DYNAMIC MECHANICAL STUDIES ON THERMO-REVERSIBLE AGEING PROCESSES IN GELS OF POLYVINYL CHLORIDE AND OF GELATIN

K. TE NIJENHUIS

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PROEFSCHRIFT

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PROF. DR. H.R.K.N. JANESCHITZ-KRIEGL

Er is een tijd om te zwijgen en een tijd om te spreken.

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K.te Nijenhuis

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LIST OF SYMBOLS

CHAPTER 1

GENERAL CONSIDERATIONS

1.1 INTRODUCTION

It is well known that in dilute solutions many linear polymers, synthetic as well as natural, have a tendency to form aggregates, whereas in more concentrated solutions gels are formed. Examples are polyacrylonitril, polyvinyl alcohol, polyvinyl chloride, isotactic polystyrene, mixtures of isotactic and syndiotactic polymethyl methacrylate, agar, gelatin etc. Although JORDAN-LLOYD (1) said in 1926 "The colloidal condition, the gel, is one which is easier to recognize than to define", HERMANS (2) defined a gel as a coherent system of at least two components, which exhibit mechanical properties characteristic of a solid, where both the dispersed component and the dispersion medium extend themselves continuously throughout the whole system. FLORY (3), in classifying gels, states that they can be subdivided into four types:

- Well ordered lamellar structures, including gel mesophases, as soap gels and clays; the forces between the lamellae may be electrostatic or dipolar.
- Covalent polymer networks, completely disordered; examples are vulcanized rubbers, the protein elastin, vinyl-divinyl copolymers, alkyd and phenolic resins and silicagel.
- 3. Polymer networks formed through physical aggregation; predominantly disordered, but with regions of local order; the primary molecules, usually of linear structure of finite size, are bound together either through the formation of crystallites, involving bundles of chains, or by multiple stranded helices. The crystalline domains may be viewed as cross-linkages of large functionality.
- 4. Particulate, disordered structures, as flocculent precipitates, which usually consist of particles of large geometric anisotropy, e.g. needles or fibrils in brush-heap disarray or reticular networks of fibres as in V_00_5 gels. Other examples are gels formed by aggregation of proteins,

fibrillar as well as globular.

In this thesis the investigation of the thermo-reversible gelation (often called ageing) of solutions of polyvinyl chloride in various plasticizers and of gelatin in water by measurement of their dynamic moduli (i.e. the storage modulus G' and the loss modulus G"), is described. These gels belong to type 3, predominantly disordered but with regions of local order, in the case of polyvinyl chloride through the formation of crystallites (cf. Fig. 1.1) and in the case of gelatin by multiple strand helices (cf. Fig. 1.2).



Fig. 1.1 Schematic view of a gel network of PVC/plasticizer systems.

1.2 REVIEW OF HISTORY AND PROPERTIES OF POLYVINYL CHLORIDE AND GELATIN

1.2.1 Polyvinyl chloride

Already in 1922 PLOTNIKOW (4) published his investigations on the photopolymerization of vinyl chloride. Besides his measurements of the kinetics of the polymerization he also paid attention to properties of the product and he stated that gels are obtained by solving the product in aniline (50-72%) or in tetraline (70-85%). In 1926 FLUMIANI (5) published his colloid chemical findings on the photopolymerization product of vinyl chloride. He reported that "für die Bestimmung des Molekulargewichts musste berücksichtigt werden, dass die Temperatur, die verschiedene Erwärmungs-

dauer, das Abstehen der Lösung, das Lösungsmittel selbst, sowie die Art und Weise der Herstellung der Lösung und die Konzentration derselben den Zustand des dispersen Systems beeinflussen könnten" and also that "Lösungen, welche längere Zeit einer höheren Temperatur ausgesetzt wurden, zeigten eine grössere Depression, d.h. ein kleineres Molekulargewicht, als solche Lösungen, die längere Zeit hindurch bei einer niedrigeren Temperatur behandelt wurden. Wurde die Lösung auf 110°C gebracht und etwa eine Stunde lang auf dieser Temperatur gehalten, so näherte sich die Depression einem Grenzwerte, der dem höchtsen Dispersionsgrad, sonach dem kleinsten Molekulargewicht entsprach". In 1928 FLUMIANI (6) published his findings on his studies of the structure of gels. One of his interesting statements is the following: "Das Gebiet der Strukturforschung von Gelen entzog sich bis heute einer systematischen Untersuchung. Eingehend erforscht wurden eigentlich nur die Gallerten der Gelatine und des Agars, sowie die Gele der Kieselsäure (7). Die kolloiddispersen Systeme sind aber so verwickelter Natur, dass sie sich als Objekte allgemeiner Strukturstudien wenig eignen und es auch verständlich erscheint, dass Strukturforschungen an diesen Gebilden oft sogar zu widersprechenden Resultaten führten (8). Wenn man hingegen bedenkt, dass das Photoprodukt des Vinylchlorides relativ einfache Systeme ergibt, was schon dadurch bedingt ist, dass jenes ein einheitliches chemisches Individuum darzustellen scheint(5), wird man leicht einsehen, dass eingehende Studien der Struktur dieser Gele vom physikochemischen Standpunkte aus als lohnenswert erscheinen". From then on an avalanche of investigations on polyvinyl chloride has been published. In 1943 LEADERMAN (9) observed a rubberlike behaviour of plasticized polyvinyl chloride in creep experiments. He assumed the existence of secondary forces between the molecules, which decrease in magnitude with increasing temperature and plasticizer content. REED (10) noticed that ageing took place in plasticized polyvinyl chloride. This held for homopolymers as well as copolymers with up to ten per cent vinyl acetate. Heating to 100° C restored the original properties. DOTY, WAGNER and SINGER (11) studied dilute solutions of polyvinyl chloride in dioxane. Aggregates were formed after cooling a solution from 70° C to room temperature. Sedimentation measurements showed the existence of a minimum aggregation number. From sedimentation measurements on solutions in butanone HENGSTENBERG and SCHUCH (12) calculated this number to be 11 with an upper limit of 25. From additional viscosity

measurements these authors derived an effective hydrodynamic diameter (120-180 Å) which appears to be of the same order of magnitude as that of the primary molecules. From dissymetry of scattered light, however, DOTY and coworkers (11) calculated an aggregation diameter of about 2000 Å. As was pointed out by other authors, these large dimensions could be the consequence of microgel particles (13-16). Apparently, these microgel particles must be formed by a larger number of primary aggregates which are connected by macromolecules being entrapped in more than one of these aggregates. As reported by HENGSTENBERG and SCHUCH (12) HENDUS showed with the aid of small angle X-ray scattering (SAXS) that the radius of the primary aggregates is indeed rather small, viz. 70-80 Å.

