about 40 μm. For all coatings studied here the TTT is much lower than the T_g. Figure 4.11 does not show more than a very rough tendency of an increased ductility with decreasing T_g. There is a trend that the temperature difference between TTT and T_g increases with decreasing T_g. However, from this figure it can be seen that some coatings with a high T_g deviate from this general (coarse) behaviour and possess a low value of the TTT. Clearly, these coatings have a high potential to be used in automotive applications as they combine a high T_g with a very high ductility. From figure 4.11 it is clear that a general relationship between the ductility and the T_g of a material does not exist as has already been discussed in detail in the introduction.

In figure 4.12 the tear transition temperature is given as a function of the secondary transition temperature for the same coatings as in figure 4.11. The coatings that did not show a significant peak in the tanδ curve below T_g are omitted in this figure. The coatings for which the TTT was found below the lowest measuring temperature in the DMTA-
experiment are represented by an open symbol. For these coatings it cannot be excluded that the TTT is equal to a secondary transition below $T_\beta$. The other coatings are represented by a filled symbol. From this figure it is very clear that a correlation between the secondary transition temperature and the tear transition temperature is completely missing for these coatings. Of all coatings studied showing a secondary transition, the coating with the lowest $T_\beta$ has one of the highest measured values of TTT.

![Graph](image1)

**Fig. 4.11** Tear transition temperature as a function of the glass transition temperature for the PUR-SS coatings (●) and various other clear coatings (○).

![Graph](image2)

**Fig. 4.12** Tear transition temperature as a function of the secondary transition temperature $T_\beta$ for various clear coatings. Same coatings as in figure 4.11. Open symbols: TTT is lower than the lowest temperature used in the DMTA-experiment (please note that the temperature range studied with DMTA is not equal for all coatings).
We can define a ductility parameter $q'$ in a similar way as the ductility parameter $q$ defined in equation 1:

$$q' = 1 - \frac{T_{TT}}{T_g}$$  \[10\]

where $T_{TT}$ is the absolute tear transition temperature. This definition results in a $q'$-value of 0.29 for the PUR-SS100 coating and a $q'$-value of 0.57 for the PUR-SS60 coating. It is clear that these ductility parameters can only be used as a very crude indication of the ductility of materials. The values of the ductility parameters are not very sensitive to changes in the fracture behaviour of the material. As an example, if the $T_{TT}$ of the PUR-SS100 would shift over 20°C to -30°C this would result in a $q'$-value of 0.35. This is only a minor increase in the value of $q'$, although the shift of $T_{TT}$ over 20°C is very significant for the practical applicability of a coating.

The ductility factor $q'$ of the coatings shown in figure 4.11 is plotted as a function of entanglement density in figure 4.13. The entanglement density was calculated from the rubber modulus at 150°C using equation 2. In this figure the ductility factor $q$ for the polymers described previously in table 2.1 is also given. For these polymers the $T_{DB}$ was obtained from the literature (references given in chapter 2). The value of the entanglement density for these polymers was taken from Wu [15,17].

![Graph showing the relationship between ductility parameter and entanglement density](image)

**Fig. 4.13** The ductility factor $q$ ($1 - T_{DB}/T_g$) for various polymers and the ductility factor $q'$ ($1 - T_{TT}/T_g$) for various coatings as a function of the entanglement density. The data for $T_{DB}$, $T_g$ and $T_{TT}$ of the polymers were taken from the literature (same polymers as in table 2.1). The coatings are the same as in figure 4.11. Open symbols: value of $q$ calculated using equation 5.

Although the ductility parameters $q$ and $q'$ are defined slightly differently and were measured under different loading conditions, these parameters can be compared qualitatively. From figure 4.13 it can be seen that the ductility parameter $q$ increases with
increasing entanglement density at low entanglement densities. In the region of high entanglement density the ductility parameter q' decreases with increasing entanglement density. For this reason it seems justified to assume that there is a maximum in the ductility parameter at intermediate entanglement density. This maximum can be explained as follows. At very low values of the entanglement density stable crazes are not formed in the material as the chains are easily pulled out of the polymer network. As a consequence the material is very brittle. In a highly cross-linked material the chains can extend only to a limited degree due to the restriction caused by the entanglements and the material is brittle again. This behaviour has also been found experimentally for epoxy resins. Both Bell et al. [44,45] and Kim et al. [46] found a maximum in the fracture energy as a function of entanglement density for various epoxy resins.

4.4.3 Effect of coating thickness on TTT

It is known that the failure mode of polymers may change from ductile to brittle on increasing the thickness of the specimen [18,47-49]. This transition is generally attributed to a change in the ratio between the amount of material deforming under plane-stress conditions (material close to the free surfaces of the specimen) and the amount of material deforming under plane-strain conditions (the centre part of the specimen). If the thickness of the material increases this ratio decreases which may result in a more brittle behaviour of the sample [48,49]. In this study the influence of the thickness of the coating on the tear transition temperature was investigated for the PUR-A coating.

![Tear transition temperature of the PUR-A coating as a function of the thickness of the specimen.](image)

In figure 4.14 the measured tear transition temperature of the PUR-A coating is given as a function of the thickness of the free film. From this figure it is obvious that increasing the thickness of the coating results in a significant increase in the TTT, and thus in an increased brittleness of the coating. Although the thickness range studied for this coating is not very
wide, the observed shift in TTT of more than 20°C is indeed large. As the glass transition temperature of the coating was not influenced by changing the film thickness the q\textsuperscript{\textcircled{a}}-value changes from 0.23 for the thin coatings to 0.30 for the thick coatings. Unfortunately it was not possible to determine the tear transition temperature of coatings with a thickness of less than about 20 μm. The transition from ductile tearing to brittle fracture is very difficult to observe for these very thin coatings.

The results of these experiments clearly indicate that the influence of the layer thickness on the ductility of coatings cannot be neglected but should always be taken into account.

4.5 CONCLUSIONS

With a modified trouser tear test the transition in the crack propagation behaviour of coatings can be easily determined. The temperature at which the crack propagation behaviour changes from ductile to brittle is called the tear transition temperature TTT and this temperature is a direct measure of the ductility of the coating. The experimental set-up for this test is simple and the measurements of the TTT can be done in a fast way. The reproducibility of the TTT is very good. With this test the ductility of coatings is determined using free films and is thus independent of e.g. the behaviour of the substrate and the level of adhesion.

In this study the TTT of various clear coatings was determined. It was shown that an unique correlation between the ductility and either the T\textsubscript{g} or the T\textsubscript{β} of the coating does not exist. An optimum in ductility was found at an entanglement density of approximately 1 mmol/cm\textsuperscript{3}. It was further found that the ductility of coatings decreases with increasing thickness of the specimen.

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A QUANTITATIVE ADHESION TEST FOR COATED PLASTICS

5.1 INTRODUCTION

Currently, coatings for plastic is a fast growing market. In the automotive industry in particular, more and more plastic parts are being used for components such as bumpers, wheel and mirror housings and spoilers. Frequently, these plastic parts are provided with a coating both for decorative reasons and for protection of the plastic against degradation due to ultraviolet rays or solvents (petrol, etc.). In both cases good adhesion between coating and substrate is of vital importance. For most engineering plastics, coatings have been developed that have excellent adhesive properties. Even for plastics that are difficult to paint such as apolar or very crystalline plastics, coatings have been developed with a sufficient level of adhesion. For apolar materials the adhesion can be improved further by applying suitable surface treatments such as corona discharge and flame treatment [1]. Attempts aimed at raising the adhesion of water-borne and high-solids coatings - which are becoming increasingly important - to a sufficiently high level have also been successful.

The development of coatings with good adhesive properties has been more successful than the development of a theoretical model for adhesion. Many theories have been developed [2–8], but a universal model is lacking [8]. One of the problems is that there is insufficient consensus about a good definition of adhesion. In such discussions a distinction can be made between the so-called basic adhesion and practical adhesion. Basic adhesion is the level of adhesion that is reached by intermolecular attractive forces if two materials are brought into close (molecular) contact. Basic adhesion neglects the influence which defects at the interface may have on the level of adhesion. Practical adhesion is described in terms of the amount of energy required to cause delamination. In this chapter we are concerned with practical adhesion only.

There are several tests to measure the adhesion of a coating to a (plastic) substrate, such as the peel test [9–11], the pull-off test [12–14] and the cross-cut test [15,16]. The problem of many of the existing adhesion tests is that they are often only qualitative or very time-consuming. No single adhesion test is fully satisfactory. In this study a quantitative test is presented for the determination of the adhesion of coatings on plastics.

Roche and co-workers [17–20] introduced a flexure test to measure the adhesion of coatings to metal substrates. We have adapted this test so that it can be used as quantitative adhesion test for coatings on plastic substrates. This modified test is called the double cantilever adhesion test (DCAT)\(^1\). It is based on linear elastic fracture mechanics and results in a value for the energy release rate for the initiation of coating delamination. The energy release rate

---

\(^1\) There is also a fracture toughness/adhesion test which is called the double cantilever beam (DCB) test (see, for example, reference 7). However, the geometry of this test deviates from that of the DCAT described here.
is the amount of energy required to delaminate the coating from the substrate per unit area. The advantage of the DCAT is that the value of the energy release rate should be a characteristic value of the level of adhesion, independent of the test geometry used. This makes the DCAT well-suited for characterizing the level of adhesion of coatings and consequently for developing and comparing coatings.

The derivation of the expression for the energy release rate for the DCAT is described in detail below. The validity of the formulae derived for the DCAT is tested in a series of model experiments. The DCAT is then used to determine the influence of adhesion promoters, testing temperature and of the substrate cleaning procedures on the level of adhesion. Both strongly adhering and poorly adhering coatings are tested. Finally, the DCAT results are compared with those of the cross-cut test.

The DCAT measures the energy release rate for the initiation of coating delamination. For crack growth in homogeneous materials, it is generally found that the energy required to initiate a crack is higher than that needed to propagate an existing crack. As a result, we may expect that for a certain coating/substrate system the energy release rate for initiation of coating debonding ($G_c$) is higher than the energy release rate for a stable, propagating crack between the coating and plastic substrate ($G_p$). This implies that the adhesion between two materials cannot be fully described with only one value for the level of adhesion (leaving aside the effects of temperature and test rate on adhesion levels). To verify this, we developed a second quantitative adhesion test based on the above-mentioned DCAT. This modified test is the single cantilever adhesion test (SCAT) and it can be used to determine the energy release rates for both initiation of coating debonding and stable crack propagation. The SCAT is discussed in detail in the Appendix.

5.2 THEORY

The DCAT, shown schematically in figure 5.1, uses a rectangular piece of coated substrate. In the middle of the coated side of the substrate a stiff, perfectly adhering, rectangular block is applied. If this sample is loaded in a three-point flexure test, the adhesion between the coating and the substrate fails when a critical force $F_c$ is reached. Delamination starts at one of the outer edges of central block and a crack propagates between the coating and the substrate. Owing to this delamination, the stiffness of the sample decreases. If the crack growth rate is high relative to the test rate, the force drops as soon as the coating starts to debond.

When a coating delaminates from a substrate, a crack grows between both materials. So we can compare the level of adhesion between coating and substrate, or rather the resistance to delamination, with the resistance to crack growth between coating and substrate. Crack growth in materials can often be described using linear elastic fracture mechanics. The theory of fracture mechanics can be found in many textbooks [21–24]. A measure of the
resistance of a material to cracking is the energy release rate \( G \). By definition, the energy release rate is the total amount of energy required to propagate a crack in a homogeneous material over unit area of fracture. Analogously, the energy release rate for delamination between a coating and a substrate can be defined as the amount of energy required to debond the coating from the substrate per unit area. Consequently, the energy release rate is a direct measure of the level of adhesion between coating and substrate. Below, we present the derivation of a quantitative expression for the energy release rate for the DCAT.

![Schematic diagram of the set-up used for the DCAT.](image)

**Fig. 5.1** Schematic diagram of the set-up used for the DCAT.

At the moment of initiation of delamination between coating and substrate, the value of the energy release rate is equal to the critical energy release rate \( G_c \). \( G_c \) is equal to the sum of the applied external energy \( \delta U_{\text{ext}} \) and the change in the stored elastic energy \( \delta U_{\text{elast}} \) per unit area \( A \) over which delamination took place:

\[
G_c = \frac{\delta U_{\text{ext}}}{\delta A} - \frac{\delta U_{\text{elast}}}{\delta A} \quad [1]
\]

The width of the delaminated area of the DCAT specimen is limited by the width of the central block. The increase in the size of the delaminated area \( \delta A \) may be written as \( B_{\text{block}} \delta a \), where \( B_{\text{block}} \) is the width of the central block and \( \delta a \) is the increase of the length of the delaminated area (equal to the crack length). If the sample deforms linear elastically, equation 1 can be written as follows [21]:

\[
G_c = \frac{\delta U_{\text{ext}}}{\delta A} - \frac{\delta U_{\text{elast}}}{\delta A} = F \frac{\delta u}{\delta A} - \frac{\delta (\frac{1}{2} Fu)}{\delta A} = \frac{F}{2} \frac{\delta u}{\delta A} - \frac{u}{2} \frac{\delta F}{\delta A} \ \ [2]
\]

\[
= \frac{F}{2} \frac{\delta (FC)}{\delta A} - \frac{u}{2} \frac{\delta F}{\delta A} = \frac{F^2}{2B_{\text{block}}} \frac{\delta C}{\delta a}
\]

where \( u \) and \( F \) are the central deflection and force, respectively, and \( C \) is the compliance of
the sample \((C = u/F)\).

The compliance of a rectangular bar subjected to a three-point flexure test is well-known [22]:

\[
C = \frac{u}{F} = \frac{L^3}{48EI} \cdot \left[ 1 + 3 \left( 1 + \frac{\nu}{2} \right) \frac{H^2}{L^2} \right]
\]  

where \(E\) is the flexural modulus, \(I\) is the moment of inertia of the bar, \(\nu\) is Poisson’s ratio and \(H\) is the thickness of the bar. In equation 3, \(L\) is the effective free length of the sample, that is the length over which the sample can bend. In a general three-point flexure test, \(L\) is equal to the distance between the outer supporting rods (the support length). The right-hand side term between the square brackets in equation 3 is the shear contribution, which can be neglected if \(H/L \ll 1\). In that case, the compliance is proportional to \(L^3\):

\[
C = \frac{L^3}{48EI} \quad \text{for } \frac{H}{L} \ll 1
\]  

Equation 4 may also be used to describe the compliance of the DCAT sample. As a first approximation we may assume that the central block is infinitely stiff relative to the substrate. Consequently, the effective free length of the DCAT sample is equal to the difference between the support length \(L_{\text{span}}\) and the length of the central block \(L_{\text{block}}\):

\[
L = L_{\text{span}} - L_{\text{block}}
\]  

In practice the stiffness of the central block is not infinite and the central block deforms slightly during loading. The effects of the finite stiffness of the central block can be incorporated in the model by increasing the effective free length with a small correction term \(2f\). The effective free length of the DCAT sample now becomes:

\[
L = L_{\text{span}} - L_{\text{block}} + 2f
\]  

If \(L\) is large enough so that equation 4 applies, the correction term can be calculated from the measured compliance \(C\) of the DCAT sample and the flexural modulus of the substrate \(E\):

\[
2f = \sqrt[3]{\frac{3}{48EIC}} - (L_{\text{span}} - L_{\text{block}})
\]  

The correction factor can also be estimated using finite element calculations [25]. These calculations and experiments have shown that the correction term for unreinforced plastic samples is small and can be approximated by \(2f = 1.5 \times H\).

If a crack starts to grow between the coating and the substrate, the mechanical contact between the substrate and the central block is locally lost. It therefore follows that debonding
of the coating increases the effective free length of the sample by an amount equal to the crack length. In our model the effective free length can thus be written as:

\[ L = L_{\text{span}} - L_{\text{block}} + 2f + a \]  \[8\]

Combining equations 4 and 8 we can easily calculate the first derivative of the compliance with respect to crack length required to solve equation 2:

\[ \frac{\delta C}{\delta a} = \frac{3(L_{\text{span}} - L_{\text{block}} + 2f + a)^2}{48\ E\ I} = \frac{3C}{(L_{\text{span}} - L_{\text{block}} + 2f + a)} \]  \[9\]

Finally, substitution of the result of equation 9 in equation 2 in the limit \( a \to 0 \) results in an expression for the energy release rate at crack initiation:

\[ G_c = \frac{3\ F_c^2 C}{2B_{\text{block}} (L_{\text{span}} - L_{\text{block}} + 2f)} \]  \[10\]

The critical energy release rate can be calculated from the compliance of the sample and from the force at the onset of coating delamination; both can be determined from the force–deflection curve.

5.3 EXPERIMENTAL

5.3.1 Materials and pretreatment of substrate

In this study, the adhesion of different substrate-coating combinations was investigated using the DCAT. Five different substrate materials were chosen from those frequently used for plastic parts in the automotive industry. A description of the substrate materials used is given below.

1) IM PBT/PC: a rubber-modified blend of polybutylene terephthalate (PBT) and polycarbonate (PC). This material was obtained from General Electric Plastics (Xenoy® CL101 with a thickness of 3.0 mm) and was provided with coating A (see below for more details about the coatings used).

2) TPE: thermoplastic elastomer from DSM Plastics (Arnitel® S74D, thickness of 2.1 mm). TPE was provided with coating B.

3) IM PA66/PPE: a rubber-modified blend of polyamide 66 and polyphenylene ether. This blend was supplied by General Electric Plastics (Noryl® GTX940) as sheet material with a thickness of 3.0 mm. Prior to coating, the IM PA66/PPE sheets were dried under vacuum (110 °C/20 h). IM PA66/PPE was provided with coating C.

4) PP/EPDM-copolymer: a DSM product (Stamylan® P83MF10 with a thickness of 3.0 mm) comprising polypropylene (PP) and EPDM, a copolymer of ethylene, propylene and
dicyclopentadiene. Stamylan® P83MF10 contains about 7% EPDM and was provided with coating D.

5) EPDM-modified PP: produced by Hoechst (Hostalen® PPX653 with a thickness of 3.0 mm). This blends contains about 30% EPDM and is very flexible. The EPDM-modified PP was provided with coating E.

Details of the coatings used are as follows.
A) Coating A is an experimental, water-borne coating.
B) Coating B is a two-layer system consisting of a flexible primer (floating surfacer, Akzo Coatings) and a colour coating.
C) Coating C is a polyurethane coating. An acrylate polyl with primary hydroxy groups (Setalux® 1152xx51, M_w = 9000, Akzo Coatings) was used as resin material. This resin was cross-linked with the isocyanurate trimer of hexamethylene diisocyanate. The molar ratio between hydroxy groups and isocyanate groups was 1:1. This coating was cured at 100 °C for 7 hours. Coating C is identical to the PUR-A coating used in some of the previous chapters.
D) Coating D is a pigmented primer and contains an acrylate polyl and a polyester polyl as resin material. Coating D was cured for 20 minutes at 80 °C.
E) Coating E is an experimental, pigmented, water-borne primer. This coating contains an acrylate resin and was cured at 90 °C for 30 minutes.

Coating C was applied by spincoating, the other coatings were sprayed by hand. The thickness of all coatings was about 40 μm.

Sometimes the level of adhesion of coatings can be considerably increased by incorporating specific additions (adhesion promoters) into the coating formulation. In this investigation the level of adhesion of coatings D and E was varied by the addition of suitable adhesion promoters (HV-I and HV-II, respectively).

In general the substrates were cleaned with isopropyl alcohol prior to coating. However, the effect of substrate cleaning was investigated in detail for IM PA66/PPE. For this purpose, the substrate was coated after:

- no pretreatment (uncleaned);
- cleaning with isopropyl alcohol; and
- immersion in a hot alkaline solution (2M NaOH, 85 °C), rinsing with demineralized water, followed by cleaning with isopropyl alcohol.

To decrease the level of adhesion, some samples were treated with a release agent for cold-curing epoxies (QZ11®, Ciba-Geigy).

5.3.2 Experimental procedures

Samples for the DCAT were sawn from the coated panels; sample dimensions were 14 × 50 mm². To ensure proper adhesion between the coating and the central block, the
coated side of the sample was roughened slightly with a suitable domestic abrasive. Next, the samples were rinsed with demineralized water, dried and subsequently cleaned with isopropyl alcohol. The cleaned samples were placed in a holder and a small block of cold-curing epoxy adhesive was applied to the centre of each sample (see figure 5.1). This block, measuring 10 * 10 * 15 mm\(^3\) (B * H * L), consisted of a two-component epoxy system (Araldit\(^\circ\) AW106 and Araldit\(^\circ\) HV953U, both from Ciba-Geigy). The two components were mixed in the disposable static mixer supplied with the package and cast in a silicone rubber mould. This mould had been placed on the samples to ensure correct positioning of the central block on the sample, see figure 5.2. Next the epoxy was cured for 3 days at room temperature since curing of the epoxy at elevated temperatures could lead to penetration of the epoxy through the coating.

![Application of epoxy adhesive central blocks.](image)

For the determination of \(G_c\)-values for bulk materials pre-cut samples are often used, the use of these cuts leading to a well-defined starting condition of the sample. The force at which the crack starts to grow, and consequently the value of \(G_c\), is lower for pre-cut samples. The application of a cut between coating and substrate will also lead to a lower \(G_c\)-value for the DCT, as has been observed experimentally for some coating/substrate systems. However, in practice, the application of a sharp initial cut between coating and substrate is not possible for properly adhering systems and therefore was omitted in this investigation.

In the flexure adhesion test using metal substrates, cuts are often made around the central block in the coating to ensure delamination to take place only under the central block only. In polymer substrates such cuts have not been applied because they may cause crack growth in the substrate during the flexure test and thus lead to an erroneous \(G_c\)-determination.
The three-point flexure test was carried out according to ASTM D-790M (method 1, procedure B) on a Zwick tensile tester, type 1474. The diameter of the supports was 6 mm. The centre distance between the outer supports was varied in one set of tests; in other experiments it was 45 mm. The cross-head speed was either 0.5 or 1.0 mm/min. About five samples of each material were tested. The compliance of the load transducer used was 0.6 μm/N.

The flexural modulus of the substrate material was measured on a sample without a central block at a support length of 35 mm.

After completion of the test the central block was removed from each sample. The delaminated areas were inspected under a microscope to establish the occurrence of adhesive failure (delamination; i.e., crack growth between coating and substrate) or cohesive failure (i.e., crack growth through the coating or through the substrate). We define a failure to be cohesive if the two newly created fracture surfaces have the same appearance.

In practice the level of adhesion of coatings is often determined using the cross-cut test. In this test six horizontal and six vertical cuts are made in the coating, the distance between the parallel cuts being constant. The resulting cross-cut area is provided with an adhesive tape which is subsequently removed. Next, the surface of the cross-cut area is inspected visually and evaluated. In view of its simplicity the cross-cut test is frequently used to test the level of adhesion. However, this test has some serious drawbacks: (1) the adhesion of the tape to the coating is neither reproducible nor the same for different coatings; (2) the evaluation of this test is subjective; (3) the reproducibility of this test is poor; and (4) precise cutting of the coating is difficult to achieve (especially in the case of plastic substrates). The cross-cut test was carried out according to ISO-2409. The cuts in the sample were applied mechanically (six horizontal and six vertical cuts, the mutual distance between the cuts being 1 mm). An ISO rating of 0 implies that no coating is removed (excellent adhesion) and an ISO rating of 5 indicates coating removal over a large area (poor adhesion).

5.4 RESULTS AND DISCUSSION

In the theoretical derivation of equation 10 it is assumed that the shear contribution to the compliance can be neglected if the support length is large enough. In that case equation 4 can be used to describe the compliance of the sample. Rearrangement of this equation yields:

\[ E = \frac{L^3}{48 \, IC} \]  \hspace{1cm} [11]

In figure 5.3 the experimental values of \(L^3/48IC\) are plotted against \(L\) for two different materials (TPE and IM PA66/PPE).
Fig. 5.3 Experimental values of $L^3/48IC$ as a function of the support length, $L$, measured in a three point flexure test at 23 °C for two uncoated materials.

From this figure it is clear that a constant value of $L^3/48IC$ is indeed reached at large values of $L$. By definition, this value is the flexural modulus of the material. From figure 5.3 it is apparent that the shear contribution to the compliance can be neglected if $L$ is greater than about seven times the thickness of the substrate $H$ (which, for the TPE and IM PA66/PPE samples, is 2.1 and 3.0 mm, respectively). In the DCAT we should choose the support length such that the following requirement is satisfied: $L_{\text{span}} - L_{\text{block}}$ must be greater than about 7H.

In this study the DCAT was used to determine the adhesion of different coatings to plastic substrates. Equation 10 was used to calculate $G_c$ from the measured compliance and the force at which delamination started. The correction factor $2f$ was calculated from the measured compliance of the test-piece and the flexural modulus of the (uncoated) substrate using equation 7. After each test the area where delamination started was examined microscopically. In the examples discussed below the failure was often adhesive; i.e., crack growth took place between coating and substrate. However, this does not always apply. Like any other strength test, the DCAT measures the strength of the weakest link. At a high level of adhesion between the coating and the substrate, cohesive failure may occur. Then the crack propagates entirely through the coating, or in the case of some very flexible substrates, entirely through the substrate.

Figure 5.4 shows some experimental force-deflection curves measured on IM PBT/PC provided with coating A. This figure gives a representative picture of the experimental variation in the force-deflection curves of the DCAT. The $G_c$-value for coating A on IM PBT/PC calculated using equation 10 is $0.29 \pm 0.01$ kJ/m$^2$. This value of $G_c$ is comparable with the data mentioned in the literature for bulk specimens of thermohardeners [23,26,27]. The variability in the values for $G_c$ measured with the DCAT is often about 10 – 15%.
Fig. 5.4  Example of some experimental DCAT force–deflection curves measured on IM PBT/PC provided with coating A. For convenience of comparison, each time the curves are shifted 0.2 mm over the deflection axis.

5.4.1  Model experiments

According to theory, the value of the energy release rate is independent of the geometry used. In other words, $G_c$ is a fundamental physical quantity that relates to the level of adhesion. To examine this, the value of $G_c$ for one coated substrate (TPE with coating B) was determined as a function of the support length $L_{span}$, the thickness of the central block $H_{block}$ and the stiffness of the substrate, which was increased by gluing a metal strip to the uncoated side of the substrate. The results of these model experiments are summarized in Table 5.1.

Table 5.1  Model experiments on TPE with coating B. The value of $G_c$ was determined for different values of the support length and the thickness of the central block. The stiffness of one sample was increased by reinforcing the substrate with a metal strip.

<table>
<thead>
<tr>
<th>$H_{block}$ mm</th>
<th>$L_{span}$ mm</th>
<th>$C_{exp}$ mm/N</th>
<th>$F_c$ N</th>
<th>$G_c$ kJ/m²</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>30</td>
<td>0.013</td>
<td>44.3</td>
<td>0.23</td>
</tr>
<tr>
<td>10</td>
<td>35</td>
<td>0.027</td>
<td>31.4</td>
<td>0.19</td>
</tr>
<tr>
<td>10</td>
<td>40</td>
<td>0.047</td>
<td>26.4</td>
<td>0.19</td>
</tr>
<tr>
<td>10</td>
<td>45</td>
<td>0.078</td>
<td>24.3</td>
<td>0.22</td>
</tr>
<tr>
<td>5</td>
<td>40</td>
<td>0.048</td>
<td>29.1</td>
<td>0.23</td>
</tr>
<tr>
<td>10 *</td>
<td>40</td>
<td>0.007</td>
<td>80.5</td>
<td>0.23</td>
</tr>
</tbody>
</table>

* Sample with metal strip
The results given in table 5.1 show that the value of $G_c$ is almost the same for all experiments even though the compliance varies by a factor $> 10$ and the critical force by a factor $> 3$. From these experiments it is evident that the results of the DCAT, evaluated using equation 10, are independent of the test parameters used.

### 5.4.2 Influence of concentration of adhesion promoter and test temperature

The influence of the concentration of adhesion promoter (HV–I) on the $G_c$-value measured for coating D on a PP/EPDM copolymer is shown in figure 5.5. Without the use of HV–I the level of adhesion of this coating is very low and the force at which delamination occurs in the DCAT cannot be measured properly. This very low level of adhesion is due to the apolar character of the PP/EPDM copolymer. When using HV–I the energy release rate $G_c$, and consequently the level of adhesion, increases almost linearly with the concentration of adhesion promoter.

![Critical energy release rate, $G_c$, for delamination of coating D on a PP/EPDM copolymer substrate as a function of the concentration of adhesion promoter (HV–I).](image)

In figure 5.6 the effect of adhesion promoter (HV–II) concentration on $G_c$ for coating E applied to EPDM-modified PP, measured at two different temperatures (23 °C and −20 °C) is given. In the temperature region studied the level of adhesion of coating E on EPDM-modified PP is almost independent of temperature. Both at 23 °C and at −20 °C there is a slight increase in the level of adhesion at low HV–II concentrations. Increasing the HV–II concentration to above 4% results in considerably increased adhesion between coating and substrate. At an HV–II concentration of 7.5% the level of adhesion of this coating at room temperature is higher than the cohesive strength of the very flexible EPDM-modified PP, and cohesive failure of the substrate is observed in this test. At −20 °C no cohesive failure occurs in the substrate for this concentration of adhesion promoter. Figure 5.6 shows that the $G_c$-value for delamination of this coating is high.
Cohesive failure of flexible substrates is often caused by a low yield stress of the material. When the temperature is decreased (or the test rate increased) the yield stress of polymers increases, reducing the chance of cohesive failure. At 23 °C the yield stress of this blend is 12 MPa; at -20 °C it increases to 23 MPa. This explains why at an HV–II concentration of 7.5% cohesive failure in the substrate occurs at 23 °C, whereas at -20 °C delamination between coating and substrate takes place. The decrease in test temperature also leads to an increase in the flexural modulus of the EPDM–modified PP substrate, from 700 MPa at 23 °C to 1500 MPa at -20 °C.

5.4.3 Influence of the cleaning method of the substrate

Plastic parts must often be cleaned prior to coating. Their surfaces may be contaminated by dust particles, release agents and additives from the plastic material. All these contaminations on the substrate surface may have a negative influence on the level of adhesion between coating and substrate, and should be removed prior to coating.

The effect of substrate cleaning on the level of adhesion was investigated for coating C on IM PA66/PPE. Figure 5.7 shows the level of adhesion between coating and substrate as a function of the cleaning method used. If the uncleaned substrate is coated, the $G_c$-value amounts to 0.3 kJ/m². Cleaning with isopropyl alcohol prior to coating doubles the level of adhesion, while cleaning the substrate with a hot alkaline solution increases $G_c$ to 1.4 kJ/m². The level of adhesion reached after the alkaline treatment is relatively high, but the reason for this increase is not fully clear. It is known that the adhesion can increase considerably due to mechanical interlocking [28]. However, comparison of the scanning electron micrographs does not show any difference between the uncleaned surface and the surface after the alkaline treatment. Consequently, it is not likely that this high level of adhesion can
be ascribed exclusively to an increase in surface roughness. Figure 5.7 also shows the level of adhesion after pretreatment of the surface with a release agent for thermohardeners. This pretreatment leads to an extremely weak interface and the level of adhesion measured is indeed very low.

### 5.4.4 Effect of plastic deformation of substrate

Equation 10 was derived for materials showing linear elastic mechanical behaviour. In practice the substrate may show some plastic deformation before delamination occurs in case of properly adhering coatings. If the substrate starts to yield prior to debonding of the coating, we must use the recoverable elastic energy $U_{\text{rec. elast}}$ in equation 2 instead of the total area under the force–deflection curve $U_{\text{total}}$. In hysteresis experiments, the recoverable elastic energy can be determined as the area under the unloading curve. For a material showing some plastic deformation, the force–deflection curve as measured in a hysteresis experiment is schematically represented in figure 5.8.

The recoverable elastic energy for many materials can be approximated by:

$$U_{\text{rec.elast}} = \frac{1}{2} F^2 C$$

where $C$ is the compliance at small deflection. For IM PA66/PPE the values of $U_{\text{total}}$, $U_{\text{rec. elast}}$ and $\frac{1}{2} F^2 C$ measured as a function of the maximum deflection are given in figure 5.9. From this figure it is apparent that equation 12 gives a satisfactory approximation of the recoverable elastic energy of materials, even if the material shows some plastic deformation. It can easily be seen that the expression for the energy release rate (equation 10) does not change if use is made of the above equation for $U_{\text{rec. elast}}$. We assume that equation 10 also applies if some plastic deformation occurs prior to the moment of delamination.
Fig. 5.8  Schematic representation of a hysteresis flexure force-deflection curve for a material showing some plastic deformation. $U_{\text{total}}$ is the area under the loading curve, $U_{\text{rec.elast}}$ is the area under the unloading curve. The area surrounded by the dashed line is equal to $\frac{1}{2} F^2 C$.

Fig. 5.9  Total area under the loading curve (○), total area under the unloading curve (○) and calculated value for $\frac{1}{2} F^2 C$ (solid line) for different values of the maximum deflection in a three-point flexure test measured on uncoated IM PA66/PPE.

In the case of large deflections of the substrate, the recoverable elastic energy is almost constant due to extensive plastic deformation (see also figure 5.9). Hence there is a maximum limit to the value of $G_c$ that can be measured with the DCAT. This limiting value of $G_c$ is determined by the yield stress $\sigma_y$ and the modulus $E$ of the substrate and by the
geometry of the sample:

\[
G_{c\max} = \frac{3}{8} \frac{BH}{B_{block}} \frac{\sigma_y^2}{E}
\]  \[13\]

where B and H are the width and thickness of the substrate sheet, respectively.

Equation 13 shows that the applicability of the DCAT is limited in the case of very flexible substrates (low \(\sigma_y\)) and in the case of very brittle substrates (substitution of fracture stress instead of \(\sigma_y\) in equation 13). For these materials the DCAT can only be used for poorly adhering coatings where \(G_c < G_{c\max}\).

An increase of the limiting value of \(G_c\) by increasing the substrate thickness often leads to an unacceptably high value of the correction term 2f (see equation 7) and consequently provides no solution. The same problem may occur when using very stiff substrates (metals, etc.).

5.4.5 Comparison with the cross cut test

In figure 5.10 the results of the adhesion measurements with the DCAT are compared with those of the cross-cut test. The results of the coating/substrate combinations described above and those of various other coated substrates have been included in this figure.

![Plot](image)

Fig. 5.10 Comparison of the values of the critical energy release rate, \(G_c\), for delamination with the results of the cross-cut test for various coated substrates.

There is a reasonable correlation between both tests for coatings having a poor to moderate level of adhesion. Above a specific level of adhesion, corresponding to a \(G_c\)-value of about 0.25 kJ/m², no coating is removed in the cross-cut test and all the samples are given a cross-cut rating of 0. Using the DCAT we do find clear differences in the level of adhesion
$G_c$ between the various coated substrates. These results show that there is a reasonable agreement between the DCAT and the cross-cut test. In the case of properly adhering coatings, however, the discriminating ability of the DCAT is far greater than that of the cross-cut test.

5.5 CONCLUSIONS

This chapter presents a quantitative adhesion test for coated plastics, the so-called double cantilever adhesion test (DCAT). This test can be used to determine the value for the critical energy release rate $G_c$ at the onset of coating delamination. The energy release rate is the amount of energy needed to debond a coating from a substrate per unit area. The value of $G_c$ is independent of the experimentalist and the test geometry used. It can be calculated from the compliance of the test specimen and the force level at which delamination of the coating starts. Both values can easily be determined with a standard tensile tester.

In this study the DCAT was used to determine the effectiveness of some adhesion promoters. It was demonstrated that the method of pretreating the surface of a plastic prior to coating may have a large influence on the level of adhesion. The results of the DCAT for several coated substrates have been compared with the results of the cross-cut test. There is a reasonable correlation for coatings with poor to moderate levels of adhesion. For coatings with a higher level of adhesion no differences are measured in the cross-cut test. In these cases significant differences in the level of adhesion can still be determined with the DCAT.

5.6 REFERENCES

INFLUENCE OF LEVEL OF ADHESION AND COATING THICKNESS ON THE IMPACT BEHAVIOUR OF COATED PLASTICS

6.1 INTRODUCTION

In chapter 3 a model was presented describing the fracture behaviour of coated plastics as a function of the level of adhesion of the coating on the substrate, the thickness of the coating and the mechanical properties of the coating and the substrate. It was shown that the application of a well-adhering polyurethane coating with a thickness of only 40 μm has a large detrimental influence on the mechanical impact properties of a very ductile, impact modified blend of polyamide-66 and polyphenylene ether (IM PA66/PPE). This surface embrittlement is often found if a brittle layer is present on a ductile substrate. It has been observed both for coated plastics [1-10] and for plastics after (outdoor) weathering [11-14]. Surface embrittlement is attributed to the lower fracture strain of the brittle layer compared to that of the ductile substrate. If the coated or weathered substrate is deformed the brittle layer fractures at a low strain level. The resulting crack in the brittle layer can propagate through the interface and cause premature failure of the substrate. Consequently, it can be expected that the surface embrittlement effect strongly depends on the actual fracture behaviour of the brittle layer and on the strength of the interface. The effect of the interface is described in this chapter while the effect of the fracture behaviour of the coating is described in the next chapter.

If the crack in the brittle layer reaches the interface with the substrate there is a competition between crack propagation along the interface (debonding), crack propagation perpendicular to the interface and arrest of the crack at the interface or in the substrate material. For this reason it can be expected that the level of adhesion of the coating on the substrate can play an important role in the fracture behaviour of coated plastics. Some authors [1,4,10,15,16] have indeed postulated that the surface embrittlement effect for coated plastics reduces significantly if the level of adhesion of the coating is low, although they provided little experimental data to support this hypothesis.

In the work described in this chapter the influence of the level of adhesion of a polyurethane clear coating on the fracture behaviour of IM PA66/PPE is determined experimentally. The level of adhesion of this coating on IM PA66/PPE can be varied over a broad range by changing the pretreatment of the surface of the substrate material. This has the advantage that the influence of the level of adhesion on the impact behaviour of the coated plastic can be studied without changing the (mechanical properties of) the coating. The actual level of adhesion is quantified using the DCAT method described in detail in chapter 5.

The influence of the coating thickness on the impact properties of coated IM PA66/PPE was also investigated. The thickness of the polyurethane coating was varied at both a high level of adhesion and at a moderate level of adhesion. It is known that changing the thickness of a material may influence its fracture properties. For this reason the high-speed tensile fracture
behaviour of the coating applied on the substrate was determined as a function of its thickness.