Already in 1947-1949 ALFREY and coworkers (18-20) proved by means of X-ray diffraction that the cross-links occurring in polyvinyl chloride/ plasticizer gels are formed by crystallites. According to BONART (21). HENDUS showed with the aid of SAXS that the small-angle spacing of the lamellar structures in polyvinyl chloride increases with increasing plasticizer content from 150 Å (0% plasticizer) to 300 Å (80% plasticizer), as a consequence of preferential collection of the plasticizer between the lamellae. For more syndiotactic polyvinyl chloride these values appear to be a little lower. Qualitatively, the same result are reported by GEZOVICH and GEIL (16,17). Together with increasing syndiotacticity also the degrees of aggregation in solution and of crystallinity in the solid material increase (22-30). In general it has been assumed that crystallites of polyvinyl chloride are built up merely of syndiotactic sequences. From X-ray diffraction HELLWEGE, JOHNSEN and KOCKOTT (31) showed that the minimum number of syndiotactic sequences in a crystallite should be 12. But with this postulate the commonly assumed ten per cent crystallinity of nearly atactic commercial polyvinyl chloride cannot be explained. However, according to CRUGNOLA (32), crystallization is also possible with one isotactic sequence between syndiotactic sequences. This, of course, can increase the degree of crystallinity of the solid material tremendously. JUIJN and coworkers (33,34) showed that the crystallinity of commercial polyvinyl chloride would be only 0.045% if at least 12 syndiotactic sequences should be built into a crystallite. From model investigations, however, they concluded that crystallization would also be possible if a larger but even number of isotactic sequences is placed between syndiotactic sequences. In

this way they arrived at a crystallinity of 8.5% for commercial rigid polyvinyl chloride. However, these authors did not take into consideration in their calculations the length (the weight) of the sequences. An improved calculation leads to a crystallinity of 28%, or, if one starts at a crystallinity of 8.5%, to a minimum regular sequence of 19 monomer units. This rather large tendency to form crystallites could probably provide a sufficient number of cross-links in polyvinyl chloride/plasticizer systems to make them behave so extremely rubberlike. In spite of all these and other, more recent (35-37) investigations STRAFF and UHLMANN (38) conclude from their SAXS-measurements that there is an absolute absence of any volume fractions of crystallinity.

By means of tensile measurements WALTER (39) made the following observations on gels of polyvinyl chloride in di-(2-ethylhexyl)phthalate: in the concentration range up to 20% of polymer the gels behave ideally elastic in the sense of the classical theory of rubber elasticity; from 20-50% a small energetic term is perceptible, whereas for concentrated systems

there is a rapid increase with concentration of the contribution of internal energy to the elasticity. He also showed that the duration of the ageing process strongly depends on the concentration: with low concentration an equilibrium value of the YOUNG's modulus was reached within a few months on ageing at 30° C, whereas the concentrated systems with more than 40% of polymer did not even reach an equilibrium value within two years. Oscillatory mechanical measurements were taken by FERRY and coworkers (40-44) on dilute and moderately concentrated solutions of polyvinyl chloride in plasticizers. They were not able to use the time-temperature superposition principle (45) in the normal way. This can be expected if the internal equilibrium structure of the system changes with temperature (46,47). Moreover, the thermal history which, from the present study, appears to be so extremely important, was not well defined in their systems. TEPLOV and coworkers (48) measured the compression modulus of a 62.5% (w/w) solution of polyvinyl chloride in various plasticizers and found that this modulus increased linearly with the logarithm of the ageing time. TE NIJENHUIS and DIJKSTRA (49) investigated a 10% (w/w) solution of polyvinyl chloride in di-(2-ethylhexyl)phthalate; they also found that the storage modulus was a linear function of the ageing time, its slope strongly depending on the ageing temperature.

As far as is known, the existence of crystallites has never been

proven in literature for dilute gels of polyvinyl chloride. On the following grounds, however, we assume their rubberlike behaviour to be caused by crystallites: a) for systems consisting of up to 80% plasticizer HENDUS showed the existence of crystallites by means of X-ray scattering (21); b) the more syndiotactic the polyvinyl chloride, the more rapid the ageing proceeds (22-30); c) the temperatures at which gels revert to solutions are considerably higher than the temperatures at which solutions gelatinize (50,51): this resembles crystallization from undercooled solutions. Moreover, in our laboratory the ageing process of a 10% (w/w) solution of polyvinyl chloride in various plasticizers has been investigated with the aid of SAXS. The increase of the storage modulus appears to be accompanied by an increase of the crystallinity (52).

1.2.2 Gelatin

Gelatin may be defined as a protein made soluble by hydrolysis of collagen derived from the skin, white connective tissue and bones of animals. It is distinguished from animal glue by the way gelatin is isolated from the raw material. For this purpose more purification is needed than with the preparation of glue. In this way a product of high quality is obtained (53).

A more scientific definition is given by VEIS (54): "The gelatins are a class of proteinaceous substances that have no existance in nature, but are derived from the parent protein collagen, by any one of a number of procedures involving the destruction of the secondary structure of the collagen and, in most cases, some aspects of the primary and tertiary structures. Collagen is the principal proteinaceous component of the white fibrous connective tissues, which serve as the chief, tensile stress-bearing elements for all vertebrates, whereas related proteins are found in many of the lower phylla".

Already in former days, thousands of years ago, the use of gelatin as a glutinous material was known. According to BOGUE (55) the extraction of glue by cooking hides dates back at least to the time of the ancient Pharaohs of Egypt. He cites a stone carving from 1400 B.C., found in the ancient city of Thebes, of the period of Thoetmosis III, the Pharaoh of the Exodus, which described the glueing of a thin piece of rare wood veneer of red colour to a yellow plank of sycamore. Also in the Bible, in one of the Apocrypha, the Proverbs of Jesus Sirach, 185 B.C., reference is made to glue:

"He that teacheth a fool is like one that glueth a potsherd together" (Ecclesiasticus XXII, 9) Plinius in the Roman period, about 100 A.D. wrote:

"Glue is cooked from the hide of bulls".

The earliest practical manufacture of glue dates back to the time of William III in Holland in 1690. The first mention of the manufacture of a gelatin as an edible ingredient of food-stuffs is found in a patent by Arney in 1846.

Collagen is a protein with an unusual amino acid composition. It has unusually high contents of glycine and of the imino acids proline and hydroxyproline (both with a pyrrolidine ring) and contains very small amounts of the aromatic and sulphur containing amino acids.

The amino acid composition (56) of the mammalian and avian collagens is remarkably constant. Glycine accounts for about 33% of the total number of amino acid residues, proline and hydroxyproline for about 20% and alanine for about 11%. So these four amino acids account for two-thirds of the amino acid residues in collagen. On the contrary fish collagens show a wider variation in composition, especially in the content of the imino acids. This content is lower, when the fish lives in colder water (see Table 1-I). The composition of amphibia and reptile collagens is rather variable, too, but in general between that of mammals and fishes.

Table 1-I

Number of imino acid residues per 1000 total residues of skin collagen of various animals.

rabbit	crocodile	African lungfish	pike	cod
237	221	207	199	155

The shrinkage temperature or denaturation temperature of collagen fibres appears to be strongly dependent on the content of imino acids, this temperature being lower if the imino acids content is smaller (see Table 1-II) (56-61).

Table 1-II (59)

Dependence between imino acid content and the shrinkage temperature of collagen.

collagen derived from	imino acid content per 1000 residues	shrinkage temperature ^O C
rat	226	40.8
pike	199	30.6
cod	155	20.0

These data show that the imino acid content determines strongly the stability of the structure of collagen. From partial hydrolysis studies (56) a wide spread distribution of glycine and the frequent occurrence in the polypeptide chain of the sequence GLY-PRO-X, where X can be any amino acid, and in particular of the tripeptide GLY-PRO-HYPRO have been demonstrated.