6.2 PREDICTIONS OF THE MODEL

The model presented in chapter 3 can be used to predict the influence of the level of adhesion and the coating thickness on the mechanical fracture behaviour of a coated plastic. In chapter 3 it was assumed that, after fracture of the coating layer, the crack from the coating can either cause delamination of the coating, can be arrested at or near the interface, or may cause fracture of the coated substrate. It must be mentioned that this model gives no more than a simplified description of the fracture behaviour of coated plastics as it is assumed that the coating and substrate deform in a linear-elastic manner. Although this assumption may be valid if the coated plastic fractures in a brittle way, it is certainly not valid at strains above the yield point of the substrate. Nevertheless, we may use this model for a qualitative description of the influence of the level of adhesion between coating and substrate on the fracture behaviour of coated plastics. It can also be used to predict the influence of the coating thickness on the fracture properties.

Delamination of the coating can occur if the elastic energy stored in the coating at the moment the crack reaches the interface is higher than the critical energy release rate for coating delamination \( G_{c,adh} \). This results in the following condition for coating delamination:

\[
G_{c,adh} \leq E_{coat} h \left( \frac{1}{2} \varepsilon_{f,c}^2 + \frac{1}{(1-\nu)} \varepsilon_{res}^2 \right)
\]  

[1]

where \( E_{coat} \) is the elastic modulus of the coating, \( h \) is the coating thickness, \( \varepsilon_{f,c} \) is the tensile fracture strain of the coating, \( \nu \) is poisson’s ratio and \( \varepsilon_{res} \) is the biaxial residual strain in the coating. The residual strain in the coating may be caused by e.g. solvent evaporation after solidification of the coating and by a difference between the thermal shrinkage of the coating and the substrate after cooling down from the curing temperature.

Alternatively the crack from the coating can be arrested at the interface of the coating and the substrate or in the substrate material under certain conditions. For a coating of thickness \( h \) the condition under which the crack is arrested is given by:

\[
\frac{(K_{la})_{sub}}{E_{sub}} \geq \varepsilon_{f,c} Y \sqrt{h}
\]

[2]

where \( (K_{la})_{sub} \) is the arrest toughness of the substrate, \( E_{sub} \) is the modulus of the substrate and \( Y \) is a constant depending on geometry. In the derivation of equation 2 it was assumed
that $h$ is greater than the critical thickness value $h^*$ [17] given by:

$$h^* = \left( \frac{K_{la}}{Y \sigma_y} \right)^2$$  \hspace{1cm} [3]

where $\sigma_y$ is the yield stress of the substrate material.

If neither delamination of the coating nor crack arrest occurs, fracture of the coating will lead to premature failure of the coated substrate. From equation 2 it is clear that catastrophic growth of the crack from the coating through the substrate can occur if:

$$\frac{(K_{la})_{sub}}{E_{sub}} < \varepsilon_{f,c} Y \sqrt{h}$$  \hspace{1cm} [4]

Under certain conditions it is feasible that both delamination of the coating and catastrophic crack growth are possible, that is, both the condition given by equation 1 and that given by equation 4 are satisfied. In order to predict which of these processes will occur under these conditions we have to know the relative probabilities of these processes. In our simplified model we define the likelihood for delamination of the coating $P_{deb}$ as:

$$P_{deb} = 1 - \frac{G_{c,adh}}{E_{coat} h \left( \frac{1}{2} \varepsilon_{f,c}^2 + \frac{1}{(1-v)} \varepsilon_{res}^2 \right)}$$  \hspace{1cm} [5]

Delamination of the coating can occur if $0 < P_{deb} \leq 1$, for $P_{deb} \leq 0$ the coating remains adhered on the substrate.\footnote{It must be realized that $P_{deb}$ as defined here is not equal to the (mathematical) probability for the debonding event. In this model it is only used to allow the comparison of the relative chances for coating debonding and catastrophic crack growth.}

In a similar way we can define the likelihood for catastrophic crack growth as:

$$P_{cat} = 1 - \frac{(K_{la})_{sub}}{\sigma_{s,fc} Y \sqrt{h}}$$  \hspace{1cm} [6]

where $\sigma_{s,fc}$ is the stress in the substrate at the moment of fracture of the coating. Catastrophic growth of the coating crack can occur if $0 < P_{cat} \leq 1$, for $P_{cat} \leq 0$ the crack from the coating is arrested.

We will assume here that under those conditions that both $P_{deb}$ and $P_{cat}$ are larger than zero, \textit{only} the process with the highest likelihood value takes place. This is schematically shown
in figure 6.1. In this figure it is assumed that $P_{\text{deb}}$ is independent of temperature whereas $P_{\text{cat}}$ increases linearly with decreasing temperature (discussed below). Note that for real systems other, more complicated, temperature-dependencies of $P_{\text{deb}}$ and $P_{\text{cat}}$ are possible. The temperature at which $P_{\text{deb}}$ is equal to $P_{\text{cat}}$ is the ductile-to-brittle transition temperature $T_{\text{DB}}$ of the coated substrate. Below $T_{\text{DB}}$, the crack from the coating grows catastrophically through the substrate, above $T_{\text{DB}}$ the coating delaminates from the substrate and the surface embrittlement effect is not observed. It should be mentioned here that with the definition of $T_{\text{DB}}$ used in this thesis it is more correct to define $T_{\text{DB}}$ as the temperature just below the temperature where $P_{\text{deb}}$ and $P_{\text{cat}}$ are equal.

![Diagram](image)

Fig. 6.1 Schematic representation of the likelihood of delamination $P_{\text{deb}}$ and the likelihood of catastrophic crack growth $P_{\text{cat}}$ as a function of temperature. See text for more details.

6.2.1 Implications of the model at a very low level of adhesion

If the level of adhesion of a coating is very low ($G_{c,\text{adh}} \approx 0$), fracture of the coating layer will immediately result in delamination of the coating ($P_{\text{deb}} \approx 1$). In that case the coating and the substrate can be considered to deform independently during loading of the coated sample and the fracture behaviour of the coated plastic will be equal to the fracture behaviour of the uncoated substrate. Changing the thickness of the coating while maintaining the low level of adhesion does not result in a different fracture behaviour of the coated substrate. Consequently, the surface embrittlement effect is never present if the level of adhesion of the brittle layer on the substrate is extremely low. However, on increasing the layer thickness the ductile-to-brittle transition of the coating itself can shift to higher temperatures, see chapter 4. The qualitative prediction of the fracture strain of the coated plastic and that of the coating is shown graphically in figure 6.2 as a function of temperature for a substrate coated with a non-adhering coating. The fracture strains are given for a low coating thickness ($\approx 10 \mu m$, figure 6.2a), an intermediate coating thickness ($\approx 40 \mu m$, figure 6.2b) and a high coating thickness ($\approx 100 \mu m$, figure 6.2c). Note that the absolute values of
the coating thickness given here are not calculated values but are only provided as an indication of the magnitude of the thickness.

Fig. 6.2 Schematic representation of the temperature dependence of the elongation at break of the coating, the coated substrate and the uncoated substrate predicted by the model. The level of adhesion of the coating is very low. The elongations at break are given for low coating thickness (a), intermediate coating thickness (b) and high coating thickness (c).
6.2.2 Implications of the model at a very high level of adhesion

If the level of adhesion between the coating and the substrate is very high, the prediction of the mechanical behaviour of the coated substrate is somewhat more complicated. At a high level of adhesion the condition for delamination of the coating as given by equation 1 is never satisfied and debonding of the coating does not occur ($P_{deb} < 0$). The likelihood that the crack from the coating is arrested at the interface or in the substrate increases with decreasing thickness of the coating as can be seen from equations 2 and 6. Furthermore, the likelihood of catastrophic crack growth is a function of temperature through the temperature dependencies of $\sigma_{c,fr}$ and the $K_{fr}$ value of the substrate. For practical systems it is often observed that the stress in the substrate at the moment of brittle fracture of the coating increases with decreasing temperature. It is further expected that the value of the crack arrest toughness of the substrate is either constant or decreases with decreasing temperature. For these reasons equation 6 predicts that the likelihood of catastrophic crack growth increases on lowering the temperature. Consequently, for a given coated substrate there is a minimum temperature below which arrest of the crack can not take place. This temperature is denoted $T^{min\_arrest}$ (see also figure 6.1) and it decreases with decreasing thickness of the coating. Above $T^{min\_arrest}$ crack arrest can be observed. In that case coating failure does not result in immediate fracture of the coated substrate. The fracture strain of the coated substrate can even become identical to that of the uncoated substrate if the thickness of the coating is sufficiently reduced. Unfortunately, calculation of the exact thickness of the coating layer below which the surface embrittlement effect no longer takes place is not possible with a linear–elastic fracture model (equation 6 is only valid for $h > h^*$). The qualitative predictions of the fracture strain of the coated plastic and that of the coating are shown in figure 6.3a as a function of temperature for this well–adhering coating of low thickness ($\approx 10 \mu m$).

Increasing the thickness of a well–bonded coating has several effects. Firstly, increasing the thickness of the coating results in an increase in $T^{min\_arrest}$ and in a decrease of the likelihood of crack arrest at a given temperature above $T^{min\_arrest}$. As discussed above the ductile–to–brittle transition of coatings shifts to higher temperatures on increasing the layer thickness. All these effects cause a rapid increase of the ductile–to–brittle transition temperature of the coated substrate with increasing thickness of the well–bonded coating. Observe that the ductile–to–brittle transition of the coating is the upper limit of the ductile–to–brittle transition of the coated substrate.

Due to the increase of the elastic modulus and the yield stress of the substrate on lowering of the temperature it is expected that the stress in the substrate at the moment of coating fracture increases with decreasing temperature. This results in a decreasing likelihood for crack arrest for a given coating thickness with decreasing temperature. This effect can be even more pronounced if the crack arrest toughness of the substrate decreases with temperature. As the occurrence of crack arrest depends both on temperature and on coating thickness it is not easy to predict the fracture strain of coated plastics quantitatively.
Fig. 6.3  Schematic representation of the temperature dependence of the elongation at break of the coating, the coated substrate and the uncoated substrate predicted by the model. The level of adhesion of the coating is high. The elongations at break are given for low coating thickness (a), intermediate coating thickness (b) and high coating thickness (c).

However, if the thickness of the coating is not too low, it is unlikely that crack arrest will lead to a considerably higher fracture strain of the coated plastics. This was already
discussed in chapter 3. In figure 6.3b and figure 6.3c the fracture strain of the coating and the coated substrate are given for a perfectly adhering coating with an intermediate thickness (≈ 40 μm) and a high thickness (≈ 100 μm), respectively.

6.2.3 Implications of the model at an intermediate level of adhesion

If the adhesion between the coating and the substrate is at an intermediate level, the situation is even more complex as the likelihood of delamination of the coating after coating fracture also has to be taken into account. To predict the fracture behaviour of the coated plastic at an intermediate level of adhesion the influence of temperature and coating thickness on $P_{deb}$ and $P_{cat}$ should be known. For this purpose some approximations have to be made. As a first approximation we assume that the fracture energy of a brittle coating ($\frac{1}{2}E_{coat}e_f^2$) is independent of temperature and thickness of the coating. If we further assume that the biaxial residual strain in the coating is always small compared to the fracture strain, it follows that the likelihood of delamination is linearly proportional to $G_{c,adh}$ and inversely proportional to $h$. As a further simplification, $G_{c,adh}$ can be considered to be independent of temperature in which case $P_{deb}$ is independent of temperature.

For a relatively thin coating at an intermediate level of adhesion $P_{deb}$ will be negative unless the elastic energy stored in the coating is very large. Consequently, debonding of the thin coating will not take place. For this reason the fracture behaviour of a substrate coated with a thin coating at an intermediate level of adhesion is identical to the behaviour of a substrate coated with a thin, perfectly-adhering coating. The fracture strain of the coated plastic and that of the coating is shown in figure 6.4a for a thin coating at an intermediate level of adhesion.

If the coating thickness is increased while maintaining the same level of adhesion, the likelihood that the coating delaminates after it fractures increases. On the other hand, increasing the thickness of the coating will also lead to an increase of $P_{cat}$. For this reason the fracture behaviour of this coated substrate strongly depends on the actual temperature dependence of the arrest toughness and modulus of the substrate and the temperature dependence of the debonding process. However, the fracture behaviour of the coated plastic at an intermediate level of adhesion will always be between the fracture behaviour of the substrate with the well-bonded coating and the fracture behaviour of the substrate with an extremely bad-adhering coating.

An example of possible temperature-dependencies of the fracture strain of the coated plastic and that of the coating is shown in figure 6.4b for this coating with an intermediate thickness (≈ 40 μm). Here it is assumed that the fracture behaviour of the substrate with a coating of intermediate thickness is somewhat inferior compared to that of the substrate with a thin coating.

On increasing the coating thickness further the fracture behaviour of the coated substrate
may slightly improve as $P_{\text{deb}}$ increases more rapidly with the coating thickness than $P_{\text{cat}}$ ($P_{\text{deb}}$ and $P_{\text{cat}}$ are proportional to $h$ and $h^\alpha$, respectively). This is shown in figure 6.4c.

![Diagram showing fracture strain vs. temperature for uncoated and coated materials.]

**Fig. 6.4** Schematic representation of the temperature dependence of the elongation at break of the coating, the coated substrate and the uncoated substrate predicted by the model for an intermediate level of adhesion of the coating. The elongations at break are given for low coating thickness (a), intermediate coating thickness (b) and high coating thickness (c).
6.3 EXPERIMENTAL

6.3.1 Materials

A rubber-modified polyamide-66/polyphenylene ether-blend (IM PA66/PPE), known commercially as Noryl® GTX 940 (GE Plastics), was used as substrate material. The PA66/PPE ratio of this blend is approximately 1. Noryl® GTX 940 was obtained as sheet material (170 * 170 * 3 mm³). All sheets were dried at 110°C under vacuum for 20 hours prior to the coating process.

A polyurethane (PUR-A) clear coating was used as coating material. The PUR-A coating is based on Setalux® 1152xx51 (Akzo Coatings). The Setalux resin was cross-linked with the isocyanurate trimer of hexamethylene diisocyanate (Desmodur® N3390, Bayer) at a curing temperature of 100°C for 7 hours. The molar ratio of hydroxyl groups and isocyanate groups was chosen 1:1. All coating components were filtered using a pressure filter (Millipore, 5.0 μm) before use. The PUR-A coating was also used in chapters 3-5. The PUR-A coating was applied on the IM PA66/PPE sheets using spincoating. The thickness of the coating was controlled by adjusting the rotating speed. For more details on this technique the reader is referred to paragraph 4.3.2.

The level of adhesion of the PUR-A coating was varied by using different treatments for the IM PA66/PPE sheets prior to application of the coating. A consistently low level of adhesion of the PUR-A coating was obtained after treating the substrate surface with a release agent (RA) for cold curing epoxies (QZ11®, Ciba-Geigy). An intermediate level of adhesion was obtained after a standard cleaning procedure of the substrate: wiping the surface with a cloth saturated with isopropyl alcohol (iPA). The highest level of adhesion of the PUR-A coating on IM PA66/PPE was obtained after washing the substrate sheets in a hot alkaline solution (2M NaOH, 85 °C), rinsing with demineralised water followed by cleaning the sheets with isopropyl alcohol. These pretreatments of the IM PA66/PPE substrate were also used in the previous chapter.

Dogbone-shaped tensile specimens (DIN 53 455, specimen number 3) were stamped from the coated sheets using a special cutting tool placed in a hydraulic press. Cutting was done at elevated temperature (75°C) to facilitate the cutting process and to prevent cracking of the coating layer. The length-axis of the tensile samples was parallel to the direction of injection moulding. All materials were tested after drying under vacuum at 20°C for a minimum period of 2 days.

6.3.2 High speed tensile testing

The impact behaviour of the coated samples was determined with high-speed tensile tests done at various temperatures. These tests were carried out on a servo-hydraulic material tester (Schenck VHS 25/20). A transient recorder (ADAM TC 210-4, Maurer) was used for
the analog data acquisition of the force and displacement signals during the tests. A small temperature chamber was used for the experiments done at temperatures other than room temperature. For these experiments the samples were preconditioned at the test temperature in a separate temperature chamber (Grasso, type GTTS 27.70) for a minimum period of one hour. The samples were then placed in the temperature chamber of the tensile tester for at least 10 minutes before testing. Further details on high-speed tensile testing and the testing procedure used can be found in chapter 2.

All high-speed tensile tests were done at a test speed of 1 m/s, resulting in a strain rate of approximately $10^5\text{\%min}^{-1}$ ($= 17\text{ s}^{-1}$). A minimum of four samples was tested at each temperature. The results of tests where fracture of the sample was clearly caused by the presence of an impurity in the material were ignored in the calculation of the average fracture data.

As discussed in chapter 2 we will preferentially use elongation instead of the effective engineering strain in this thesis. If the engineering strain value is required it may be calculated from the elongation data using equation 3 given in paragraph 2.2.4.

6.3.3 Determination of the level of adhesion

The level of adhesion of the PUR-A coating as a function of the pretreatment of the substrate and of the thickness of the coating was determined using the DCAT method [18]. Full details on the experimental procedure used for this test can be found in paragraph 5.3.2.

The samples (14 $\times$ 50 mm$^2$) for the DCAT were carefully sawn from the coated panels. The coated side of the sample was roughened slightly with an abrasive and subsequently cleaned. The cleaned samples were placed in a holder. Using a silicone rubber mould a small block (10 $\times$ 10 $\times$ 15 mm$^3$) of a cold-curing, two-component epoxy adhesive (Araldit® AW106 and Araldit® HV953U, both from Ciba-Geigy) was applied to the centre of each sample.

After curing the adhesive for a minimum of three days at room temperature, the DCAT samples were subjected to a three-point flexure test. These tests were carried out according to ASTM D 790M (method I, procedure B) on a Zwick tensile tester, type 1474. The diameter of the supports was 6 mm. The centre distance between the outer supports was 45 mm and the cross-head speed was 1.0 mm/min. For each material a minimum of six samples were tested. The flexural modulus of the substrate material was measured on a sample without a central block at a support length of 35 mm. After completion of the test the delaminated area of each sample was inspected under a microscope. All samples described in this chapter failed adhesively.

6.3.4 Determination of the coating fracture point using a graphite layer

For the determination of the fracture point of the coating layer on the substrate during a high
speed tensile test a very thin, conductive graphite layer (Graphit 33, Kontakt Chemie) is sprayed on top of the coating layer. During a high speed tensile test the electrical resistance of the graphite layer is measured using a transient recorder. Crack growth in the coating layer will also cause fracture of the thin graphite layer on top of it. Consequently, the first crack in the coating can be observed as a very sharp increase in the measured electrical resistance of the graphite layer. This method is described in more detail in paragraph 3.3.5.

6.4 RESULTS AND DISCUSSION

The model presented in paragraph 6.2 for the description of the mechanical fracture behaviour of coated plastics is based on several assumptions. The validity of these assumptions is studied by comparison with experimental data. Furthermore, the predicted joint effects of the level of adhesion and the thickness of the coating on the fracture behaviour of coated plastics are verified experimentally.