PRO

At first it was assumed that the combination GLY-PRO-HYPRO was of primary importance for the stability of collagen. In that way the intramolecular hydrogen bond between the carboxyl group of glycine and the hydroxyl group of hydroxyproline would be responsible for the stability. From

HYPRO

GLY

measurements of the heat of denaturation and of the shrinkage temperature of collagen, however, one had to conclude that hydrogen bonds do play a part in the stabilization of the collagen structure, but not the most important one. McCLAIN and WILEY (62) concluded from the heat and entropy of denaturation that the tertiary super helix structure of the collagen molecule is stabilized primarily by the steric restrictions imposed by the pyrrolidine residues. On the contrary PRIVALOV c.s. (59,63) suppose that the regular water structure near the macromolecule plays an essential role in stabilizing the collagen structure. On the basis of similar measurements PIEZ and SHERMAN (64) conclude that the imino acid hydroxyproline as such cannot be considered to be the only possibility in order to effectuate the stabilization of collagen, but that among others a tripeptide GLY-PRO-X can be responsible for the collagen structure. These authors suppose that the formation of a collagen type helix only requires the repeating tripeptide sequence (GLY-X-Y), where X and Y can be any amino acid, provided there is an average of at least one residue of proline or hydroxyproline every other triplet.

The structure of collagen is mainly derived from detailed X-ray diffraction and electron microscope studies. By stretching collagen COWAN c.s. (65) were able to improve the X-ray diffraction pattern considerably. With the aid of this pattern similar structures were proposed by three groups of workers (66-69). At present this model of the collagen structure is generally accepted. Essentially the model consists of three separate peptide chains coiled along a left-handed three fold screw axis with three residues in one turn (see also refs. 57,70,71 e.g.). These three residues complete their turn in about 9 Å. The three helices are arranged parallel to each other, so that, when viewed from above, their axes are set at the corners of an equilateral triangle of side 5 Å. Further, a slight righthanded super helix is formed about a common axis, with an overall repeat distance of about 86 Å and a translation of 2.86 Å from a residue on one chain to the corresponding residue on another. In this model two features have to be emphasized: the steric hindrance of rotation, as imposed by the high content of pyrrolidine residues, and the occurrence of glycine at every third residue, permitting the three chains to approach each other closely enough for the formation of hydrogen bonds. Whether one or two hydrogen bonds are involved in triplets containing only one pyrrolidine residue, is still open to question. However, studies on thermal denatura-

tion and rates of deuterium and tritium exchange have produced results in favour of the double bonded structures (56).

The denaturation process of collagen involves the melting of the ordered hydrogen bonded structure. In this process the triple helical structure is destroyed to produce one, two or three random chains gelatin molecules.

In literature much attention has been paid to the renaturation process of dilute and concentrated gelatin solutions. Already in 1904 LEICK (72) investigated the elasticity of gelatin gels. He concluded that the YOUNG's modulus was nearly proportional to the square of the concentration of gelatin up to 25%. In 1915 ARISZ (73) published his comprehensive studies of the sol and gel state of gelatin solutions. One of the findings, which surprised the author himself, was the remarkable dependency of the sol-gel transition on the thermal history (see Chapter 8). In 1925 POOLE (74) and in 1932 HATSCHEK (75) concluded, too, that the modulus of elasticity of gelatin gels is proportional to the square of the concentration. However, in 1921, SHEPPARD and SWEET (76) did not report a similar relation in the concentration range from 10 to 45%. In 1948 FERRY (77) published a review on protein gels and paid much attention to gelatin gels. From then on many investigation on gelatin have been published. Many of them were concerned with the viscoelastic behaviour of gelatin gels. Special attention has been paid to the dependency of the shear modulus, G, on molecular weight, concentration and temperature.

It appears that, with increasing concentration and molecular weight and with decreasing temperature, the shear modulus becomes higher. As already mentioned, many kinds of gelatin show a modulus which increases with the square of the concentration, up to concentrations of 25 per cent. For low molecular weight gelatins it appears that, at constant concentration, a linear relationship exists between $G^{\frac{1}{2}}$ and \overline{M}_w , where \overline{M}_w is the weight average molecular weight. On the other hand, for high molecular weight gelatin, this modulus is independent of the molecular weight (cf. ref. 78). Although the temperature range in which aqueous gelatin gels can exist, is very limited (by the melting point of the gel at about 30° C and by the freezing point of water) temperature is an important parameter in this region. For a gelatin of $\overline{M}_w = 60\ 000\ e.g.$ the shear modulus at 0° C is a factor 17 higher than at 25° C (79). This factor even increases with de-

creasing molecular weight. With every change of a parameter, which causes an increase or a decrease of the ultimate equilibrium shear modulus, also the rate of the ageing process is increased resp. decreased. Only little attention has been paid so far, however, to the rate with which the ageing process proceeds (80-83).

A mechanism for the partial renaturation of gelatin is proposed by HARRINGTON and RAO (84) and shown in Fig. 1.2. It appears that the extent and manner of reversion to collagen fold (triple helix) structure is dependent on solvent, temperature and concentration. The rate determining step in the renaturation of gelatin is still uncertain. Already in 1959 FLORY and WEAVER (85) proposed that the helix formation of a single chain should be rate determining, whereas in a second, quick step the collagen



Fig. 1.2 Schematic view of the renaturation process of gelatin (after HARRINGTON and RAO, cf. ref. 84).

structure would be achieved by aggregation of single helices. On the other hand, in 1959 VON HIPPEL and HARRINGTON (86) assumed the reverse: the single chain is converted very quickly into a helix with the aid of water. Then a slow aggregation to triple helices follows. It is difficult to distinguish between the two mechanisms, as the result (i.e. a gel) is the same in both cases. However, measurements of the optical rotation, as carried out by EAGLAND c.s. (87) seem to favour the mechanism of FLORY and WEAVER.

1.3 MATERIALS AND PREPARATION OF SAMPLE

1.3.1 Polyvinyl chloride and plasticizers

The polyvinyl chloride used was Solvic 239, a suspension polymer of Solvay. Its weight average molecular weight, $\overline{M}_{m} = 240.000$ (determined by Ir. A.J.M. Segeren), was determined by means of light scattering. As plasticizers di-(2-ethylhexyl)phthalate (DOP) from Fluka and di-butyl phthalate (DBP) from Merck and Reomol ATM from Ciba Geigy were used. Reomol is the trimellitic acid ester of alphanol 79, a mixture of branched alcohols. All samples had the same composition being expressed in weight per cent, i.e. 9.9% polyvinyl chloride, 89.9% plasticizer and 0.2% stabilizer. The stabilizer consisted of 80% dibutyl tindilaurate and 20% zincstearate. For this composition the concentration of polymer at 25° C was 0.10 g/cm 3 . The solutions were prepared by heating the thoroughly mixed slurry for 20 minutes at 160° C. For this purpose, the slurry was filled into a thick walled tube. This tube was evacuated during several hours. In order to remove any trace of oxygen it was flushed with nitrogen occasionally. Finally the tube was sealed. It was constantly turned end-over-end during the heating.

1.3.2 Gelatin

The gelatin used was a gelatin from Gelatin Delft. Its weight average molecular weight, \overline{M}_{W} = 70000 was determined (by Mrs. Dipl.ing. J. Spangenberg-Oskerova) by means of light scattering at 40[°] C in 0.15M NaCl-solution, pH = 6.40 (88). The isoelectric point, pH = 4.83, was determined by means

of viscosity measurements. The amino acid composition, determined in our Organic Department (by Mr. A. van Estrik), is given in Table 1-III.

Table 1-III

Amino acid composition of gelatin in residues per 1000 total residues.

amino acid	residues/ 1000 residues	amino acid	residues/ 1000 residues
glycine	335.3	lysine	25.5
alanine	112.1	ornithine	1.7
valine	22.7	histidine	4.4
methionine	3.6	arginine	48.1
leucine	24.7	aspartic acid	47.4
isoleucine	11.0	glutamic acid	62.7
tyrosine	1.6	proline	140.5
phenylalanine	12.5	hydroxyproline [*])	96.8
cysteine	0.2	serine	32.0
		threonine	17.2

*) Determined at CIVO-TNO, Zeist

The solutions (1-5%) were prepared by weighing gelatin in an Erlenmeyer flask and adding half the amount of needed water. After half an hour the swollen gelatin is dissolved by heating the mixture to 60° C. Then, after cooling to 30° C, water is added in order to obtain the desired concentration.

1.3.3 Filling of the apparatus

In order to measure the dynamic moduli a solution was brought into a dynamic viscometer (see Chapter 3) at 150° C in the case of polyvinyl chloride and at 60° C in the case of gelatin. This temperature was maintained for 20 min. resp. 30 min., after which it was quickly cooled to the desired ageing temperature. Ageing temperatures were varied from 110° C to -25° C, resp. from 26° C to -1.2° C.

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CHAPTER 2

LINEAR VISCOELASTICITY

2.1 INTRODUCTION

If a body with a rectangular cross section is subjected to a shear force F, this cross section is deformed into a parallelogram. The shear stress σ is given by (see Fig. 2.1):

$$\sigma = F/A \tag{2.1}$$

where A is the area which the force acts on. The angle of deformation is $\boldsymbol{\epsilon}$



Fig. 2.1 Illustration of simple shear on a rectangular cross section; σ ... shear stress, ε ... angle of shear.

and the shear deformation is defined as:

$$\gamma = \tan \varepsilon \tag{2.2}$$

For an ideally elastic body HOOKE's law holds:

$$\sigma = G\gamma \tag{2.3}$$

where G (in N/m^2) is the shear modulus. On the other hand, for an ideally viscous liquid NEWTON's law holds:

where η (in Ns/m²) is the viscosity. However, for many materials, e.g. polymers, the relation between shear stress and deformation cannot be given by the Eqs. (2.3) or (2.4). The shear stress does not cause a constant deformation or a constant rate of deformation. By the combination of elasticity and viscosity the deformation becomes a function of the time elapsed from the moment in which the shear stress is imposed on the body. The material shows elastic as well as viscous properties and is called viscoelastic. If the shear stress is small, the deformation and the rate of deformation are still proportional to the shear stress: the material behaves linearly viscoselastic. Then the ratio of shear stress and deformation is a function of time only.

The relation between a suddenly imposed constant shear stress σ_{0} and the resulting shear deformation is given by:

$$\gamma(t) = \sigma_0 J(t) \tag{2.5}$$

where J(t) is the time dependent shear compliance. This experiment is called a creep experiment. The relation between a suddenly imposed constant shear deformation $\gamma_{\rm O}$ and the shear stress is given by:

$$\sigma(t) = \gamma_0 G(t) \tag{2.6}$$

where G(t) is the time dependent shear modulus or relaxation modulus. This experiment is called a stress relaxation experiment.

2.2 CREEP EXPERIMENTS

The deformation which is obtained, if a constant shear stress σ_0 is applied on the body at time t_0 , is shown in Fig. 2.2 for a Newtonian liquid 1, a Hookean solid 2, and a viscoelastic material 3. The deformation of the liquid increases linearly with time, hence the shear rate is constant and equal to σ_0/η . The elastic solid shows a constant deformation immediately after the application of the stress. This deformation is

equal to σ_0/G . The viscoelastic material initially shows a convex course of the deformation with respect to the time scale, whereas after a certain time the deformation becomes a linear function of time. The slope of



Fig. 2.2 Creep experiment for: 1) a Newtonian liquid; 2) a Hookean solid;
3) a viscoelastic liquid. σ ... shear stress, γ ... shear deformation,
t ... time.

this linear region is again equal to σ_0/η , whereas by extrapolation to to this straight line cuts the deformation ordinate at a value $\gamma_e = \sigma_0 J_e$; J_e is called the equilibrium shear compliance. A cross-linked, viscoelastic rubber shows a horizontal course after the convex region.

2.3 STRESS RELAXATION

The time dependent shear modulus G(t) is shown in a double logarithmic plot in Fig. 2.3. G(t) is a monotonously non-increasing function of time. At short times G(t) has an almost constant value G_g , for polymers approximately equal to 10^9 N/m^2 . This value represents the rigidity in the absence of chain backbone rearrangements. At longer times G(t) falls rapidly for uncross-linked polymers of low molecular weight and eventually



Fig. 2.3 The shear relaxation modulus vs time for various systems: 1) Maxwell-element; 2) dilute solution of a polymer, low molecular weight polymer melt; 3) concentrated solution and melt of high molecular weight polymer; 4) slightly vulcanized rubber or gel; 5) densely vulcanized rubber or gel.

vanishes (cf. curve 2). In molecular terms this corresponds to the resumption of random average configurations by the macromolecular coils which have completely freed themselves from the constraints which were effective during the preceding rapid deformation.

For a slightly cross-linked rubber (cf. curve 4) a new plateau, the rubber plateau at a level of approximately 10^5 N/m^2 , follows on the first rapid decrease. This plateau is a consequence of the cross-links between the polymer molecules, by which the chain ends have no opportunity to move with respect to each other. If the cross-link density of the rubber increases, also the rubber plateau acquires a higher level (cf. curve 5). The height of the rubber plateau is determined by the following relation:

 $G_e = VkT$ (2.7)

where:

G = the equilibrium shear modulus, i.e. the shear modulus on the rubber
plateau;

v = the number of elastically effective chains between the cross-links; k = the Boltzmann constant;

T = the absolute temperature.

If the molecular weight of an uncross-linked polymer is higher than a critical molecular weight of approximately 20000, so-called entanglements are present: coils of polymer molecules are entangled. At moderately short times these entanglements behave like the cross-links in a rubber. After long times, however, these molecular coils have the opportunity to disentangle. This process causes the shear modulus to fall rapidly and to vanish (cf. curve 3). This is called the terminal zone or flow region, where the molecules as a whole are able to move with respect to each other. The width of the pseudo rubber plateau of these uncross-linked polymers increases with the molecular weight.

2.4 RELAXATION SPECTRUM

In Fig. 2.3 is also shown the shear modulus of a Maxwell-element (cf. curve 1). This model consists of an elastic element (a spring with a modulus of elasticity G) connected in series to a viscous element (a dashpot with a viscosity η). The shear modulus of this element is given by:

 $G(t) = G \exp(-t/\tau)$

(2.8)

where $\tau = \eta/G$, the relaxation time.