6.4.1 The adhesion level as a function of pretreatment and coating thickness

In figure 6.5 the level of adhesion of the PUR-A coating on IM PA66/PPE is given as a function of coating thickness for various pretreatments of the substrate. The level of adhesion was determined with the DCAT method described in detail in chapter 5 [18].

![Graph showing critical energy release rate as a function of coating thickness and pretreatment](image)

**Fig. 6.5** Critical energy release rate, $G_{c,adh}$, for the delamination of the PUR-A coating on IM PA66/PPE as a function of coating thickness and pretreatment of the substrate prior to application of the coating. The standard deviation of the $G_{c,adh}$-value are represented by the error bars.

The highest level of adhesion of the coating is obtained after the alkaline treatment of the substrate. Cleaning of the substrate surface with isopropyl alcohol (iPA-treatment) results in an intermediate level of adhesion, whereas a very low level of adhesion of the coating is
obtained after treating the substrate with a release agent (RA-treatment). These results clearly show that the level of adhesion of the PUR-A coating on IM PA66/PPE can be varied over a very broad range.

Although the scatter in the level of adhesion of these samples is relatively high, these results further show that the thickness of the coating has a pronounced influence on the level of adhesion especially for the PUR-A coating applied after the IPA-treatment. A marked influence of the coating thickness on the level of adhesion has been reported by others [19-26]. Several authors [19,21,24,25] have observed a maximum in the plot of the energy release rate as a function of the thickness of coating. Unfortunately, a satisfactory explanation for the observed influence of the thickness of the coating on the energy release rate has not been given.

6.4.2 Influence of a PUR-A coating at a very low level of adhesion

The high-speed tensile elongation at break of IM PA66/PPE coated after the RA-treatment with a 40 μm layer of PUR-A is shown in figure 6.6 as a function of temperature. In this figure the elongation at break of uncoated IM PA66/PPE is also shown.

![Graph showing elongation at break as a function of temperature](image)

**Fig. 6.6** Elongation at break as a function of temperature measured in a high-speed tensile test of uncoated IM PA66/PPE (solid line), coated IM PA66/PPE (○) and the PUR-A coating (○) for a coating thickness of 40 μm. The coating was applied after the RA-treatment.

After the RA-treatment the level of adhesion of the PUR-A coating on IM PA66/PPE is extremely low, $G_{c,adh}$ is only 0.02 kJ/m². From figure 6.6 it can be seen that the high-speed mechanical tensile properties of IM PA66/PPE coated after the RA-treatment with a 40 μm PUR-A coating are very similar to those of uncoated IM PA66/PPE and it is clear that the application of the 40 μm PUR-A coating at this level of adhesion does not cause a significant change in the ductile-to-brittle transition temperature of the substrate material. In the temperature range studied it was found that the PUR-A coating always completely
debonded from the substrate during the high-speed tensile test. It was further observed that fracture in all tested samples started somewhere in the bulk of the specimen. The same behaviour was observed with the high-speed tensile tests on uncoated samples, see chapter 2.

The elongation at break of the PUR-A coating as a function of temperature is also shown in figure 6.6. The elongation at break of the coating was determined during the high-speed tensile tests by measuring the electrical resistance of a thin graphite layer sprayed on top of the coating layer. A consistently low value for the elongation at break of the PUR-A coating over the temperature range investigated was observed. Such behaviour is as expected taking into account the brittleness of the PUR-A coating.

In chapter 3 the results of the determination of the elongation at break of a 40 µm PUR-A coating applied on IM PA66/PPE after the alkaline treatment were presented (these results are shown again in figure 6.8b, see below). Comparison of these sets of results shows that the elongation at break of the coating applied after the RA-treatment is somewhat lower compared to that of the alkaline treated samples. This is most probably due to the cutting process used to make the tensile specimen. As the level of adhesion of the coating with the RA-treatment is extremely low, the coating partly debonds from the substrate during the cutting process. In this case debonding of the coating during the cutting process is most certainly unavoidable as the level of adhesion of the coating will be low compared to the stored elastic energy due to residual stresses in the coating. This can cause spontaneous delamination as explained in detail in paragraph 3.2.1. Delamination of the coating from the substrate easily leads to small cracks in the coating at the cutting edges. On loading the specimen in a tensile test these cracks can cause fracture of the coating at a lower strain level compared to that of a well-bonded, uncracked coating.

The model presented in paragraph 6.2 predicts that at a very low level of adhesion the mechanical fracture behaviour of coated substrates is not influenced by the thickness of the coating. In the case of very weakly adhering coatings, fracture of the coating during loading of the specimen will immediately result in debonding and, consequently, the mechanical fracture behaviour of the substrate is not worsened by the application of a non-adhering coating. As discussed above, preparation of samples with a weakly adhering layer is hampered by spontaneous delamination of the coating especially for thick coatings. For these reasons, the influence of the thickness of the PUR-A coating on the impact properties of IM PA66/PPE after the RA-treatment was not further studied.

### 6.4.3 Influence of the coating thickness at a high level of adhesion

The high speed mechanical tensile properties of IM PA66/PPE coated with PUR-A after the alkaline treatment were determined as a function of coating thickness. The measured elongation at break of the coated substrate and that of the coating are given as a function of temperature in figure 6.7a, 6.7b and 6.7c for a thickness of the PUR-A coating of 13 µm, 40 µm and 65 µm, respectively. The elongation at break of uncoated IM PA66/PPE is also
Fig. 6.7  Elongation at break as a function of temperature measured in a high-speed tensile test of uncoated IM PA66/PPE (solid line), coated IM PA66/PPE (○) and the PUR-A coating (○). The coating was applied after the alkaline treatment. The thickness of the coating is (a) 13 μm, (b) 40 μm and (c) 65 μm.
shown in these figures. For all samples tested delamination of the coating was not observed. This observation supports the high level of adhesion of the PUR-A coating following the alkaline treatment as measured with the DCAT.

The mechanical properties of IM PA66/PPE coated with a 40 μm PUR-A coating after the alkaline treatment were already discussed in chapter 3. The impact properties of these coated samples were found to differ significantly compared to those of the uncoated substrate. The ductile-to-brittle transition temperature $T_{DB}$ of the coated material was found at 15°C whereas for the uncoated substrate it was found at -60°C. On application of the perfectly adhering PUR-A coating with a thickness of 40 μm the $T_{DB}$ is shifted over 75°C. Below the ductile-to-brittle transition of the coated substrate, fracture of the coated substrate was always initiated at the coated side of the specimen. Above $T_{DB}$ of the coated substrate, both fracture initiated at the coated side and fracture initiated in the bulk of the substrate was observed. This was found to be caused by the increased elongation at break of the coating at these higher temperatures.

In figure 6.7a the elongation at break of the coated substrate for a coating thickness of 13 μm is shown in comparison with the elongation at break of the uncoated substrate. In this figure the temperature dependence of the elongation at break of the coating is also given. The fracture behaviour of the coated substrate with a coating thickness of 13 μm is completely different from that with a coating thickness of 40 μm. On lowering the thickness of the PUR-A coating from 40 μm to 13 μm the ductile-to-brittle transition temperature of the coated substrate decreases from +15°C to -30°C. From figure 6.7 it is clear that this shift of the ductile-to-brittle transition is not caused by a change in the fracture behaviour of the coating. Although the ductile-to-brittle transition temperature of the thinner coating is somewhat lower ($T_{DB}$ is 10°C for the 13 μm coating compared to 15°C for the 40 μm coating), the shift in the ductile-to-brittle transition of the coated substrate is much larger. At -30°C fracture of the 13 μm coating caused immediate fracture of the substrate. Crack arrest did not occur under these conditions. For every sample tested at -30°C it was observed that only one crack had developed in the coating layer during the test. From the detailed observations on the fracture surfaces it could be concluded that fracture in these samples always started at the coated side. In the temperature range from -20°C to 15°C it was found that the (first) crack from the coating was arrested at the interface of the coating and the substrate or in the substrate material and often more than one crack was found to develop in the coating layer. This latter observation also gives an indication that the first crack in the coating is arrested in the ductile substrate material.

The elongation at break of the coated substrate for a high coating thickness (65 μm) is given in figure 6.7c as a function of temperature. The elongation at break of the coating and the elongation at break of the uncoated substrate are also shown in this figure. The results shown in figure 6.7c are very similar to the elongations at break of the coating and the substrate measured for the substrate with the 40 μm coating. For both coating thicknesses the elongation at break of the coated substrate is almost equal to the elongation at break of
the coating over the entire temperature range studied and, consequently, the ductile-to-brittle transition temperatures of the coating and the coated substrate are almost identical. For a coating thickness of 65 \( \mu m \) the ductile-to-brittle transition temperature of the coated substrate is 35°C, that of the coating is found at a slightly lower temperature (30°C). These ductile-to-brittle transition temperatures are somewhat higher than those measured for the 40 \( \mu m \) coating. The higher ductile-to-brittle transition temperature of the 65 \( \mu m \) coating indicates that the ductility of the coating decreases with increasing thickness. This was also found in the trouser tear experiments described in chapter 4 of this thesis.

Below the ductile-to-brittle transition temperature of the coated substrate at 30°C, the elongation at break of the substrate is practically identical to the elongation at break of the coating. Above this temperature the elongations at break of the substrate and the coating differ slightly. This indicates that in this temperature range crack arrest does occur in the coated samples. Yet, these results show that crack arrest is only of minor importance for the actual fracture behaviour of the coated substrate in this case.

Debonding of the coating was never observed for these samples despite the higher thickness of the coating and the slightly lower level of adhesion.

The results shown in figure 6.7 are in good agreement with the qualitative predictions made using the model presented in paragraph 6.2 for a substrate with a well-adhering coating (figure 6.3). As predicted in paragraph 6.2 the \( T_{DB} \) of the coated substrate increases with increasing thickness of the coating. On decreasing the coating thickness the likelihood of crack arrest increases at a given temperature. The results presented in figure 6.7 show that in the temperature range between -20°C and 10°C the elongation at break of the PUR-A coated IM PA66/PPE strongly depends on the thickness of the coating. This is caused by crack arrest taking place for the 13 \( \mu m \) coating resulting in a significant improvement of the fracture behaviour of the coated substrate compared to that found for the substrate coated with thicker coatings. The influence of the coating thickness on the mechanical behaviour of the coated substrate observed above 10°C for these coatings is mainly due to the shift of the \( T_{DB} \) of the coating on changing its thickness. A strong dependence of the surface embrittlement effect on the thickness of the brittle layer has also been described in the literature [2,8,12,27-30].

Using the fracture properties determined in this study for the coating and the coated substrate the validity of equation 2 can be examined. The value of the stress intensity factor \( K_t \) of the crack reaching the interface between the coating and the substrate can be calculated from the stress in the substrate at the moment of coating fracture using equation 2. It is assumed that the notch length is equal to the coating thickness. Details on these calculations are given in chapter 2. As the calculation of \( K_t \) using equation 2 is only valid under linear-elastic conditions, experiments in which the fracture strain of the coating exceeded the yield strain of the substrate were omitted. The results of the samples coated with the 13 \( \mu m \) coating were also omitted as this coating thickness is below the critical value \( h^* \).

The calculated values of \( K_t \) for the coated samples are given in figure 6.8 as a function of temperature and coating thickness. The solid symbols in this figure mark the experiments in
which crack arrest occurred. An experiment is represented by an open symbol if the fracture point of the coating and the coated substrate were equal (catastrophic crack growth).

![Temperature dependence of the value of the stress intensity factor of the crack from the coating reaching the interface calculated for individual tests. The coating was applied on the substrate after the alkaline treatment. The thickness of the coating is 40 μm (circles) or 65 μm (triangles). The dashed line represents a possible temperature-dependency of $K_{la}$ of IM PA66/PPE.](image)

Fig. 6.8

Temperature dependence of the value of the stress intensity factor of the crack from the coating reaching the interface calculated for individual tests. The coating was applied on the substrate after the alkaline treatment. The thickness of the coating is 40 μm (circles) or 65 μm (triangles). The dashed line represents a possible temperature-dependency of $K_{la}$ of IM PA66/PPE.

The fracture mechanics model presented above predicts that crack arrest in a coated substrate can only occur if $K_1$ of the crack from the coating is below a critical value. This critical value is called the crack arrest toughness $K_{la}$ of the substrate. The value of $K_{la}$ of a substrate depends on the actual testing conditions. Figure 6.8 shows that, at a given temperature, the value of $K_1$ for samples in which crack arrest was found is indeed always lower compared to the value of $K_1$ for samples which failed by catastrophic crack growth. These results further show that the stress intensity factor for crack arrest $K_{la}$ of IM PA66/PPE increases slightly with temperature, at least in the temperature range between 0°C and 30°C. Note that the value of $K_1$ of the crack (and thus the value of $\sigma_{s,fc}$) increases with decreasing temperature as was assumed in paragraph 6.2.

6.4.4 Influence of the coating thickness at an intermediate level of adhesion

After the iPA-treatment the adhesion of the PUR-A coating on IM PA66/PPE is at a level intermediate between that found after the RA-treatment and that found after the alkaline treatment. As shown in chapter 5 the level of adhesion obtained after the iPA-treatment is still moderately high compared to the adhesion level obtained in industrial practice (cross-hatch ranking of zero). It was found that the level of adhesion after an iPA-treatment of the substrate depends on the thickness of the coating. The high-speed mechanical tensile properties of IM PA66/PPE coated with PUR-A after the iPA-treatment were determined as a function of coating thickness. In figure 6.9a, 6.9b and 6.9c,
Fig. 6.9  Elongation at break as a function of temperature measured in a high-speed tensile test of uncoated IM PA66/PPE (solid line), coated IM PA66/PPE (○) and the PUR-A coating (○). The coating was applied after the IPA-treatment. The thickness of the coating is (a) 13 μm, (b) 40 μm and (c) 65 μm.
the measured elongation at break of the coated substrate and of the coating are given as a function of temperature for a PUR-A coating thickness of 13 μm, 40 μm and 75 μm, respectively. In these figures the elongation at break of uncoated IM PA66/PPE is also given.

In paragraph 6.2 it was predicted that for a coated substrate with a thin coating and an intermediate level of adhesion between the coating and the substrate delamination of the coating would not occur. Under these conditions the fracture behaviour is predicted to be equal to that of a well-adhering coating with the same thickness. Comparing the results of the high-speed tensile tests for IM PA66/PPE with the thin, well-adhering coating and the thin coating with an intermediate level of adhesion as shown in figure 6.7a and figure 6.9a, respectively, it is obvious that the fracture behaviour of these materials is indeed strikingly similar. Note that the level of adhesion of these coatings is very different. The ductile-to-brittle transition temperature for both materials is found at −30°C. Above T_{DB} of the coated substrate arrest of the crack from the coating is observed in all samples and the fracture points of the coating and the coated substrate start to differ considerably. At temperatures above −20°C no surface embrittlement effect is observed.

It must be mentioned that delamination of the thin coating was not completely absent in the samples with an intermediate level of adhesion of the coating. At a testing temperature of −10°C and −20°C partial debonding of the coating was observed in some of the tested samples. This is probably caused by the relatively low level of adhesion that is obtained after the IPA-treatment with very thin coatings.

The elongation at break of the coating and of the coated substrate as a function of temperature are shown in figure 6.9b for a coating thickness of 40 μm. The ductile-to-brittle transition temperature of the coated substrate is found at −20°C. Comparison of these results with the results shown in figure 6.7b shows that the T_{DB} of IM PA66/PPE coated with a 40 μm PUR-A layer shifts over 35°C if the level of adhesion is lowered from 1.3 kJ/m² to 0.6 kJ/m². This shift of T_{DB} of the coated substrate is not accompanied by a change in the fracture behaviour of the coating. The elongations at break determined for the 40 μm coating after the alkaline-treatment and that after the IPA-treatment coincide in the temperature range studied. The T_{DB} of the coating is found at 15°C for both levels of adhesion.

With the samples coated after the IPA-treatment the occurrence of debonding of the 40 μm coating during the high speed tensile test was found to depend strongly on temperature. This is shown in figure 6.10 where the elongation at break of all the tested coated substrate samples is given as a function of the testing temperature. In this figure the unfilled symbols represent the samples where the coating debonded over a large area during the tensile test. The black symbols denote the samples for which coating debonding did not occur during the test. With some samples the coating was found to be debonded over only a very small area. In some of these cases this debonded area did not coincide with the fracture area of the sample. The samples showing partial debonding of the PUR-A coating are represented by the shaded symbols in figure 6.10. In this figure it is also shown whether fracture of the sample initiated at the coated side of the sample (denoted by the circles in the figure) or somewhere
in the bulk of the sample (denoted by the triangles).

![Graph showing elongation at break vs. temperature](image)

- **Circles**: fracture initiated at coated side
- **Triangles**: fracture initiated in the bulk

Fig. 6.10  Fracture and delamination behaviour observed for iM PA66/PPE coated with a 40 μm PUR-A coating after the iPA-treatment in high-speed tensile testing.

As predicted by the model presented above, debonding of the coating mainly occurs at higher temperatures. If the coating debonds completely from the substrate this leads almost always to a fracture behaviour of the coated sample which is comparable to that of the uncoated substrate. Some exceptions of this observation are found at -15°C. At this temperature some samples fracture at a relatively low elongation although the coating completely debonds from the substrate during the test. At low temperatures coating debonding is no longer observed. The absence of coating debonding is always accompanied by a low elongation at break of the coated sample. Fracture in these samples always initiated at the coated side of the sample.

The temperature dependence of the elongation at break of the coating and the coated substrate for a coating thickness of 75 μm is given in figure 6.9c. For this coated substrate the T_{DB} is found at 0°C. These results show that also at high coating thickness the fracture behaviour of the coated substrate strongly depends on the actual level of adhesion of the coating on the substrate. The shift of the T_{DB} of iM PA66/PPE caused by coating the substrate with a thick PUR-A layer is smaller if the level of adhesion of the coating is lowered as was also found for a coating thickness of 40 μm. Again, this reduced shift of T_{DB} of the coated substrate is not caused by a change in the fracture behaviour of the coating itself. The elongations at break determined for the well-bonded, thick coating and the thick coating at an intermediate level of adhesion are very similar.
The results of the determination of the fracture behaviour of IM PA66/PPE coated with PUR-A after the iPA-treatment can be used to calculate the value of the biaxial residual strain in the coating. In paragraph 6.2 it was stated that the $T_{DB}$ of a coated plastic is found just below the temperature where $P_{deb}$ is equal to $P_{cat}$. In figure 6.11 the calculated values of $P_{deb}$ and $P_{cat}$ are given as a function of the value of the residual biaxial strain for IM PA66/PPE coated with PUR-A with a thickness of 40 µm and 75 µm. The values of $P_{deb}$ and $P_{cat}$ were calculated for the temperature corresponding to the $T_{DB}$ of the coated material. In these calculation it was assumed that $G_{c,adh}$ is independent of temperature. For $K_{In}$ a constant value of 0.9 MPa h$^{1/2}$ is used. If the model is correct the biaxial residual strain in the coating is the value for which $P_{deb}$ is equal to $P_{cat}$.

![Graph showing likelihood of delamination $P_{deb}$ and likelihood of catastrophic crack growth $P_{cat}$ as a function of biaxial residual strain calculated for IM PA66/PPE coated with PUR-A after the iPA-treatment for two different values of the coating thickness.](image)

Fig. 6.11  **Likelihood of delamination $P_{deb}$ and likelihood of catastrophic crack growth $P_{cat}$ as a function of the biaxial residual strain calculated for IM PA66/PPE coated with PUR-A after the iPA-treatment for two different values of the coating thickness.**

From this figure it can be seen that this value of the biaxial strain is 4.2% and 4.0% for a coating thickness of 40 µm and 75 µm, respectively. These values of the biaxial residual strain are comparable with values reported in the literature. It is generally found that the biaxial residual strain is independent of the layer thickness [31-34]. For polyimide coatings residual strain values ranging from 0.25%–2% have been measured depending on curing temperature [33,35], for coatings based on PIBM and PS the residual strain values were measured of 0.6% and 1.8%, respectively [31] and for epoxy coatings cast from a solution based on a slow evaporating solvent residual strain values up to 9% were reported [32].

### 6.4.5 Influence of the adhesion level on the surface embrittlement effect

The measured high-speed tensile fracture energy of IM PA66/PPE coated with a 40 µm layer of PUR-A is shown in figure 6.12 as a function of temperature for three different
pretreatments of the substrate. In this figure the fracture energy of the uncoated substrate is also shown.

![Graph showing fracture energy vs temperature for coated and uncoated substrates](image)

**Fig. 6.12** High-speed tensile fracture energy as a function of temperature of uncoated **IM PA66/PPE** and of **IM PA66/PPE** coated with 40 μm **PUR-A** after various pretreatments.

A comparison of the results of the high-speed tensile tests on **IM PA66/PPE** coated with a 40 μm **PUR-A** coating after the RA-treatment and after the alkaline treatment clearly shows that the level of adhesion between the brittle coating and the ductile substrate may have an enormous influence on the actual (detrimental) surface embrittlement effect. The ductile-to-brittle transition temperature $T_{DB}$ of the substrate shifts over about 75°C after application of the perfectly adhering **PUR-A** coating with a thickness of 40 μm. The ductile-to-brittle transition temperature of the coated substrate and that of the coating were both found at 15°C. Figure 6.6 shows that for the same coated substrate this surface embrittlement effect completely disappears if the level of adhesion of the coating is at a sufficiently low level. In that case the coated sample has the same mechanical impact behaviour as the uncoated sample resulting in the same ductile-to-brittle transition temperature of the coated substrate and the uncoated substrate.

In figure 6.13 the ductile-to-brittle transition temperatures of uncoated **IM PA66/PPE**, of the **PUR-A** coating and of **IM PA66/PPE** coated with 40 μm **PUR-A** after various pretreatments are given. It is clear that the ductile-to-brittle transition of a coated sample can vary between the ductile-to-brittle transition of the uncoated substrate and that of the coating. These results clearly indicate that the ductile-to-brittle transition of coated samples depends, among others, on the level of adhesion of the coating.
The ductile-to-brittle transition temperature $T_{DB}$ of IM PA66/PPE coated with 40 µm PUR-A as a function of the level of adhesion $G_c, adh$. The $T_{DB}$ of IM PA66/PPE and of the 40 µm PUR-A are also shown.

Fig. 6.13

The experiments presented here demonstrate that application of a brittle coating on a ductile substrate may result in a profound shift of the ductile-to-brittle transition if the level of adhesion is high, whereas application of the same brittle coating on the same ductile substrate may not cause a shift of the ductile-to-brittle transition if the level of adhesion is very low. This is also shown in figure 6.14.

Fig. 6.14

The ductile-to-brittle transition temperature $T_{DB}$ of IM PA66/PPE coated with PUR-A as a function of the pretreatment of the substrate and of the coating thickness. The $T_{DB}$ of PUR-A as a function of thickness and the $T_{DB}$ of IM PA66/PPE are also shown.

alkaline  iPA  RA

IM PA/PPE
In figure 6.14 the measured ductile-to-brittle transition temperatures of the coated substrates are given as a function of coating thickness for various levels of adhesion. The ductile-to-brittle transition temperatures of uncoated IM PA66/PPE and of the PUR-A coating as a function of thickness are also presented. Clearly, the \( T_{DB} \) of coated plastics is strongly influenced by the thickness of the coating and by the level of adhesion of the coating. If delamination of the coating takes place this has a positive effect on the fracture behaviour of the coated plastic. On lowering of the coating thickness the likelihood of crack arrest increases which may also have a positive effect on the fracture behaviour of the coated plastic.

6.5 CONCLUSIONS

The fracture behaviour of PUR-A coated IM PA66/PPE was studied as a function of the thickness of the coating and as a function of the level of adhesion between the coating and the substrate. It was found that the fracture properties of the substrate remain unchanged if the substrate is coated with a very weakly-adhering, brittle coating. If the level of adhesion is high the surface embrittlement effect caused by the application of the same brittle coating results in a very significant deterioration of the fracture properties of the ductile substrate. The detrimental surface embrittlement effect caused by the well-adhering coating can be reduced by decreasing the coating thickness leading to crack arrest. At an intermediate level of adhesion there is a competition between delamination of the coating and catastrophic growth of the coating crack after coating fracture. If the thickness of the coating at an intermediate level of adhesion is low, coating delamination does not occur and the mechanical behaviour of the coated substrate can be compared to that of the substrate coated with a well-adhering coating having the same thickness. The fracture behaviour of a coated substrate having an intermediate level of adhesion is superior to that of the substrate with the well-adhering coating at higher values of the coating thickness. This is caused by the delamination of the coating taking place at the intermediate level of adhesion. The fracture mechanics model presented gives a good prediction of the influence of the coating thickness and the adhesion level on the fracture behaviour of the coated substrate.

6.6 REFERENCES

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INFLUENCE OF COATING DUCTILITY AND DEFORMATION RATE ON THE IMPACT PROPERTIES OF COATED PLASTICS

7.1 INTRODUCTION

In chapter 3 it was shown that the high-rate mechanical tensile properties of a ductile, rubber-modified blend of polyphenylene ether and polyamide-66 (IM PA66/PPE) are largely reduced over a broad range of temperatures if this material is coated with a brittle, perfectly adhering polyurethane coating (PUR-A) with a thickness of only 40 µm. This effect is called surface embrittlement and manifests itself by the large reduction of the fracture strain of the coated substrate under conditions that the uncoated substrate deforms in a ductile manner.

In chapter 6 the influence of the level of adhesion and the influence of the thickness of the coating on the high-rate mechanical tensile behaviour of PUR-A coated IM PA66/PPE was studied. It was shown that the surface embrittlement effect can be largely reduced if the level of adhesion is low enough to cause delamination of the coating during loading of the coated substrate. The surface embrittlement effect caused by the brittle coating can even be completely absent if the level of adhesion of the coating is very low. Furthermore, it was shown that the surface embrittlement effect caused by perfectly adhering coatings can be reduced by lowering of the thickness of the coating. For these thin coatings the crack from the coating can effectively be arrested at the interface or in the substrate. If the level of adhesion of the coating is high and the thickness of the coating is not very small, neither coating delamination nor (significant) crack arrest occurs. Under those conditions it was found that the ductile-to-brittle transition of the coated substrate practically coincides with that of the coating layer and, consequently, the coated ductile substrate deforms (almost) as brittle as the coating layer. For these coated plastics it can thus be expected that the surface embrittlement effect caused by the coating is mainly determined by the ductility of the coating. It has indeed been often observed that the surface embrittlement effect induced by the coating is significantly reduced if the ductility of the coating is increased [1-10]. For this reason it seems advisable to use coatings with a low glass transition temperature $T_g$ and a low cross-link density. Unfortunately, as discussed in chapter 3, lowering of the $T_g$ and the cross-link density of automotive coatings also has some serious disadvantages, like low solvent and weather resistance [5], low gloss, prolonged drying time [2,4,6] and low surface hardness resulting in an insufficient level of polishability [4,6,10,11]. Consequently, for commercial automotive coatings an optimum balance in the mechanical, physical and chemical properties of the coating has to be found.

The influence of the ductility of the coating on the surface embrittlement effect observed for coated plastics was investigated in detail in the study presented in this chapter. For this purpose the mechanical tensile properties of IM PA66/PPE coated with various well-adhering polyurethane clear coatings were determined. The ductility of the coatings used varies over a very broad range from brittle to very tough depending on the binder composition. In
chapter 6 it was shown that the thickness of the coating can play a significant role on the surface embrittlement effect. To avoid interference of the effect of coating thickness on the mechanical properties of the coated plastic, the thickness of all coatings applied on IM PA66/PPE was kept constant at 40 $\mu$m. This thickness is close to the coating thickness used in industrial automotive practice.

Coating ductility not only depends on coating composition but also on the rate of strain. Therefore, to check the general validity of the model presented in chapter 6 the mechanical tensile properties of the polyurethane coated IM PA66/PPE samples were determined at a very high as well as at a low deformation rate.

In this thesis the ductility of materials is described by the ductile-to-brittle transition temperature $T_{DB}$. If the $T_{DB}$ of a material is low its ductility is regarded as high and vice versa. In chapter 4 it was speculated that a good indication of the ductility of coatings could be obtained in a fast and simple way by determining the tear transition temperature TTT. In this chapter this hypothesis is further examined by relating the mechanical fracture properties of various coated materials to the mechanical tear properties determined at low test speed on free films of the coating.

Finally, the fracture behaviour of the coated plastic is also related with other properties of the coating, like the $T_g$ and the surface hardness. Such a comparison is often made in the literature. It is shown that the TTT is a much better indicator for the surface embrittlement effect of coatings than the standard indicators $T_g$ and surface hardness.

7.2 EXPERIMENTAL

7.2.1 Materials

A rubber-modified polyamide-66/polyphenylene ether-blend (IM PA66/PPE), known commercially as Noryl® GTX 940 (GE Plastics), was used as substrate material. Noryl® GTX 940 was obtained as sheet material (170 $\times$ 170 $\times$ 3 mm$^3$). All sheets were dried at 110°C under vacuum for 20 hours prior to the coating process.

A rubber-modified polycarbonate/polybutylene terephthalate-blend (IM PC/PBT), known commercially as Xenoy® CL101 (GE Plastics), was used as substrate material in some additional experiments.

The influence of coating ductility on the fracture behaviour of coated IM PA66/PPE was studied by using various polyurethane clear coatings. As a brittle coating PUR-A was used. This coating is based on a hard polyacrylic resin with a high $T_g$ (Setalux® 1152xx51, Akzo Coatings). The resin was cross-linked with the isocyanurate trimer of hexamethylene diisocyanate (Desmodur® N3390, Bayer) at a curing temperature of 100°C for 7 hours.

Polyurethane coatings with a higher ductility compared to PUR-A were made by mixing the same polyacrylic resin with a much softer polyester resin. The polyester resin (Setal® 168,
Akzo Coatings) is an aliphatic/aromatic resin containing hydroxyl groups. It has a low $T_g$ and is fully miscible with the polyacrylic resin. These coatings are named PUR-SSXX, where XX denotes the percentage of the polyacrylic resin in the coating. The PUR-SS coatings were made by mixing the resins in the desired compositions, followed by cross-linking with the biuret of hexamethylene diisocyanate (Desmodur® N75, Bayer) for 4 hours at 100°C. A small amount of dibutyltin dilaurate (0.03 w/w-% based on solid weight of isocyanate cross-linker) was used as a catalyst. Under these curing conditions conversion of the reactive hydroxyl groups is almost complete.

For all polyurethane coatings the molar ratio of hydroxyl groups and isocyanate groups was chosen 1:1. The coating components were filtered using a pressure filter (Millipore, 5.0 μm) before use. The same polyurethane coatings were also used in (some) of the experiments described in the previous chapters.

Prior to application of the coating the substrate sheets were immersed in a hot alkaline solution (2M NaOH, 85 °C), rinsed with demineralised water followed by cleaning of the sheets with isopropyl alcohol. The coatings were applied on the cleaned sheets using spincoating. The thickness of the coating was controlled by adjusting the rotating speed, see also paragraph 4.3.2. In this study the thickness of all coatings was approximately 40 μm.

The influence of coating ductility on the high-speed tensile behaviour of coated plastics was also studied using IM PC/PBT coated with four different experimental clear coatings. All coatings were based on polyester resins and cured at 90°C for 40 minutes and subsequently annealed at 80°C for 24 hours.

Dogbone-shaped tensile specimens (DIN 53 455, specimen number 3) were stamped from the coated sheets using a special cutting tool placed in a hydraulic press. Cutting was done at elevated temperature (75°C) to facilitate the cutting process and to prevent cracking of the coating layer. The length-axis of the tensile samples was parallel to the direction of injection moulding. All materials were tested after drying under vacuum at 20°C for a minimum period of 2 days.

### 7.2.2 Determination of the level of adhesion

The level of adhesion of the polyurethane clear coatings was determined using the DCAT method [12]. The samples (14 × 50 mm²) for the DCAT were carefully sawn from the coated panels. The coated side of the sample was roughened slightly with an abrasive and subsequently cleaned. The cleaned samples were placed in a holder. Using a silicone rubber mould a small block (10 × 10 × 15 mm³) of a cold-curing, two-component epoxy adhesive (Araldit® AW106 and Araldit® HV953U, both from Ciba–Geigy) was applied to the centre of each sample.

After curing the adhesive for a minimum of three days at room temperature, the DCAT samples were subjected to a three-point flexure test. These tests were carried out according to ASTM D 790M (method I, procedure B) on a Zwick tensile tester, type 1474. The
diameter of the supports was 6 mm. The centre distance between the outer supports was 45 mm and the cross-head speed was 1.0 mm/min. For each material a minimum of 6 samples were tested. The flexural modulus of the substrate material was measured on a sample without a central block at a support length of 35 mm. Full details on the experimental procedure used for this test can be found in paragraph 5.3.2.

After completion of the test the delaminated area of each sample was inspected under a microscope. It was found that all samples tested in this study failed adhesively between the coating and the substrate.

7.2.3 High-speed tensile testing

The mechanical behaviour of the coated samples at high-rates of strain was determined with high-speed tensile tests done at various temperatures. These tests were carried out on a servo-hydraulic material tester (Schenck VHS 25/20). A transient recorder (ADAM TC 210-4, Maurer) was used for the analog data acquisition of the force and displacement signals during the tests. The displacement of the lower clamp was determined using a fibre optics extensometer. A small temperature chamber was used for the experiments done at temperatures other than room temperature. For these experiments the samples were preconditioned at the test temperature in a separate temperature chamber (Grasso, type GTTS 27.70) for a minimum period of one hour. The samples were then placed in the temperature chamber of the tensile tester for at least 10 minutes before testing. Further details on high-speed tensile testing and the testing procedure used can be found in paragraphs 2.2.2 - 2.2.4 of this thesis.

All high-speed tensile tests were done at a test speed of 1 m/s, resulting in a strain rate of approximately 10^5 %min^{-1} (≈ 17 s^{-1}). A minimum of four samples was tested at each temperature. The results of tests where fracture of the sample was clearly caused by the presence of an impurity in the material were ignored in the calculation of the average fracture data. The ductile-to-brittle transition temperature T_{DB} was defined as the highest temperature at which all tested samples failed in a brittle manner.

7.2.4 Tensile testing at low test speeds.

Low-rate tensile testing was done on a Zwick 1474 tensile testing machine at a test speed of 6 mm/min (= 10% min^{-1} = 0.0017 s^{-1}). The displacement of the cross-head was measured using an incremental extensometer (Heidenhain MT101K, resolution: 0.5 μm). A temperature chamber (Brabender type TEE52) was used for testing at low temperatures. The temperature was measured using a Cr–Al thermo-couple (Comark type 6110) positioned close to the mounted sample.

7.2.5 Determination of the coating fracture point using a graphite layer

The elongation at break of the coating layer on the substrate during a tensile test was
determined by measuring the electrical resistance of a very thin, conductive graphite layer (Graphit 33, Kontakt Chemie) sprayed on top of the coating layer. Crack growth in the coating layer also causes fracture of the thin graphite layer on top of it. Consequently, the first crack in the coating can be observed as a very sharp increase in the measured electrical resistance of the graphite layer. This method is described in more detail in paragraph 3.3.5.

7.3 RESULTS AND DISCUSSION

In chapter 6 it was shown that the level of adhesion is an important factor determining the impact properties of coated plastics. For this reason the level of adhesion on IM PA66/PPE was determined for all coatings investigated. The results are shown in figure 7.1. In all cases the value of $G_{c,adh}$ was found to be higher than 1 kJ/m$^2$ indicating a very high level of adhesion. As expected, delamination of these polyurethane coatings was never found in the mechanical tensile tests of the coated samples described hereafter. In the analysis of the results all systems can be regarded as perfectly adhering.

![Graph showing $G_{c,adh}$ values for various polyurethane coatings](image)

**Fig. 7.1** Critical energy release rate, $G_{c,adh}$, for delamination measured for various polyurethane coatings on IM PA66/PPE. The variation of the measured $G_{c,adh}$ is about 20%. The thickness of the coatings is kept constant at 40 µm. All coatings were applied on IM PA66/PPE after an alkaline treatment of the substrate.

7.3.1 Influence of coating ductility on the high-rate fracture behaviour of polyurethane coated IM PA66/PPE

In figure 7.2 the elongation at break of IM PA66/PPE coated with a 40 µm layer of PUR-SS85 is given as a function of temperature. The fracture properties were measured in uniaxial tensile tests at a strain rate of $10^5$% min$^{-1}$. The elongation at break of uncoated IM PA66/PPE and that of the well-bonded coating are also shown in this figure. From the data shown in
coating ductility and deformation rate

this figure it is clear that application of the PUR-SS85 coating on IM PA66/PPE results in a significant surface embrittlement effect. At temperatures at or below the $T_{DB}$ of the coated substrate fracture of the coating layer and the coated substrate always coincide. The fracture strains of the coating and the coated substrate are much smaller than that of the uncoated substrate at these temperatures (about 6% and 28%, respectively). Visual inspection of the fracture surfaces of these samples clearly showed that fracture always started at the coated side of the specimen. Arrest of the crack from the coating does not occur below the $T_{DB}$ of the coating layer. At higher temperatures a small difference between the elongation at break of the coated substrate and that of the coating is observed. Evidently, this crack arrest effect does not lead to a significant improvement of the mechanical properties of the coated substrate as was also found for IM PA66/PPE coated with a perfectly-adhering 40 $\mu$m PUR-A layer. For some of the samples tested at 20°C it was observed that fracture did not initiate at the coated side but in the bulk of the specimen. This observation can be explained by the sharp increase of the elongation at break of the PUR-SS85 coating at this temperature.

![Graph](image)

**Fig. 7.2**  *Elongation at break of uncoated IM PA66/PPE (solid line), PUR-SS85 coated IM PA66/PPE (○) and the PUR-SS85 coating (○) measured as a function of temperature in high-speed tensile tests. The thickness of this well-adhering coating was 40 $\mu$m.*

Although the application of the 40 $\mu$m PUR-SS85 coating clearly leads to a significant reduction of the mechanical impact behaviour of IM PA66/PPE, this reduction is not as pronounced as that found for IM PA66/PPE coated with a PUR-A coating of equal thickness. The shift of the $T_{DB}$ caused by the application of the well-adhering coating with a thickness of 40 $\mu$m is 55°C for the PUR-SS85 coating compared to 75°C for the PUR-A coating. For both coatings it is found that the $T_{DB}$ of the coated substrate coincides with the $T_{DB}$ of the coating layer. From these results it can be concluded that the observed improvement of the fracture behaviour of PUR-SS85 coated IM PA66/PPE compared to PUR-A coated IM PA66/PPE is solely due to the higher ductility of the PUR-SS85 coating.