With proceeding time a very rapid decay of the shear modulus is perceptible in the neighbourhood of $t = \tau$. A material with a number of relaxation times will show a more gradual decrease of the shear modulus with proceeding time, as is revealed by curve 2. The width of this transition depends on the difference between the smallest and largest relaxation time. If the material has two groups of relaxation times, G(t) shows a gradual decrease from the glassy region to a new plateau as a consequence of the first group of relatively short relaxation times. When the time reaches a value comparable with the second group of relatively long relaxation times, a second transition follows (cf. curve 3). If the times in the second group of relaxation times become infinite, the plateau persists up to immeasurably long times (cf. curves 4 and 5). If the number of relaxation times increases without limit, a continuous spectrum of relaxation times is obtained. This relaxation spectrum is defined as $H(\tau)$ d ln τ , i.e. as the number of relaxation times whose logarithms lie in the range between ln τ and ln τ + d ln τ . From the theory of linear viscoelasticity the following relation between G(t) and $H(\tau)$ can be derived:

$$G(t) = G_{e} + \int_{-\infty}^{\infty} H(\tau) \exp(-t/\tau) d \ln \tau$$
 (2.9)

The constant G_e is added to allow for a finite contribution to the spectrum at $\tau = \infty$. This form of Eq. (2.9) is useful for permanently cross-linked viscoelastic rubbers. For uncross-linked polymers one can put $G_e = 0$.

2.5 DYNAMIC MECHANICAL BEHAVIOUR

If an ideally elastic material is deformed sinusoidally according to:

$$\gamma = \gamma_0 \sin \omega t \tag{2.10}$$

the shear stress is given by:

$$\sigma = \sigma_{o} \sin \omega t = G\gamma_{o} \sin \omega t$$
 (2.11)

where $\boldsymbol{\omega}$ is the angular frequency. For an ideally viscous liquid, however, the shear stress is then given by:

$$\sigma = \eta \, d\gamma/dt = \gamma_0 \, \eta \, \omega \, \sin(\omega t + \frac{1}{2}\pi) = \sigma_0 \, \sin(\omega t + \frac{1}{2}\pi) \tag{2.12}$$

In the case of a Hookean solid the stress is in phase with the deformation. In the case of a Newtonian liquid it is $\frac{1}{2}\pi$ rad out of phase. A phase angle



Fig. 2.4 Simple shear experiment on a viscoelastic liquid with shear varying sinusoidally with time. σ_0 ... amplitude of shear stress, γ_0 ... amplitude of shear deformation, δ ... phase difference, ω ... angular frequency, t ... time.

 δ between 0 and $\frac{1}{2}\pi$ rad is characteristic for a viscoelastic material (cf. Fig. 2.4):

 $\sigma = \sigma_{\alpha} \sin(\omega t + \delta) = \sigma_{\alpha} (\sin \omega t \cos \delta + \cos \omega t \sin \delta)$

= $\gamma_{c}(G' \sin \omega t + G'' \cos \omega t)$ (2.13)

where G' = $(\sigma_0/\gamma_0) \cos \delta$ and G'' = $(\sigma_0/\gamma_0) \sin \delta$. G' is called the storage modulus: it determines the elastic part of the stress, according to the storage of mechanical energy. G'' is called the loss modulus: it determines the viscous part of the stress, according to the dissipation of mechanical energy. G' and G'' are functions of the angular frequency. G'(ω) resembles G(t) for $\omega = 1/t$. This is shown in Fig. 2.5 for uncross-linked polymers of various molecular weights and for a slightly vulcanized rubber. In this figure both dynamic moduli are plotted vs the angular frequency on logarithmic scales. In the transition regions the loss modulus reaches maximum values. In the plateau region it possesses a minimum value.

From the theory of linear viscoelasticity the following relations can be derived for the dependencies of $G'(\omega)$ and $G''(\omega)$ on $H(\tau)$:

G'(
$$\omega$$
) = G_e + $\int_{-\infty}^{\infty} H(\tau) \left[\omega^2 \tau^2 / (1 + \omega^2 \tau^2) \right] d \ln \tau$ (2.14)



Fig. 2.5 The dynamic moduli as functions of angular frequency for uncrosslinked polymer of high (----), intermediate (---) and low (....) molecular weight and for a slightly vulcanized rubber (-----).

$$G''(\omega) = \int_{-\infty}^{\infty} H(\tau) \left[\omega \tau / (1 + \omega^2 \tau^2) \right] d \ln \tau$$
(2.15)

For uncross-linked polymers it is easily shown that:

$$\lim_{\omega \to 0} G'/\omega^2 = \int_{-\infty}^{\infty} H(\tau) \tau^2 d \ln \tau = \text{constant}$$
(2.16)

$$\lim_{\omega \to 0} \mathbf{G}''/\omega = \int_{-\infty}^{\infty} \mathbf{H}(\tau) \ \tau \ \mathbf{d} \ \ln \tau = \text{constant}$$
(2.17)

From these equations it follows that at low frequencies the slope of the curve for the storage modulus equals 2 whereas the slope of the curve for the loss modulus equals 1 (on a double logarithmic plot).

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CHAPTER 3

THE DYNAMIC VISCOMETER

3.1 INTRODUCTION

The dynamic viscometer is based on a principle developed by MORRISON, ZAPAS and DE WITT (1). It is an improved version of the apparatuses described by DUISER (2) and by DEN OTTER (3,4). There were several reasons for the construction of an improved version:

a) In our laboratory we are investigating the ageing process of polymer/plasticizer systems, as there are e.g. polyvinyl chloride in di-(2ethylhexyl) phthalate, di-n-butyl phthalate, Reomol etc. or gelatin in water, by means of dynamic mechanical measurements and other methods (5-7). From these investigations it appears that, with proceeding ageing, the storage modulus increases almost linearly with the logarithm of the ageing time. Hence, in the early beginning of the ageing process a large number of measurements have to be taken, whereas after some time (e.g. one day) the necessary number of measurements drastically diminishes. However, pursuing the ageing process for a long time (four weeks and longer) is very interesting in order to obtain information about the mechanism of the ageing process. This means that we need an apparatus which offers the possibility to interchange measuring cells without disturbing the ageing process of the gel. An apparatus without this facility would be occupied by only one sample for a long time.

b) The loss as well as the storage moduli, plotted as functions of the frequency for several ageing times, give a considerable amount of information about the growing mechanism of the gel network, especially for systems with a special thermal history (6). As these gels behave nearly as ideal as rubbers, the values of the loss modulus are only small fractions of the corresponding values of the storage modulus. This means that we have to measure very small phase angles in an accurate way.

c) In our laboratory we are also interested in the low frequency be-

haviour of polymer melts (8-11). It is well known that for these systems the storage modulus is much smaller than the loss modulus. This obliges us to measure phase angles which deviate only slightly from ninety degrees.

In this way we arrived at the conclusion that a dynamic viscometer had to be constructed which enables us: a) to interchange measuring cells without disturbing ageing systems and b) to measure very small phase angles as well as phase angles very close to ninety degrees.