If the ductility of the coating is further increased the surface embrittlement effect caused by
the coating decreases even more. In figure 7.3 the high-rate tensile elongation at break of IM PA66/PPE coated with PUR–SS70 is given as a function of temperature. The elongations at break of the coating layer and of the uncoated substrate are also shown in this figure. The \( T_{DB} \) of PUR–SS70 coated IM PA66/PPE is found at \(-25^\circ C\). Compared to PUR–SS85 coated IM PA66/PPE the \( T_{DB} \) of this coated substrate is shifted over 20°C. Again, the \( T_{DB} \) of the coated substrate and the \( T_{DB} \) of the coating layer coincide. As was also found for the IM PA66/PPE samples coated with either PUR–A or PUR–SS85 with the same thickness, fracture most often initiated at the coated side of the sample. Only at temperatures well above the \( T_{DB} \) of the coated substrate fracture sometimes initiated in the bulk of the material. From the results shown in figure 7.3 it is evident that in the PUR–SS70 coated IM PA66/PPE samples arrest of the crack from the coating is almost completely absent in the temperature range studied.

![Figure 7.3](image)

**Fig. 7.3** Elongation at break of uncoated IM PA66/PPE (solid line), PUR–SS70 coated IM PA66/PPE (○) and the PUR–SS70 coating (◇) measured as a function of temperature in high-speed tensile tests. The thickness of this well-adhering coating was 40 \( \mu \)m.

In figure 7.4 the high-rate tensile elongation at break is given as a function of temperature for IM PA66/PPE coated with a 40 \( \mu \)m layer of PUR–SS40 and for IM PA66/PPE coated with a 40 \( \mu \)m layer of PUR–SS0. Again, the elongation at break of the uncoated substrate is also shown. For all tested samples it was found that the elongation at break of the coating and that of the coated substrate were exactly equal. For this reason the measured elongation at break of the coating layers is omitted in this figure. From figure 7.4 it can be seen that the surface embrittlement effect is not observed if IM PA66/PPE is coated with a 40 \( \mu \)m layer of either PUR–SS40 or PUR–SS0. From these results it can be concluded that for these coatings the \( T_{DB} \) of the coating layer will be equal to or lower than the \( T_{DB} \) of the uncoated substrate and, consequently, the \( T_{DB} \) of the substrate is not shifted to higher temperatures if the substrate is coated with one of these coatings. In this case the elongation at break of the substrate is lower than that of the coating layer, at least at low temperatures. On loading the coated sample fracture will start in the substrate causing also immediate fracture of the
coating layer. This explains the observation that the elongations at break of the coating and the coated substrate are equal for all tested samples. Visual inspection of the fracture surfaces of these coated samples gives further evidence of the higher fracture strain of the coating compared to that of the substrate at low temperatures. Unlike the fracture behaviour observed in the IM PA66/PPE samples coated with PUR-A, PUR-SS85 or PUR-SS70, fracture in the IM PA66/PPE samples coated with PUR-SS40 or PUR-SS50 always initiated in the bulk of the specimen at low temperatures. At temperatures well-above the T_{DB} of the coated substrate it was found that fracture in the PUR-SS40 coated samples also sometimes initiated at the coated side. This is caused by the somewhat lower fracture strain of the ductile coating compared to the fracture strain of the ductile substrate.

![Graph](image)

Fig. 7.4  *Elongation at break of uncoated IM PA66/PPE (solid line), IM PA66/PPE coated with PUR-SS40 (○) and IM PA66/PPE coated with PUR-SS50 (○) measured in high-speed tensile tests as a function of temperature. The thickness of these well-adhering coatings was 40 μm.*

In the previous chapters it was demonstrated that arrest of the crack from the coating layer can only occur if the value of the stress intensity factor at the crack tip reaching the interface between the coating and the substrate (K_I) is below a certain value K_{la}. The value of K_{la} is known as the crack arrest toughness of the substrate and is assumed to be a material property depending on the temperature at the crack tip. Provided that the coating is not very thin and that the deformation of the sample can be regarded as linear-elastic, the value of K_I of the coating crack reaching the interface can be calculated from the thickness of the coating layer and the stress in the substrate at the onset of fracture of the coating using equation 5 presented in chapter 3.

The calculated values of K_I for the crack from the polyurethane coating reaching the interface are given in figure 7.5 as a function of temperature. In this figure the value of K_I is given for all experiments within the linear-elastic limit for IM PA66/PPE coated with a 40 μm layer of PUR-A, PUR-SS85 or PUR-SS70. For comparison, the K_I-data calculated for IM PA66/PPE coated with a 65 μm layer of PUR-A are also shown (same data as presented
previously in figure 6.8). The solid symbols in this figure represent the experiments in which the crack from the coating was arrested at the interface or in the substrate. The other symbols are used for experiments in which fracture of the coating and of the coated substrate were found to coincide. Crack arrest did not occur at low strains in any of the coated substrates described in this chapter. This is in agreement with the model presented in chapter 6 which predicts that crack arrest can only occur if the value of the stress intensity of the crack is below a critical, temperature-dependent value. In figure 7.5 it can be further observed that the value of $K_I$ for all coatings of equal thickness is roughly the same at a given temperature. This is in accordance with the observation that the brittle fracture strain is practically equal for all these coatings.

![Graph showing temperature dependence of the stress intensity factor](image)

**Fig. 7.5** Temperature dependence of the value of the stress intensity factor of the crack from the coating reaching the interface calculated for individual high-speed tensile tests on IM PA66/PPE coated with PUR-A (40 μm, circles), PUR-A (65 μm, triangles), PUR-SS85 (40 μm, squares) and PUR-SS70 (40 μm, asterisks). Experiments in which crack arrest was observed are represented by filled symbols, all other experiments by open symbols. The dashed line represents the estimate of $K_{Ic}$ of IM PA66/PPE as a function of temperature.

7.3.2 Influence of coating ductility on the low-rate fracture behaviour of polyurethane coated IM PA66/PPE

The influence of deformation rate on the surface embrittlement effect observed for coated plastics was investigated using the same set of polyurethane coated IM PA66/PPE samples as described above. For this purpose, the mechanical tensile behaviour of these materials was also determined at a much lower deformation rate, namely 10% min$^{-1}$.

In figure 7.6 the results of the low-speed tensile tests on IM PA66/PPE coated with PUR-A,
coated with PUR-SS85 and coated with PUR-SS70 are summarized. The thickness of these well-adhering coatings was 40 μm. In this figure the elongation at break of the coated substrate and that of the coating are given as a function of the temperature. The elongation at break of the uncoated substrate (see chapter 2) is also shown in figure 7.6. From this figure it is evident that these coatings cause surface embrittlement of the substrate (also) at this low strain rate. The deterioration of the tensile properties of IM PA66/PPE on application of these coatings measured at a low strain rate of 10% min⁻¹ is very similar to that observed at a strain rate of 10²% min⁻¹. As was also observed in the high-speed tensile tests, arrest of the crack does not occur at low temperatures and the TDB of the coated substrate exactly coincides with the TDB of the coating. As expected, the TDB measured at low strain rate is lower than the TDB found for the same material tested at high strain rate.

Fig. 7.6  **Elongation at break of uncoated IM PA66/PPE (solid line), of polyurethane coated IM PA66/PPE (solid symbols) and of the coating (open symbols) measured in low-speed tensile tests as a function of temperature. Data are shown for PUR-A (circles), PUR-SS85 (squares) and for PUR-SS70 (triangles). The thickness of these coatings is 40 μm.**

For IM PA66/PPE coated with PUR-SS40 and for IM PA66/PPE coated with PUR-SS80 the surface embrittlement effect was not observed (data not shown). The TDB of these coated substrates were both identical to the TDB of −100°C determined for uncoated IM PA66/PPE.

The stress intensity factor KI for the crack from the coating reaching the interface was calculated for the low-speed tensile tests in the same way as discussed previously. Only those experiments in which the coating failed within the linear-elastic limit were used for these calculations. In figure 7.7 the calculated values of KI are given as a function of temperature for IM PA66/PPE coated with PUR-A, PUR-SS85 or PUR-SS70. Crack arrest was not observed in any of the coated samples that fractured within the linear-elastic limit. The values of KI for the same materials calculated from the results of the tensile tests at high strain rate are also shown. As found previously, arrest of the crack from the coating does not occur if the stress intensity factor of the crack is above a critical value. From the results
presented in this figure it can be concluded that this critical value $K_{Ia}$ is equal to or smaller than roughly 0.9 MPa m$^{1/2}$ in the temperature range shown. Evidence of a strain rate dependency of $K_{Ia}$ can not be found from these results.

![Graph showing temperature dependence of the stress intensity factor](image)

Fig. 7.7 Temperature dependence of the value of the stress intensity factor of the crack from the coating reaching the interface calculated for individual low-speed tensile tests on IM PA66/PPE coated with PUR-A (circles), PUR-SS85 (squares) and PUR-SS70 (triangles) measured in high-speed and low-speed tensile tests. The thickness of all coatings was 40 μm. Experiments in which crack arrest was observed are represented by filled symbols, all other experiments by open symbols.

7.3.3 Relation between the fracture behaviour of coated plastics and various properties of the coating

From the results presented above it is clear that the ductile-to-brittle transition of IM PA66/PPE coated with a 40 μm PUR-A, PUR-SS85 or PUR-SS70 coating is entirely determined by the ductility (that is, the ductile-to-brittle transition) of the coating. In chapter 4 it was shown that the ductility of coatings at low deformation rate can be determined in a simple and quick way using the trouser tear test. In that study the tear transition temperature TTT was determined for the PUR-A coating as a function of thickness and for the PUR-SS coatings as a function of composition. Below we will compare the tear transition temperature of the coating free film with the ductile-to-brittle transition of the coating. Furthermore, the ductile-to-brittle transitions will be compared to other properties which may indicate the ductility of the coating.

In figure 7.8 the $T_{DB}$ of IM PA66/PPE coated with various polyurethane clear coatings measured at a strain rate of $10^5$ %/min$^{-1}$ is given as a function of the TTT of the coating. In this figure the data for the 40 μm PUR-SS coatings as described in paragraph 7.3.1 are given
together with the data for PUR-A with a thickness of 40 μm and for PUR-A with a thickness of 65 μm (chapter 3 and 6, respectively). The dashed line in this figure indicates the $T_{DB}$ of the uncoated substrate. At high values of TTT an almost linear relationship between the TTT of the coating and the $T_{DB}$ of the coated substrate is found. For most of these coated samples it was found that the $T_{DB}$ of the coated substrate coincides with the $T_{DB}$ of the coating. The only exception is the 65 μm PUR-A coating for which the $T_{DB}$ of the coated substrate was found 5°C lower than the $T_{DB}$ of the coating. This slight difference was caused by the occurrence of crack arrest in this temperature range. The plot of the $T_{DB}$ of the coated substrate as a function of the TTT of the coating has a slope approximately equal to 1. This indicates that a change in the ductility of the coating causes roughly equal changes in the low-speed TTT and in the high-speed $T_{DB}$ on an absolute temperature scale. Please note that the TTT and the $T_{DB}$, by definition, are not identical due to the differences in loading geometry and deformation rate between the trouser tear test and the high-speed tensile test.

![Graph showing DB-transition of coated substrate vs. TTT of coating](image)

**Fig. 7.8** The high-speed tensile ductile-to-brittle transition temperature of coated IM PA66/PPE as a function of the tear transition temperature TTT of the coating. Data are shown for PUR-A, PUR-SS85, PUR-SS70, PUR-SS40 and PUR-SS0 with a thickness of 40 μm and for PUR-A with a thickness of 65 μm. The triangle represents the high-speed tensile $T_{DB}$ of PUR-A for a thickness of 13 μm as a function of the extrapolated value of TTT corresponding to this thickness.

On increasing the ductility of the coating, the TTT of the coating decreases. For the coated materials investigated here, a decrease of the TTT of the coating results in a decrease of the $T_{DB}$ of the coated substrate. Below a TTT of the coating of approximately −90°C, the high-speed $T_{DB}$ of the coating layer is lower than the $T_{DB}$ of the uncoated substrate. As the ductile-to-brittle transition of the uncoated substrate determines the lower limit of the ductile-to-brittle transition of the coated substrate, the $T_{DB}$ of the coated substrate is equal to that of the uncoated substrate for these very ductile coatings. Evidently, this lower limit does not exist with the trouser tear test.
From the PUR-A data shown in figure 7.8 it can be seen that the TTT determined with the trouser tear test also gives a good indication of the change of the $T_{DB}$ of the coated substrate as a function of coating thickness. Unfortunately, the TTT of the PUR-A coating could not be accurately determined below a coating thickness of approximately 20 μm. If we assume a linear relationship between the TTT of the coating and the layer thickness, the extrapolated value of the TTT for a PUR-A coating of 13 μm is $-17^\circ$C. In figure 7.8 the high-rate $T_{DB}$ of the 13 μm PUR-A coating on IM PA66/PPE as a function of this value of the TTT is represented by the triangle. Again the TTT gives a good estimate of the $T_{DB}$ of the coating. Here we have used the $T_{DB}$ of the coating instead of the $T_{DB}$ of the coated substrate as the latter is determined by crack arrest and not by the ductility of the coating.

To investigate the general validity of the relationship between the $T_{DB}$ of coated substrates and the TTT of the coating, the surface embrittlement effect was also determined for some other coated systems using a different substrate material. For this purpose, the influence of four different experimental clear coatings on the mechanical tensile properties of IM PC/PBT was determined at a strain rate of $10^5$%min$^{-1}$. The thickness of these coatings was approximately 40 μm and delamination of these coating during high-speed tensile testing was never observed.

In figure 7.9 the measured $T_{DB}$ of the four coated IM PC/PBT materials is given as a function of the TTT of the clear coating. The $T_{DB}$ of uncoated IM PC/PBT was found to be also $-60^\circ$C.

![Fig. 7.9](image)

The high-speed ductile-to-brittle transition temperature of coated IM PA66/PPE (○, same data as shown in Fig. 7.8) and of coated IM PC/PBT (◇) as a function of the tear transition temperature TTT of the coating. Data are shown for various coatings, see text for details.

In this figure the data for the well-adhering polyurethane coatings on IM PA66/PPE are also shown. Except for the coating with a very low TTT applied on IM PC/PBT, there is a reasonably good correlation between the $T_{DB}$ of the coated substrate measured with high-speed tensile testing and the TTT of the coating measured with the trouser tear test for
all tested coated materials indicating the general validity of the trouser tear test and the subsequent analysis. Note that the $T_{DB}$ for these two substrates is equal.

It is often assumed in the literature that the mechanical properties of coated plastics are strongly related to the glass transition temperature $T_g$ of the coating. This assumption is checked here for the same set of coated materials as presented in figure 7.9. In figure 7.10 the $T_{DB}$ of these coated materials is given as a function of the $T_g$ of the coating. Clearly, the correlation is worse than in figure 7.9. This is especially valid for the coating with a $T_g$ of 85°C and a TTT of -140°C. The $T_{DB}$ of IM PC/PBT coated with this clear coating determined in a high-speed tensile test is -50°C which is much lower than the $T_{DB}$ predicted from the high $T_g$ of the coating. Furthermore, the $T_g$ of PUR-A was found to be independent of the thickness of the coating, at least in the thickness range studied (13 μm – 100 μm). Therefore, no unique relation between $T_g$ and TTT can exist. However, the dependence of the $T_{DB}$ on coating thickness correlates well with that observed for the TTT.

![Graph showing the relationship between glass transition temperature of coating and DB transition of coated substrate](image)

**Fig. 7.10** The high-speed tensile ductile-to-brittle transition temperature of coated IM PA66/PPE (○) and of coated IM PC/PBT (◇) as a function of the glass transition temperature of the coating. Data are given for the same coatings as shown in Fig 7.9.

In the introduction it was explained that good polishability and low-temperature ductility are often conflicting requirements for automotive coatings. Routes to obtain coatings with a high ductility, even at low temperatures and high deformation rates, often result in a low $T_g$ of the coating. A low $T_g$ may result in a low surface hardness of the coating which hampers the polishability. In practice a surface hardness of the coating of 75 MPa at room temperature can often be taken as a lower limit to ensure a sufficiently high level of polishability. In figure 7.11 the $T_{DB}$ of the same set of coated substrates as presented in figure 7.9 is plotted as a function of the surface hardness of the coating. Although there seems to be a tendency that the $T_{DB}$ of the coated substrate increases with increasing hardness of the coating, the relation is not unique. For some coatings a much better balance between good polishability and high ductility at low temperature has been realized. Coatings
which combine sufficiently high surface hardness with low-temperature ductility have promising potential as commercial automotive coatings.

![Diagram](image)

Fig. 7.11 The high-speed tensile ductile-to-brittle transition temperature of coated IM PA66/PPE (○) and of coated IM PC/PBT (△) as a function of the hardness of the coating. Data are given for the same coatings as shown in Fig 7.9.

Finally, the effect of strain rate on the relation between the $T_{DB}$ of the coated substrate and the TTT of the coating was also investigated for polyurethane coated IM PA66/PPE. Also at low strain rates the $T_{DB}$ of the coated substrate coincides with that of the coating. In figure 7.12 the ductile-to-brittle transition temperature of the coated substrate measured at two different deformation rates is given as a function of the tear transition temperature of the coating. In this figure the data are shown for IM PA66/PPE coated with the 40 μm PUR-SS coatings, IM PA66/PPE coated with 40 μm PUR-A and for IM PA66/PPE coated with 65 μm PUR-A. For both tensile strain rates there is a remarkably good correlation between the $T_{DB}$ of the coated substrate and the TTT of the coating layer. Note that the dependence on strain rate is only determined for the $T_{DB}$ of the coated substrate. The TTT of all coatings is determined at a constant tearing speed.

From figure 7.12 it can be seen that the $T_{DB}$ of the well-adhering polyurethane coatings PUR-A, PUR-SS85 and PUR-SS70 on IM PA66/PPE are shifted over roughly 55°C if the strain rate is changed from $10^5 \text{%min}^{-1}$ to $10\%\text{min}^{-1}$. Assuming a logarithmic dependence of the $T_{DB}$ on strain rate, the average shift of the $T_{DB}$ over the range of strain rates studied is about 14 K per decade of strain rate for these coating and, in this case, thus for the coated materials. For uncoated IM PA66/PPE the average shift of the $T_{DB}$ with strain rate is about 10 K per decade, although it must be mentioned here that the low-speed $T_{DB}$ of uncoated IM PA66/PPE could not be determined very accurately as this temperature is very close to the lowest temperature that can be attained with the temperature chamber used for the low-speed tensile tests.
coating ductility and deformation rate

![Graph showing DB-transition of coated substrate vs TTT of coating](image)

**Fig. 7.12** The ductile-to-brittle transition temperature of coated IM PA66/PPE measured in high speed tensile tests (△) and in low speed tensile tests (○) as a function of the tear transition temperature TTT of the coating. Data are shown for the same polyurethane coatings as in Fig 7.8.

The measured shift of the TDB with strain rate for IM PA66/PPE and the polyurethane coatings is of the same magnitude as the shift values that can be obtained from the results of mechanical tests reported in the literature. From the tensile test results on various polymers reported by Wu [13] shifts of the TDB ranging from 8 K/decade to 11 K/decade can be derived. For PVC measured over a very broad range of tensile strain rates an average shift of the TDB of roughly 15 K/decade was reported by Radon [14], whereas for PVC tested in three-point bending this shift was found to be about 20 K/decade [15].

It was found that the shift of the TDB of uncoated IM PA66/PPE with strain rate could not be related with the shift of the Tg of the rubber used in this blend with loading rate. In torsional DMTA tests it was found that the shift of Tg is only 4 K/decade. This observation gives further proof that the Tg is not a reliable measure of the ductility of materials.

### 7.3.4 Summary of the relationship between the fracture behaviour of coated plastics and the ductility of automotive clear coatings.

In the previous paragraph it was shown clearly that, if crack arrest does not occur, the TTT of well-adhering coatings can be used to give a precise prediction of the fracture behaviour of coated plastics. However, as demonstrated in chapter 6, when crack arrest or coating delamination occurs, this can have a significant influence on the fracture behaviour of the coated substrate. The relationship between the TDB of the coated plastic and the TTT of the coating can also be derived for those cases where coating delamination or crack arrest occurs. Figure 7.13 gives a schematic representation of the relationship between the TDB of the coated plastic and the TTT of the coating. For the construction of this figure it was assumed that the (relative) likelihoods of coating delamination and catastrophic crack growth are adequately described by the expressions derived in paragraph 6.2. For simplicity it was
further assumed that the likelihood of delamination is independent of temperature and the likelihood of catastrophic crack growth is inversely proportional with temperature.

Fig. 7.13  Schematic representation of the $T_{DB}$ of coated substrates as a function of the TTT of the coating. Region I: the $T_{DB}$ is equal to that of the substrate. Region II: the $T_{DB}$ is equal that of the coating. Region III: the $T_{DB}$ is determined by crack arrest or coating delamination. $T_{DB}^{sub}$ is the $T_{DB}$ of the uncoated substrate.

In figure 7.13 three different regions can be observed. In region I the TTT of the coating is very low causing the $T_{DB}$ of the substrate to be higher than that of the coating. As a result surface embrittlement is not observed and the fracture behaviour of the coated substrate is equal to that of the uncoated substrate.

In region II the ductility of the substrate is larger than the ductility of the coating. Furthermore, for these coated substrates crack arrest and coating delamination do not occur in the temperature range below the $T_{DB}$ of the coating, i.e., $P_{deb} < P_{cat}$ and $P_{cat} > 0$. For these coated systems there is a linear dependence of the $T_{DB}$ of the coated plastic on the TTT of the coating with a slope about equal to unity (assuming that the dependence of $T_{DB}$ on testing conditions is similar for all coatings). Under these conditions brittle fracture of the coating always immediately results in fracture of the coated substrate. This can be considered as the situation where surface embrittlement has the most detrimental effect on the fracture behaviour of the coated substrate and, consequently, the plot of the $T_{DB}$ of the coated plastic against the TTT of the coating in region II can be regarded as the upper limit for surface embrittlement irrespective of other experimental conditions. At temperatures above this limiting value of $T_{DB}$ the coating deforms in a ductile manner and the surface embrittlement effect is not observed.

In region III the $T_{DB}$ of the coated substrate is lower than that of the coating, that is, in the temperature range between the $T_{DB}$ of the coated substrate and that of the coating, the coated substrate deforms ductile despite the fact that the coating fractures in a brittle manner. The
difference in $T_{DB}$ of the coating and the coated substrate is caused by crack arrest or by coating delamination. The value for the $T_{DB}$ of the coated substrate in region III is determined by $P_{cat}$ and $P_{deb}$.

The lower limit of the $T_{DB}$ of the coated substrate in region III, represented by the dashed line in figure 7.13, is found for those coated plastics for which in the temperature range above $T_{DB}^{ub}$ either $P_{cat} < 0$ (always crack arrest), or $P_{deb} > P_{cat}$ and $P_{deb} > 0$ (always coating delamination). In these cases the surface embrittlement effect is not observed and the $T_{DB}$ of the coated plastic is equal to that of the uncoated substrate. Note that region II is not present in this case.

The cases for which the $T_{DB}$ of the coated substrate is found between the $T_{DB}$ of the coating and that of the uncoated substrate correspond to situations in which $P_{deb}$ is positive and equal to $P_{cat}$. For these coated plastics there is a competition between catastrophic crack growth and coating delamination in the temperature range above $T_{DB}^{ub}$. At temperatures above the $T_{DB}$ of the coated plastic the coating debonds from the substrate upon deformation whereas at lower temperatures fracture of the coating immediately results in fracture of the substrate. If the biaxial residual strain can be neglected the condition of $P_{deb} = P_{cat}$ can be approximated by:

$$\sigma_{s,fc}(T_{DB}) = \frac{K_{la} \varepsilon_{fc}^2 \sqrt{h} E_{coat}}{2 \gamma G_{c,adh}} \quad (h > h^*) \quad \text{[1]}$$

where $K_{la}$ is the arrest toughness of the substrate, $\varepsilon_{fc}$ is the tensile fracture strain of the coating, $h$ is the coating thickness, $E_{coat}$ is the elastic modulus of the coating, $\gamma$ is a constant depending on geometry and $G_{c,adh}$ is the level of adhesion. The $T_{DB}$ of the coated substrate is found at the temperature where the stress in the substrate at the moment of fracture of the coating is equal to $\sigma_{s,fc}(T_{DB})$. As an example, the $T_{DB}$ of a ductile plastic ($K_{la} = 1 \text{ MPa m}^{1/2}$) coated with a brittle coating ($E_{coat} = 6 \text{ GPa}$; $\varepsilon_{fc} = 0.04$) of 40 $\mu$m with a moderate level of adhesion ($G_{c,adh} = 0.2 \text{ kj/m}^2$) is found at that temperature for which the stress in the substrate at the strain equal to the fracture strain of the coating is 76 MPa. When the stress/strain curve of the substrate material at the appropriate strain rate is known at a range of relevant temperatures, the $T_{DB}$ of the coated substrate can be predicted exactly using an interpolation procedure.

In the discussion above it is assumed that the occurrence of crack arrest always results in a significant reduction of the surface embrittlement effect. As the experiments in chapter 6 have shown, this assumption is not always true for practical systems. In practice, it is likely that crack arrest will only result in a significant reduction of the surface embrittlement effect if $P_{cat} \ll 0$.

The determined influence of various material parameters on the fracture behaviour of coated plastics as shown schematically in figure 7.13 can be used to design coated plastics which show minor, or even no, surface embrittlement. Evidently, the most simple solution to diminish the surface embrittlement effect observed in coated plastics is the use of very
ductile coatings. However, for automotive coatings it is very important that the high ductility of the coating is not accompanied by a low \( T_g \) as this has a detrimental effect on various other important coating properties. Although it was shown in this chapter that some coatings indeed combine a high \( T_g \) with a high ductility, it is often found that the development of hard and ductile coatings is very difficult in practice.

The surface embrittlement effect observed using hard and brittle coatings can be reduced by crack arrest. Crack arrest is favoured by a high arrest toughness of the substrate or a low coating thickness. The latter option can often not be used in practical situations as the coating must protect the substrate from solvents, scratches and UV-degradation and provide sufficient colour and appearance matching with the other parts of the car body.

The surface embrittlement effect can also be largely reduced by decreasing the level of adhesion leading to delamination of the coating upon loading of the coated plastic. The same effect can be obtained by using a second coating layer (primer), applied between the brittle coating and the ductile substrate, having a low strength. When this coated plastic is deformed the primer will fracture cohesively leading to delamination of the brittle coating. In the ideal case the level of adhesion (or the cohesive strength of the primer) is low at high deformation rates or low temperatures only. In that case the (top)coating will remain adhered when the coated plastic is loaded under conditions where the coating deforms in a ductile manner, i.e., low rate at higher temperatures.

7.4 CONCLUSIONS

After application of a brittle coating the fracture properties of ductile materials can be significantly reduced. If the level of adhesion between the coating and the substrate is high and the coating is thick enough to prevent important beneficial effects of crack arrest on the mechanical properties, the fracture strain of the coated plastic is practically identical to the fracture strain of the coating. This was clearly demonstrated for a series of well-adhering polyurethane coatings applied on IM PA66/PPE where the ductile-to-brittle transition of the coated plastic was found to coincide with that of the coating. As expected, for these materials it was found that the \( T_{DB} \) of the coated substrate decreases with increasing ductility of the coating. Depending on the ductility of the coating, the \( T_{DB} \) of the coated plastic measured in high-speed tensile tests was found to vary between \( -60^\circ\text{C} \) (equal to the \( T_{DB} \) of the uncoated plastic) for very ductile coatings and \( 35^\circ\text{C} \) for brittle coatings.

Testing the same series of polyurethane coatings on IM PA66/PPE at a much slower rate resulted in very similar surface embrittlement effects as measured in high-speed tensile tests. Again, it was found that the \( T_{DB} \) of the coated substrate practically coincides with the \( T_{DB} \) of the coating. In the low-speed tensile test the \( T_{DB} \) of the coated substrate was also found to decrease with increasing coating ductility and the surface embrittlement effect was not observed for very ductile coatings. As expected, the ductile-to-brittle transition of all materials shifts to lower temperatures on lowering the strain rate. Decreasing the tensile deformation rate over four decades caused a shift of the \( T_{DB} \) of the coating, and in this case thus of the coated plastic, by roughly \( 60^\circ\text{C} \), whereas the shift of the \( T_{DB} \) of the uncoated
substrate was found to be 40°C.
In this study it was found that the $T_{DB}$ of these polyurethane coated IM PA66/PPE samples determined at both high-speed and low-speed as a function of coating ductility could be very well related to the tear transition temperature of the coating. This relation seems to have general validity suggesting that the trouser tear test provides a quick and reliable method for screening the $T_{DB}$ of coated plastics. In this study it was further demonstrated that the $T_{DB}$ of these coated substrates is hardly correlated to the $T_g$ or the hardness of the coating.

7.5 REFERENCES

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The same text can be found in chapter 5 of this thesis.

SINGLE CANTILEVER ADHESION TEST (SCAT)

The test described previously in chapter 5 (DCAT) can be used to measure the energy release rate required for the initiation of coating delamination. As discussed in the introduction of chapter 5, it may be expected that the energy needed to initiate a crack between a coating and a substrate is higher than that needed to propagate an existing crack between a coating and a substrate. To verify this, we have developed a modified quantitative adhesion test derived from the DCAT. This test is called the single cantilever adhesion test (SCAT) [1]. In the SCAT the shape of the samples is modified to allow the determination of both the energy release rate for initiation of coating debonding (= $G_c$) and the energy release rate for a stable, propagating crack between coating and substrate (= $G_p$).

The geometry of samples used in the SCAT is shown in figure A1. The adhesive block is partly tapered to increase the required energy as debonding develops. The wedge angle of the tapered part is determined by the shape factor $k$. As shown in this figure, the samples are tested in a single cantilever clamped flexure configuration. The initial free length of the SCAT sample is $L_0$.

\[ k = 2 \tan \alpha \]

\[ L_0 = \text{initial free length} \]

Fig. A1  Schematic overview of the shape of the samples and the test set-up used for the SCAT.

For the sample shown in figure A1 we can derive an expression for the energy release rate in a similar way as done earlier for the DCAT. If the crack propagates in a stable manner, we can neglect the contribution of the kinetic energy and the energy release rate in this case is equal to:

\[ G = \frac{\delta U_{ext}}{\delta A} - \frac{\delta U_{elast}}{\delta A} = \frac{F^2}{2} \frac{\delta C}{\delta A} = \frac{F^2}{2B_{bloc}(a)} \frac{\delta C}{\delta a} \]  \hspace{1cm} A[1]

This expression is similar to equation 2 used for the derivation of $G_c$ for the DCAT. The width of the adhesive block of the SCAT sample (and thus the width of the delamination area)
is a function of the crack length \( a \). The width of the adhesive block can be written as:

\[
B_{\text{block}}(a) = B_{\text{block},0} + k \ a
\]

\[ A[2] \]

To solve equation A1 we have to find an expression for the compliance of the partly tapered substrate as a function of the length of the debonded area.

The deflection of an elastic beam is given by [2]:

\[
\frac{d^2 u}{dx^2} = \frac{M}{E I}
\]

\[ A[3] \]

where \( u \) is the deflection of the beam in the direction of the applied load, \( x \) is the distance from a chosen origin to any section of the beam, \( M \) is the bending moment, \( E \) is the bending modulus of substrate and \( I \) is the moment of inertia (= \((BH^3)/12\)).

Starting from equation A3 and using the known boundary conditions at \( x=L_0 \) and at \( x=L_0+a \), we can calculate the compliance of the SCAT sample:

\[
C = \frac{12}{EH^3} \left[ \frac{L_0^3}{3B_0} + \frac{a(a+4L_0)}{2k} - \frac{aB_0}{k^2} - \frac{(kL_0-B_0)^2}{k^3} \ln \left( \frac{B_0+k a}{B_0} \right) \right]
\]

\[ A[4] \]

where \( H \) is the thickness and \( B_0 \) the smallest width of the substrate. From this equation \( \delta C/\delta a \) can be calculated and the formula for the energy release rate is found:

\[
G = \frac{6F^2(L_0+a)^2}{EH^3(B_0+k a)(B_{\text{block},0}+k a)}
\]

\[ A[5] \]

Equation A5 can be further simplified by adjusting the shape of the SCAT sample and choosing a proper value of the initial free length. If \( k=1 \), and \( B_0=B_{\text{block},0}=L_0 \), the energy release rate is independent of \( a \):

\[
G = \frac{6F^2}{EH^3}
\]

\[ A[6] \]

For this configuration of the SCAT we expect the following force/deflection behaviour. Initially, there is a linear increase of the force with deflection. At a certain critical force \( F_c \) initiation of coating debonding starts. After initiation of debonding, the force decreases until it reaches a constant value \( F_p \) characteristic of the energy release rate for stable crack propagation. Using equation A6 we can calculate \( G_c \) and \( G_p \) from the values of \( F_c \) and \( F_p \), respectively.
In practice, the condition $B_0 = B_{\text{block},0}$ is not met and we have to use equation A5 to calculate the values of the energy release rate.

In the above equations $L_0$ is the *corrected* initial free length, that is, $L_0$ is equal to the distance between the edge of the epoxy and the position where the load is applied plus a correction term due to the finite stiffness of the epoxy adhesive block. The corrected value of $L_0$ can be calculated from the measured compliance:

$$L_0 = \sqrt[3]{\frac{CEB_0 H^3}{4}} \quad \text{A[7]}$$

We assume that the experimental error in the calculated value of the energy release rate due to the use of equation A7 is small.

---

**Fig. A2** Experimental SCAT force-deflection curves for two different coatings on IM PC/PBT: (a) cohesive failure (crack growth in coating AA layer); (b) adhesive failure between coating AB and IM PC/PBT. Calculated values for $G_c$ and $G_p$ are given in the figure.
The experimental procedure of the SCAT is similar to that described for the DCAT. We have used the SCAT to determine the level of adhesion of a limited set of coated plastics. Figure A2 presents two examples of SCAT force–deflection curves. These curves were measured for two different coatings on IM PC/PBT (coating AA and coating AB, respectively). Coating AA failed cohesively and coating AB failed adhesively in these tests. As expected, the force–deflection curve shows a maximum followed by a plateau characteristic for stable crack growth. The values of $G_c$ and $G_p$, calculated using equation A5, are given in the figure. For coating AA the difference between the energy release rate for initiation $G_c$ and that for propagation $G_p$ is small. On the other hand, this difference is enormous (a factor of 10!) for coating AB. These results clearly show the importance of determining both $G_c$ and $G_p$.

In figure A3–a, the SCAT force–deflection curve for a water–borne coating on IM PC/PBT is shown. This coating failed adhesively in this test.

Fig. A3  (a) Experimental SCAT force–deflection curve for a water–borne coating on IM PC/PBT; (b) values of $G$ as a function of the length of the debonded area (crack length) calculated from the force–deflection curve of (a).
From the force/deflection curve we have calculated the energy release rate as a function of crack length (= length of the debonded area). The result for this sample is shown in figure A3–b. The crack length was calculated from the measured compliance. For this sample $G_c$ is about 0.36 kJ/m², and the value of $G_p$ is approximately 0.20 kJ/m². The value of $G_p$ is almost independent of crack length.

The results of the SCAT presented here show that this new quantitative adhesion test is suited for determination of both the energy release rate for initiation of coating debonding and the energy release rate for stable crack propagation between a coating and a plastic substrate. Both values are needed for a complete, meaningful characterization of the level of adhesion of coatings on plastics.

**REFERENCES**


Abstract

One of the major problems encountered with coated plastics is the so-called surface embrittlement. Due to this surface embrittlement effect the mechanical fracture behaviour of ductile plastics coated with a thin, brittle coating is often inferior compared to that of the uncoated plastic. The observed reduction of the fracture properties is caused by the brittleness of the coating. On loading the coated plastic the brittle coating fractures at a low strain. If the crack in the coating reaches the interface between the coating and the substrate, the crack can often propagate through the substrate due to the high stress intensity at the tip of the crack. In this way, fracture of the brittle coating causes premature (brittle) fracture of the coated plastic.

In the study described in this thesis, the surface embrittlement effect observed with coated plastics is investigated in detail. The influence of the properties and thickness of the coating, the level of adhesion between the coating and the substrate, the temperature and the strain rate on the embrittlement of coated plastics is determined experimentally. The aim of this study was the development of a model describing the mechanical fracture behaviour of coated plastics on the basis of the properties of the coating and the substrate and the level of adhesion.

For this study a ductile, rigid engineering plastic (IM PA66/PPE) was used as a model substrate. One of the advantages of this material is its high solvent resistance; the solvents from the paint formulations used in this study do not affect its mechanical properties. The influence of temperature on the mechanical tensile properties of coated and uncoated IM PA66/PPE was studied at both a very high (10^5\% min^{-1}) and a low strain rate (10\%/min^{-1}). On decreasing the temperature, or increasing the strain rate, the fracture behaviour of plastics can change from ductile to brittle. The temperature at which this transition is observed at a given strain rate is the ductile-to-brittle transition temperature $T_{DB}$. The $T_{DB}$ is an important parameter for materials as it determines the temperature range in which the material is applicable in practice. In this thesis the ductility (fracture behaviour) of coated and uncoated plastics is described by the $T_{DB}$. The difference in $T_{DB}$ of the coated substrate and that of the uncoated substrate is used as a measure for the surface embrittlement effect.

At a strain rate of 10^5\%/min^{-1} the $T_{DB}$ of uncoated IM PA66/PPE is found at -60°C. This low value of $T_{DB}$ shows the high ductility of this material. On lowering the strain rate to 10\%/min^{-1} the $T_{DB}$ decreases to -100°C. Application of a perfectly-adhering, brittle coating (PUR-A) of only 40 μm causes a dramatic reduction of the mechanical properties. The $T_{DB}$ of this coated plastic is 15°C at a strain rate of 10^5\%/min^{-1} corresponding to a $T_{DB}$ shift of 75°C compared to uncoated IM PA66/PPE. A similar change in $T_{DB}$ was observed at low strain rate. For this coated system it was shown that fracture of the coating almost always causes immediate fracture of the substrate. Consequently, the $T_{DB}$ of the coated substrate is equal to that of the coating.