3.2 PRINCIPLE OF THE APPARATUS (1,2,12)

In Fig. 3.1 the principle of the dynamic viscometer is shown. It consists of two concentric cylinders. The outer cylinder is fixed whereas the



Fig. 3.1 Principle of the coaxial cylinder type viscometer; $h \dots$ height of the inner cylinder; $R_i \dots$ outer diameter of the inner cylinder; $R_o \dots$ inner diameter of the outer cylinder; D_1 and $D_2 \dots$ torsion wires; A1 ... driving shaft; ε_a and $\varepsilon_c \dots$ angular displacements of the driving shaft and inner cylinder respectively.
inner cylinder is suspended between two torsion wires. The sample of investigation is placed into the gap between these cylinders. A sinusoidal rotational oscillation is applied to the driving shaft Al. This movement of the shaft is transferred to the inner cylinder by the upper torsion wire. As a consequence of the (damped) oscillation of the inner cylinder the sample in the gap is sheared with the same frequency. In fact, in the case of a sinusoidal oscillation of the driving shaft also the inner cylinder performes a neat sinusoidal oscillation, provided the sample behaves linearly viscoelastic. The oscillation of the inner cylinder, however, shows a smaller amplitude and a phase difference with respect to that of the driving shaft. These changes of amplitude and phase are consequences of a) the viscoelastic properties of the sample, b) the elasticity of the torsion wires and c) the moment of inertia of the inner cylinder.

If the oscillation of the driving shaft is given by:

$$\varepsilon_{a} = \varepsilon_{ao} \sin \omega t$$
 (3.1)

the oscillation of the inner cylinder becomes:

$$\varepsilon_{\rm c} = \varepsilon_{\rm co} \sin(\omega t - \phi) \tag{3.2}$$

The dynamic moduli of the sample can be calculated from the following equations (for the derivation of these equations see ref. 12, for a simplified derivation see ref. 2):

$$G' = \frac{D_1}{E} \left(\frac{\varepsilon_{ao}}{\varepsilon_{co}} \cos \phi - 1 \right) - \frac{D_2}{E} + \frac{I\omega^2}{E}$$

$$(3.3)$$

$$G'' = \frac{D_1}{E} \frac{\varepsilon_{ao}}{\varepsilon_{co}} \sin \phi$$

$$(3.4)$$

where:

Eao	=	amplitude	of	the	drivin	g shaft	(in	rad);
8	=	amplitude	of	the	inner	cylinder	(in	rad);

ω	=	angular frequency (in rad/s);					
φ	=	phase difference between the movements of the driving shaft and of					
		the inner cylinder (in rad);					
G '	=	storage modulus (in N/m^2);					
G''	=	loss modulus (in N/m ²);					
D ₁	=	torsion constant of the upper torsion wire (in Nm);					
D_2	=	torsion constant of the lower torsion wire (in Nm);					
E	=	a constant, characteristic for the apparatus equal to					
		4π h $R_{i}^{2} R_{o}^{2} / (R_{o}^{2} - R_{i}^{2})$ (in m ³);					
h	=	length of the inner cylinder (in m);					
R	=	radius of the inner cylinder (in m);					
R	=	radius of the outer cylinder (in m);					
I	=	moment of inertia of the inner cylinder (in Nm s^2).					

 D_1 is a constant, which can be determined from low frequency measurements on a purely viscous liquid of known dynamic viscosity. At sufficiently low frequencies the following relation holds between dynamic viscosity and loss modulus (see e.g. ref. 13):

 $\eta = \frac{G''}{\omega} = \frac{D_1}{E\omega} \frac{\varepsilon_{ao}}{\varepsilon_{co}} \sin \phi$ (3.5)

Once D₁ is known, D₂ can be determined with the aid of measurements of ε_c as a function of ε_a in a stationary configuration. For this purpose the apparatus is filled with a purely viscous liquid in order to damp vibrations which would otherwise occur. The relation between ε_a and ε_c is then given by:

$$D_1 \varepsilon_a = (D_1 + D_2) \varepsilon_c$$
(3.6)

The moment of inertia I can be determined from measurements of the eigenfrequency of the unfilled system, according to:

$$\omega_{0}^{2} = (D_{1} + D_{2})/I$$
(3.7)



Fig. 3.2 Schematic survey of the arrangement of the dynamic viscometer. In the centre the measuring cell is shown; on the left hand side and top side the detecting system and on the right hand side the driving system are shown.

3.3 DESCRIPTION OF THE APPARATUS

In Fig. 3.2 the dynamic viscometer is shown schematically. In the centre the measuring cell is sketched, on the right side the driving system and on the left side the equipment for the determination of amplitudes and phase angle are shown.

3.3.1 The driving system *)

The requirements for the electric drive are:

- a control range of 1 : 30 in order to enable a continuous adjustment within one decade, but also to ensure a sufficient overlap with adjacent decades;
- a speed stability of 1 : 4000;
- a quick response;
- an upper speed limit of 6000 rev/min in order to realize frequencies up to 100 Hz.

In a control system according to the block diagram of Fig. 3.3 these requirements are fulfilled. The field of a D.C. motor is fed by an unstabilized D.C. voltage. The armature is fed by a full thyristor bridge. The speed is controlled with the armature voltage. As a measuring device for the speed a precision D.C. tachogenerator (Thorn Automation Ltd. England)



Fig. 3.3 Block diagram of the electrical circuit in behalf of the engine control of the D.C. motor.

*) The author is much indebted to Mr. R. van Donselaar for preparing this part of the manuscript.

is used. The tacho voltage is amplified with the aid of amplifier A1. The output voltage of this amplifier is used in order to fire the thyristor bridge with the aid of a phase shift unit (phase shifting control) sooner or later. The dynamic behaviour of this control is established by two carefully chosen time constants. The long term stability of this system is ensured by equalizing the temperature coefficients of the tacho generator and the reference voltage source. In order to limit high armature currents, which always occur with these fast control systems, a second amplifier A2 is used. At the input of A2 a voltage, proportional to the armature current of the motor, is compared with a reference voltage. If the armature current becomes too high, the output voltage will shorten the firing unit of the thyristor bridge during a short time. The mean value of the armature voltage will become somewhat lower or will change less quickly in that way.

The speed of the motor is determined with the aid of a chopper disc, mounted to the motor shaft. This chopper disc furnishes a digital tacho output signal.

3.3.2 The generation of the sinusoidal oscillation

The revolution of the motor is transformed into a sinusoidal rotational vibration with the aid of an eccentric gear, schematically shown in Fig. 3.4. The right disc is driven by the motor. As a consequence, it performs a



Fig. 3.4 Crank case for the generation of the sinusoidal oscillation.

rotational movement of constant speed. If the crank is long enough, the disc on the left side is given a sufficiently beautiful sinusoidal rotational vibration. The amplitude of this oscillation can be adjusted on the right disc by changing the eccentricity of the pin, on which the right bore of the crank fits.

3.3.3 The retardation

In order to increase the frequency range a system of two interchangeable gear boxes (G&K Osborne Ltd.) is used. These boxes comprise several retardations, e.g. 1:1, 10:1 and 100:1. In this way the total possible retardation varies from 1:1 (two gear boxes of 1:1) up to 10000:1 (two gear boxes of 100:1). Between this retardation system and the motor an extra retardation of 10:1 can be placed. On account of the frequency range of the motor, the frequency of the oscillation can be varied over a range from 7×10^{-5} Hz up to 80 Hz (that is a range of more than six decades), with an accuracy of 0.025%.

3.3.4 The measuring cells

The measuring cell, which is shown in Fig. 3.5, consists of the following parts:

- an inner cylinder of anodically oxidized duraluminium tube with a diameter of 8 mm and a length h = 150 mm. On the top this cylinder has a thinner end. As a consequence of this design, the exact height, to which the cell is filled with the sample of investigation, is no longer of importance, since the portion of the sample located around the narrow part of the cylinder furnishes only a negligible contribution to the shearing moment anyway. By the same measure edge effects due to the liquid surface can be neglected;
- an outer cylinder of Pyrex precision glass tube with an inner diameter of 10 mm;
- a thermostat mantle that can be connected to a pumping thermostat;
- torsion wires of stainless steel of several diameters and a length of 48 mm. The upper wire is attached in such a way that it is easily interchangeable. Torsion wires of the following diameters are available: 0.10 0.15 0.20 0.30 0.45 0.70 and 1.00 mm. As the torsion constant is pro-



Fig. 3.5 The measuring cell of the dynamic viscometer.

portional to the fourth power of the diameter, we have the following rough ratios in torsion constants: 1:5:16:80:400:2400:10000. Since the torsion constant of the lower wire (the tension wire) appears as a correction in Eq. (3.3) for the storage modulus, it is advisable to choose the diameter of this wire to be not bigger than that of the upper wire, but by preference, a factor of two smaller at least;

- two small mirrors, one on shaft 1, below the leaf spring, and the other one on the top of the inner cylinder; these parts play an important role in the determination of ε_{ao} , ε_{co} and ϕ ;
- a double leaf spring like a Maltese cross, which serves for a slight tension on the torsion wires, in order to accomplish coaxiality of the inner and outer cylinders;
- an axial ball bearing in the upper plate in order to fix the shaft in axial direction;
- three springs in order to hold the loose upper plate of the thermostat mantle in position against the pressure of the streaming thermostat liquid; this upper plate is loosely mounted in order to permit thermal expansion and shrinkage of the glass parts. At the same time it should prevent leakage.

The assembled measuring cell is connected to the driving system by pushing shaft 1 into the hole of the driving shaft. Simultaneously the upper plate of the measuring cell is pressed against the framework; with three clamping screws the measuring cell is attached. Finally shaft 1 is coupled to the driving system by tightening the screw in the driving shaft.

As a consequence of this careful construction the measuring cell is suspended vertically and the inner and outer cylinders are coaxial.

Through the tap the liquid of investigation is brought into the measuring cell.

The described construction enables us to disconnect a filled measuring cell at shaft 1, without exposing an ageing sample to forces. The sample can be aged further without occupying the apparatus.

Besides this measuring cell, which is appropriate for rather thin liquids and gels, also a measuring cell for the measurement on polymer melts is available. It consists of an outer glass cylinder with a diameter of 9 mm and an inner stainless steel cylinder with a length of 5 cm and a diameter of 5 mm or with another one with the same length but with a diameter of 7 mm.

3.3.5 The detection

For the determination of the dynamic moduli the angular frequency ω , the phase angle ϕ and both amplitudes ε_{20} and ε_{c0} have to be measured.

3.3.5.1 The determination of the angular frequency ω

For the determination of the angular frequency use is made of a chopper disc mounted on the shaft of the D.C. motor.

3.3.5.2 The determination of the amplitudes ε_{a0} and ε_{c0}

With the aid of a high pressure mercury lamp two beams of light are created with the aid of a simple optical system, which contains a monochromator and an optical slit. One beam is directed on mirror 1, which is connected to the driving shaft and the other one on mirror 2, which is connected to the inner cylinder. Each of the two beams of light is reflected to a separate scale. These scales are engraved on segments of cylindrical surfaces with a diameter of about 2 m. The common centreline of these scales coincides with the axis of the measuring cell. Each beam is focussed in such a way that a sharp vertical image of the slit, with a width of about 1 mm, is formed on the pertinent scale. At rest, with unloaded torsion wires, these images are positioned at the zero points of the scales.

If the driving shaft is brought into oscillation, the light spots move over the scales. Their maximal lateral deflections are measures for ε_{ao} and ε_{co} . The amplitude ε_{ao} has an (adjustable) preset value. It can easily be read with the eye. On the contrary, ε_{co} does not have a fixed value, but has to be determined at every value of the frequency. In order to simplify this determination, use is made of the high intensity of the light spots. For that purpose, three photomultiplier tubes, each of them being protected by two narrow slits in series, are placed on the ε_c -scale at equal but adjustable distances. The central one is put at the zero point of the scale. At the moments of coincidence the beam of light penetrates through the said slits and a simple lens to the photomultiplier tube. By this tube an electrical current is generated immediately, which is able either to start or to stop a digital counter. If a light spot is deflected over such a distance from the centre that one of the eccentric photomulti-

plier tubes is activated, the counter is started. After that moment the light spot continues its movement until it reaches its maximum deflection. On its return it passes the activated photomultiplier. Only at the moment when it hits the central photomultiplier, the counter is stopped. When the light spot now swings to the other side, the eccentric photomultiplier tube on this side is activated with analogous consequences. From the (equal) distances between the photomultipliers, the width of the optical image of the slit, the angular frequency and the two measured time differences the amplitude of the sinusoidal oscillation is calculated with the aid of an iterative calculation process of three to five steps (for the method of calculation see Appendix I of this Chapter).

For this determination it is not necessary that the central photomultiplier is positioned exactly in the zero passage of the sine, provided the other ones are at exactly equal distances from the central one.

3.3.5.3 The determination of the phase angle φ

The measurement of the phase angle occurs in a similar way. For that purpose, in the zero point of the ε_a -scale a fourth photomultiplier tube is placed. The phase of the light spot, reflected by the mirror on the driving shaft, is always in front of the one reflected by the mirror on the inner cylinder. If the fourth photomultiplier tube is hit by the respective light spot, a second digital counter is started. This counter is stopped at the moment when the light spot from the mirror on the inner cylinder hits the central photomultiplier tube on the ε_a -scale.

Also with this measurement it is not necessary that both photomultiplier tubes are positioned exactly in the zero passages of the respective sines. A prerequisite, however, is that in each half cycle the spots have to come from the same side, i.e. from the left or from the right. From the two measured time differences, the width of the optical images of the slit and the angular frequency the phase angle is calculated (for the method of calculation see Appendix II of this Chapter).

3.4 OPERATION LIMITS

3.4.1 Preamble

The following physical limits determine the possibilities of the dynamic viscometer:

- the angular frequency;

- the ratio of ε_{ao} and ε_{co} ;
- the available torsion wires;
- the width of the optical image of the slit;

- the dimensions of the inner and outer cylinders.