Crack arrest was found to occur in some of the PUR-A coated IM PA66/PPE samples during high-speed tensile testing, although this did never lead to a significant improvement of the
fracture behaviour. A simplified fracture mechanics model was used to describe the conditions under which crack arrest occurs after coating fracture. The model further predicts that the coating will debond from the substrate after coating fracture if the level of adhesion between the coating and the substrate is insufficiently high. Surface embrittlement will not be observed if coating delamination occurs.

To study the influence of coating ductility and adhesion level on the fracture behaviour of coated plastics two new test methods were developed. The trouser tear test is used to study the tear behaviour of coatings as a function of temperature at low testing speeds. The temperature at which the crack propagation behaviour changes from stable, ductile tearing to unstable, brittle fracture is called the tear transition temperature TTT. The TTT is a measure of the ductility of the coating. In this study the TTT is determined as a function of coating composition. It was shown that a unique relation between the TTT and the Tg of coatings does not exist. For PUR-A it was found that the TTT increases with increasing coating thickness.

The second test, the double cantilever adhesion test (DCAT), is a quantitative adhesion test for coated plastics. It determines the critical energy release rate $G_{c,adh}$ for the onset of coating delamination. The energy release rate is the amount of energy required to debond the coating from the substrate per unit area. Using the DCAT it was demonstrated that the level of adhesion of PUR-A on IM PA66/PPE depends strongly on the surface pretreatment of the substrate.

The simultaneous influence of both the level of adhesion and the coating thickness was determined for PUR-A coated IM PA66/PPE at a strain rate of $10^5\%\text{min}^{-1}$. It was shown that these two parameters both have a large influence on the degree of surface embrittlement caused by a given coating. Depending on the coating thickness and the adhesion level the $T_{DB}$ of PUR-A coated IM PA66/PPE varies from -60°C to 35°C.

If the adhesion level is very low ($G_{c,adh}=0.02$ kJ/m²) the PUR-A coating delaminates entirely from the substrate after coating fracture. In this case the mechanical properties of IM PA66/PPE do not change on application of the brittle coating.

If the level of adhesion is very high ($G_{c,adh}>1$ kJ/m²) delamination of the PUR-A coating does not occur. Application of the well-adhering PUR-A leads to a significant deterioration of the mechanical properties of IM PA66/PPE. The $T_{DB}$ of PUR-A coated IM PA66/PPE for a coating thickness of 40 µm and 65 µm is 15°C and 35°C, respectively. For these materials the fracture strain of the coated substrate is almost identical to that of the coating. The detrimental surface embrittlement effect caused by the well-adhering, brittle coating can be reduced by decreasing the coating thickness. For IM PA66/PPE provided with a 13 µm PUR-A coating the $T_{DB}$ is -30°C. The reduced surface embrittlement effect is caused by crack arrest taking place at the interface between substrate and coating or in the substrate material. At low temperatures ($\leq-30°C$) crack arrest does not occur and the coated substrate fractures in a brittle manner.

For a coating thickness of 40 µm and 75 µm the $T_{DB}$ of PUR-A coated IM PA66/PPE at an intermediate level of adhesion ($G_{c,adh}=0.7$ kJ/m²) is -20°C and 0°C, respectively. These
$T_{DB}$'s are about 35°C lower than the $T_{DB}$ of the coating. The observed difference in $T_{DB}$ of the coating and the coated substrate is caused by delamination of the coating. For thin PUR-A coatings at an intermediate level of adhesion delamination of the coating is (almost) absent. This observation explains the resemblance of the fracture properties of IM PA66/PPE coated with 13 μm PUR-A at an intermediate ($G_{e,adh}=0.3$ kJ/m²) adhesion level and at a high ($G_{e,adh}>1$ kJ/m²) adhesion level.

These results show that, depending on the thickness of the coating and the adhesion level, the crack from the coating can (i) be arrested at the interface or in the substrate, (ii) cause delamination of the coating or (iii) propagate through the substrate resulting in brittle fracture of the substrate. The fracture mechanics model presented in this thesis predicts which process will occur under given conditions. It was found that this model gives a good description of the observed influence of coating thickness and adhesion level on the fracture behaviour of the coated plastic.

If crack arrest does not occur the fracture behaviour of plastics with a perfectly-adhering coating is determined by the ductility of the coating only. This was experimentally verified by determining the fracture behaviour of coated IM PA66/PPE as a function of the ductility of the coating at $10^5$%min⁻¹ and $10%$min⁻¹. The ductility of the coatings applied varied from extremely tough to very brittle. It was found that brittle coatings cause a significant surface embrittlement effect and the $T_{DB}$ of the coated IM PA66/PPE is much higher than that of uncoated IM PA66/PPE. An increase of the coating ductility causes a decrease of the $T_{DB}$ of the coated substrate. In the case of very ductile coatings the $T_{DB}$ of coated IM PA66/PPE becomes even identical to that of uncoated IM PA66/PPE. Lowering of the strain rate results in a decrease of the $T_{DB}$ of uncoated and coated IM PA66/PPE. For both strain rates used it was found that the $T_{DB}$ of the coated substrate can be accurately described by the TTT of the coating. With the results of a series of well-adhering coatings on a different engineering plastic the general validity of the relation between the $T_{DB}$ of the coated substrate and the TTT of the coating was shown. The TTT also gives a correct prediction of the influence of the coating thickness on the fracture behaviour of coated plastics. The TTT was shown to be a much better indicator for embrittlement than the $T_R$ or the hardness of the coating which are usually used as indicators.

Finally, the general implications of the model for the development of coated engineering plastics are described.
Samenvatting

Het gebruik van kunststoffen is de afgelopen jaren in de automobielfabricage sterk toegenomen. Toepassing van kunststoffen biedt een aantal voordelen, zoals gewichtsbesparing, leidend tot een vermindering brandstofverbruik en vermindering uitstoot van schadelijke stoffen, corrosiebestendigheid, laag energieverbruik tijdens fabricage en ontwerpflexibiliteit. Ongeveer 35% van het gewicht van de gebruikte hoeveelheid kunststoffen wordt toegepast in carrosserieën, zoals bumpers, spatborden en spoilers. Kunststof carrosserieën worden veelal van een lak voorzien. Dit gebeurt enerzijds om het kunststof deel dezelfde kleur en hetzelfde uiterlijk te geven als de rest van de carrosserie en anderzijds om de kunststof te beschermen tegen degradatie ten gevolge van UV-straling en tegen oplosmiddelen, zoals benzine.

Een belangrijke eigenschap van veel carrosserieën is het mechanisch gedrag tijdens stootbelasting, ook wel slagvastheid genoemd. Tijdens een botsing bij geringe snelheid dient het geraakte carrosseriedeel intact te blijven. Een autodeur, of ander deel dat in contact kan komen met de inzittenden, mag bij een botsing bij hogere snelheid weliswaar bezwijken, maar zeker niet bros breken (versplinteren).

Een belangrijk probleem bij gelakte kunststoffen is de oppervlakteverbossing die op kan treden bij het gebruik van een of meer harde laklagen. Door deze oppervlakteverbossing is het mechanisch gedrag van een kunststof met een goedhechtinge lak inferieur in vergelijking met het gedrag van dezelfde kunststof zonder laklaag. Ondanks de geringe dikte van de lak, veelal slechts circa 50 μm (=0.05 mm), kan de gelakte kunststof bros breken onder omstandigheden waarbij dezelfde kunststof zonder lak taai deformeert. Oppervlakteverbossing van gelakte kunststoffen wordt veroorzaakt door de brosheid van de gebruikte lak. Bij vervorming van het gelakte onderdeel, bijvoorbeeld tijdens een botsing, zal de brosse lak reeds bij lage rek gaan scheuren. De in de lak ontstane scheur kan door de grenslaag tussen de lak en de kunststof groeien en op deze wijze voortijdig breuk van de kunststof veroorzaken. Oppervlakteverbossing van gelakte kunststoffen treedt vooral bij lage temperatuur en hoge deformatiesnelheid op.

In het onderzoek dat beschreven is in deze dissertatie is de invloed van de eigenschappen en dikte van de lak, de hechtingsniveau, de temperatuur en de treksnelheid op het mechanisch gedrag van gelakte kunststoffen onderzocht. Doel van het onderzoek was het opstellen van een model dat de mechanische eigenschappen van gelakte kunststoffen kan voorspellen aan de hand van de (op onafhankelijke wijze bepaalde) eigenschappen van de lak en de kunststof en de experimentele testcondities.

In dit onderzoek is een taai, stijve kunststof (IM PA66/PPE) gebruikt als model-substraat. Een van de voordelen van dit materiaal is dat de oplosmiddelen, die in dit onderzoek gebruikt worden om de lak aan te brengen, geen invloed hebben op het mechanisch gedrag van deze kunststof. De invloed van de temperatuur op het breukgedrag van ongelakt en gelakt IM PA66/PPE werd onderzocht bij zowel zeer hoge (10^5%min^-1) als bij lage (10%min^-1) treksnelheid. Bij verlaging van de temperatuur, of verhoging van de deformatiesnelheid, kan
het mechanisch gedrag van kunststoffen veranderen van taai naar bros. De temperatuur waarbij deze overgang plaatsvindt bij een bepaalde snelheid wordt de bros/taai-overgang $T_{DB}$ genoemd. De $T_{DB}$ is een belangrijke maatstaf voor het mechanisch gedrag van kunststoffen aangezien deze het temperatuurgebied aangeeft waarin het materiaal in de praktijk toegepast kan worden. In dit onderzoek wordt de $T_{DB}$ veelvuldig gebruikt om de ductiliteit (breukgedrag) van gelakte en ongelakte kunststoffen te beschrijven. Materialen met een lage $T_{DB}$ deformeren zelfs bij lage temperatuur taai en hebben, volgens de in dit proefschrift gehanteerde definitie, een hoge ductiliteit. Het verschil in $T_{DB}$ tussen de gelakte en de ongelakte kunststof wordt gebruikt als een maat voor oppervlakteverbrosting.

De $T_{DB}$ van ongelakt IM PA66/PPE is -60°C bij een trek snelheid van $10^5 \text{% min}^{-1}$. Deze lage $T_{DB}$ toont de hoge ductiliteit van deze kunststof. Bij verlaging van de trek snelheid tot $10 \text{% min}^{-1}$ daalt de $T_{DB}$ tot -100°C. Indien IM PA66/PPE voorzien wordt van een bross, goedhechtende lak (PUR-A) met een dikte van slechts 40 µm leidt dit tot een dramatische verslechtering van de mechanisch eigenschappen. De $T_{DB}$ van dit gelakte IM PA66/PPE is 15°C bij een trek snelheid van $10^5 \text{% min}^{-1}$, hetgeen overeenkomt met een verschuiving van de $T_{DB}$ over 75°C ten opzichte van ongelakt IM PA66/PPE. Een vergelijkbare verschuiving van de $T_{DB}$ werd gevonden bij lage trek snelheid. Voor dit gelakte materiaal werd aangetoond dat breuk van de lak vrijwel altijd direct breuk van het substraat tot gevolg heeft. Consequentie hiervan is dat de $T_{DB}$ van het gelakte substraat identiek is aan de $T_{DB}$ van de lak op het substraat.

Voor enkele PUR-A gelakte IM PA66/PPE monsters werd een verschil waargenomen tussen het breukmoment van de lak en die van het substraat, maar dit had geen duidelijke verbetering van het breukgedrag van deze monsters tot gevolg. Met een vereenvoudigd breukmechanica model is beschreven onder welke condities de scheur van de lak zich niet (direct) door het substraat kan voortplanten, dit wordt ook wel scheurstop genoemd. Met dit model is tevens te voorspellen dat onthechting van de lak op kan treden na lakbreuk ingeval het hechtingsniveau tussen de lak en het substraat onvoldoende hoog is. Indien de lak onthecht van het substraat, zal oppervlakteverbrosting niet optreden.

Voor de bestudering van de invloed van de ductiliteit van de lak en het hechtingsniveau op het breukgedrag van gelakte kunststoffen was het noodzakelijk een tweetal testen te ontwikkelen. De eerste test wordt de trouser tear test genoemd en kan gebruikt worden om de invloed van de temperatuur op het scheurpropagatiegedrag van vrijstaande lakkagen te bestuderen bij lage testsnelheid. De temperatuur waarbij het scheurpatroon in de lakkfilm verandert van een taai, stabiele scheur in een bross, instabiele scheur noemen we de scheur-overgangstemperatuur TTT. De TTT is te beschouwen als een directe maat voor de ductiliteit van de lak. In deze studie is de TTT gemeten als functie van de samenstelling van de lak. Uit de metingen kan geconcludeerd worden dat er geen eenduidige relatie bestaat tussen de TTT en de glasovergangstemperatuur van lakken. Voor PUR-A werd aangetoond dat de TTT naar hogere temperatuur verschuift indien de lakdikte toeneemt.

De tweede test, de double cantilever adhesion test (DCAT), is een kwantitatieve hechtingstest voor gelakte kunststoffen. Met de DCAT wordt de hoeveelheid energie ($G_{c,adh}$) bepaald die
per oppervlakte nodig is voor de initiërtion van onthechting van de lak. Met de DCAT werd ondermeer aangetoond dat het hechtingsniveau van PUR-A op IM PA66/PPE zeer sterk beïnvloed wordt door de gebruikte schoonmaakmethode van het substraat vóór het lakken.

Voor IM PA66/PPE gelakt met PUR-A is de gecombineerde invloed van het hechtingsniveau en de lakkide op het breukgedrag van de gelakte kunststof bepaald bij een treksnelheid van 10^5 % min^-1. Uit deze experimenten blijkt dat deze parameters de mate van oppervlakteverbossing sterk beïnvloeden. Afhankelijk van de lakkide en het hechtingsniveau varieert de T_{DB} van PUR-A gelakt IM PA66/PPE van -60°C tot 35°C. Bij een zeer laag hechtingsniveau tussen PUR-A en IM PA66/PPE (G_{c,adh}=0.02 kJ/m²) onthecht de lak volledig van het substraat na lakbreuk. In dit geval veroorzaakt het aanbrengen van een brosse lak geen verandering in het breukgedrag van IM PA66/PPE.

Bij een zeer hoog hechtingsniveau (G_{c,adh}>1 kJ/m²) treedt onthechting van de PUR-A lak niet op. Het aanbrengen van de goedhechtende PUR-A lak leidt tot een enorme afname van de slagvastheid van de kunststof. Voor een dikte van de PUR-A lak van 40 µm en 65 µm is de T_{DB} van het gelakte IM PA66/PPE respectievelijk 15°C en 35°C. Voor deze monsters was de breukrek van het gelakte substraat vrijwel identiek aan de breukrek van de lak. De afname van de slagvastheid van IM PA66/PPE is minder groot bij zeer lage lakkide; de T_{DB} van IM PA66/PPE met 13 µm PUR-A is -30°C. De verminderde afname van het breukgedrag van IM PA66/PPE bij lage lakkide wordt veroorzaakt door het afstoppen van de lakscheur aan de grenslaag tussen lak en substraat of in het substraat (scheurstop). Bij lage temperatuur (≤ -30°C) treedt scheurstop niet meer op en breekt het gelakte substraat brok.

Voor lakkides van 40 µm en 75 µm werd de T_{DB} van PUR-A gelakt IM PA66/PPE bij een middelmatig hechtingsniveau (G_{c,adh}=0.7 kJ/m²) gevonden bij respectievelijk -20°C en 0°C. Deze T_{DB}'s zijn circa 35°C lager dan de T_{DB} van de lak. Het verschil in T_{DB} van de lak en van het gelakte substraat wordt veroorzaakt door onthechting van de lak. Bij lage lakkides wordt onthechting van het matig-hechtende PUR-A nauwelijks waargenomen. Dit verklaart de grote overeenkomst tussen het breukgedrag van IM PA66/PPE met een 13 µm PUR-A lak bij een matig hechtingsniveau (G_{c,adh}=0.3 kJ/m²) en dat bij een hoog hechtingsniveau (G_{c,adh}>1 kJ/m²).

Bovenstaande resultaten tonen dat, afhankelijk van de lakkide en het hechtingsniveau, de in de lak ontstane scheur (i) kan worden afgestopt in het substraat of aan de grenslaag, (ii) onthechting van de lak kan veroorzaakt of (iii) zich kan voortplanten door het substraat en zo voortijdig breuk van de gelakte kunststof kan veroorzaakt. Het in deze dissertatie gepresenteerde breukmechanica-model voorspelt welk van deze processen optreedt onder gegeven omstandigheden. Dit model geeft een goede beschrijving van de experimenteel bepaalde invloed van de lakkide en het hechtingsniveau op het breukgedrag van de gelakte kunststof.

Indien scheurstop niet, of niet in belangrijke mate optreedt, is te verwachten dat het breukgedrag van kunststoffen met een perfect-hechtende lak volledig bepaald wordt door de ductiliteit van de lak. In dit onderzoek werd dit experimenteel geverifieerd aan de hand van
de bepaling van de invloed van verschillende lakken op het breukgedrag van gelakt IM PA66/PPE. De ductilitéit van de gebruikte lakken varieerde van zeer bros tot zeer taai. Het breukgedrag van de gelakte materialen werd bepaald bij $10^5 \text{% min}^{-1}$ en bij $10 \text{% min}^{-1}$. Zeer brossé lakken veroorzaken een dramatische oppervlakteverbrossing en de $T_{DB}$ van het gelakte substraat is aanzienlijk hoger dan dat van ongelakt IM PA66/PPE. Indien de ductiliteit van de lak toeneemt, daalt de $T_{DB}$ van het gelakte substraat. Voor zeer taai lakken is de $T_{DB}$ van het gelakte substraat zelfs identiek aan dat van ongelakt IM PA66/PPE. Verlaging van de deformatiesnelheid leidt tot een verlaging van de $T_{DB}$ van zowel gelakt als ongelakt IM PA66/PPE. Voor beide treksnelheden kan de $T_{DB}$ van het gelakte substraat nauwkeurig voorspeld worden door de TTT van de lak. Aan de hand van de resultaten voor een aantal goedhechttende lakken op een ander type substraat werd de algemene geldigheid van de relatie tussen de $T_{DB}$ van de gelakte kunststof en de TTT van de lak aangetoond. De TTT geeft tevens een goede voorspelling van de invloed van de laddikte op het breukgedrag van gelakte kunststoffen. Alhoewel het breukgedrag van gelakte kunststoffen vaak beschreven wordt aan de hand van de glasovergangstemperatuur of de hardheid van de lak, is in deze studie aangetoond dat deze parameters het breukgedrag van gelakte kunststoffen aanzienlijk minder nauwkeurig beschrijven dan de TTT.

Tenslotte worden, aan de hand van het in dit proefschrift gepresenteerde model, aanbevelingen gedaan voor de ontwikkeling van nieuwe gelakte kunststoffen met een verbeterd verbrossingsgedrag.
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Curriculum vitae


Op 1 september 1987 trad de auteur in dienst van Akzo, nu Akzo Nobel, als research chemicus. In de periode tot 1 januari 1994 was hij werkzaam op de afdeling fysische chemie (CRU, o.l.v. Dr. Ir. J.J. van Aartsen) van Akzo corporate research te Arnhem. In dit proefschrift wordt een deel van het aldaar verrichte onderzoek beschreven.