3.4.2 The angular frequency

It has already been mentioned that the frequency range is limited to:

 $5 \times 10^{-4} < \omega < 500 \text{ rad/s}$

3.4.3 The ratio between ε_{a0} and ε_{c0}

The ratio of ε_{ao} and ε_{co} which is still measurable, determines the smallest measurable phase angle as well as the extreme values of the loss modulus and the maximum value of the storage modulus. (N.B. the minimum value of the storage modulus is limited by the correction terms in Eq. (3.3)). The maximum value of ε_{ao} on the scale is 50 cm, whereas the maximum value of ε_c is determined by the torsion constants of both torsion wires according to Eq. (3.6). The minimum value of ε_c is determined by the central photomultiplier and both outer photomultipliers; this minimum distance is 5.5 cm. Slightly arbitrarily a value of ε_{co} (min) = 6 cm is found, so that

 $6 < \varepsilon_{co} < \varepsilon_{ao} D_1 / (D_1 + D_2) cm$

3.4.4 The available torsion wires

In the foregoing, it already is mentioned that the available torsion wires vary in diameter from 0.1 to 1 mm. In using thicker torsion wires, the limited rigidity of the inner cylinder, especially of the narrow section, will play a certain role. On the other hand thinner torsion wires are mechanically weak. From Section 3.5.1 it will appear that the torsion constants vary according to:

$$0.13 \times 10^{-4} \leq D_1 \leq 0.13 \text{ Nm}$$

Hence, it follows for the biggest measuring cell (h = 15 cm, $R_i = 4$ mm, $R_o = 5$ mm):

 $0.16 \leq D_1/E \leq 1600 \text{ N/m}^2$

and for the smallest measuring cell (h = 5 cm, $R_1 = 2.5$ mm, $R_0 = 4.5$ mm):

$$6.7 \leq D_1/E \leq 67000 \text{ N/m}^2$$

The diameter of the thinnest tension wire is 0.05 mm. Hence, its torsion constant is 16 times smaller than that of the thinnest torsion wire. This means that we can write for the biggest measuring cell:

 D_{0}/E (min) = 0.01 N/m²

3.4.5 The widths of the light spots

The widths of the light spots determine the smallest measurable phase angle. From Eq. (3.37) (in Appendix II) it appears that the minimum phase angle is given by:

$$\phi(\min) = \frac{1}{2} (\gamma_c / \varepsilon_c - \gamma_a / \varepsilon_{ao})$$
(3.8)

where γ_c and γ_a are the widths of the light spots on the ε_c -scale and the ε_a -scale. With a width of the spots of $\gamma_a = \gamma_c = 1 \text{ mm}$, full deflection on the ε_a -scale ($\varepsilon_{ao} = 50 \text{ cm}$) and minimum deflection on the ε_c -scale ($\varepsilon_{co} = 6 \text{ cm}$) it follows that $\phi(\min) = 25'$. If the deflection on the ε_c -scale is much larger, e.g. $\varepsilon_{co} = 45 \text{ cm}$, one obtains for the smallest determinable phase angle the extremely low value of $\phi(\min) = 25''$.

3.4.6 The distance between the walls of the inner and outer cylinders

The wavelength of the shearing wave, developed in the viscoelastic medium during oscillation, is not allowed to be smaller than e.g. 10 times the thickness of the sample. Hence, with a distance between the walls in the measuring cell of 1 mm, it follows for the wavelength $\lambda > 0.01$ m.

3.4.7 Calculation of the limitations of G' and G"

For the wavelength in a viscoelastic medium we can write the following equation (see e.g. ref. 14):

$$\lambda = \left[2G^{*}/(\rho\omega^{2})\right]^{\frac{1}{2}} \cdot \left(1 + \cos \delta\right)^{\frac{1}{2}} \cdot 2\pi$$
(3.9)

where G* is the absolute value of the dynamic shear modulus, ρ the specific mass of the sample and δ the loss angle of the viscoelastic medium at the angular frequency ω . With λ (min) = 0.01 m and a specific mass ρ = 1000 kg/m³ we obtain:

$$2G^* v^2 (1 + \cos \delta) > 0.1 \text{ kg/m}$$

where ν is the frequency,equal to $\omega/2\pi$. If $\cos \delta = 1$, $G^* = G'$, so that

$$G' > 0.025 v^2 N/m^2$$
 (3.10)

If $\cos \delta = 0$, $G^* = G''$, so that

$$G'' > 0.05 v^2 N/m^2$$
 (3.11)

From the Sections 3.4.3 and 3.4.4 it follows that the largest value of G' can be calculated from $(D_1/E)(max) = 6.7 \times 10^4 \text{ N/m}^2$, $(\epsilon_{ao}/\epsilon_{co})(max) = 50/6$ and $\cos \phi(max) = 1$. With these values we obtain:

 $G'(max) = 5 \times 10^5 \text{ N/m}^2$

and with sin $\phi(\max) = 1$:

$$G''(max) = 5.6 \times 10^5 N/m^2$$

The smallest value of G' is determined by the slightly arbitrary criterion that the correction $D_2^{/E}$, due to the lower torsion wire, should not be larger than the value of G' itself, so that:

$$G'(min) = 0.01 \text{ N/m}^2$$

For the smallest value of G" we find with $\varepsilon_{ao}/\varepsilon_{co} = 47$ (that is according to Eq. (3.6) for the case $D_1 = 16 D_2$) and $\sin \phi(\min) = \phi(\min) = 0.00011$ (see Eq. (3.8)):

 $G''(min) = 0.001 \text{ N/m}^2$

Moreover, the smallest values of G' and G'' are determined by Eqs. (3.10) and (3.11), which play an important role at high frequencies.

These calculations of the limitations of G'(ω) and G"(ω) lead together



Fig. 3.6 Operating region of the dynamic viscometer; (---)... storage modulus; (---)... loss modulus.

with other operation limits, to Fig. 3.6, where the operational range of the dynamic viscometer is shown.

3.5 RESULTS

3.5.1 Determination of the torsion constant D,

According to Eq. (3.5) the torsion constant D_1 of the upper wire can be determined from measurements on a Newtonian liquid. As an example, the calibration of a stainless-steel wire with a length of 48 mm and a diameter of 1 mm is chosen. As a calibration liquid silicon oil MS 200 - 12500 cS (Midland Silicons Ltd.) is used. The dynamic viscosity of this liquid has been measured in an Ubbelohde viscometer at 25° C; its value is 11.598 Ns/m².

In Fig. 3.7 the experimental results are shown: log $[\epsilon_{ao} \sin \phi/\epsilon_{co}]$ is plotted vs. log ω . According to Eq. (3.5), a straight line must be



Fig. 3.7 Calibration measurements of a 1 mm torsion wire with silicon oil MS 200 - 12500 cS.

found, with a slope equal to 1. A least squares fit results in:

$$\log [\varepsilon_{ao} \sin \phi/\varepsilon_{co}] = 0.9942 \log \omega - 2.1235$$

with a correlation coefficient $\rho = 0.99997$. The value of $(\epsilon_{ao} \sin \phi)/(\epsilon_{co})$ which, for a Newtonian liquid, must be a constant equal to $\eta E/D_1$, is 0.00743, with a standard deviation of 0.00010 (cf. Eq. (3.5)). In making use of the constant E = 8.373 x 10^{-5} m³ characteristic for the apparatus, we obtain $D_1 = 0.130$ Nm.

3.5.2 The dynamic moduli of silicon oil MS 200 - 12500 cS

As an example for the behaviour of a purely viscous liquid the behaviour of the silicon oil, which was used for the calibration of the torsion wire (cf. section 3.5.1), may be considered. The data which were obtained for the calibration of the torsion wire, can also be used for the calculation of G' and G", provided D_2 and I are determined separately. The results of these calculations are shown in Fig. 3.8: the storage and loss moduli are plotted vs the angular frequency on logarithmic scales.



Fig. 3.8 Double logarithmic plot of the storage and loss moduli as a function of angular frequency of the silicon oil mentioned in Fig. 3.7. $(\bigcirc) \dots G''; (\triangle) \dots G'$. Temperature 25.0° C.

For viscoelastic liquids the following equations hold (13):

 $\lim_{\omega \to 0} \frac{\mathbf{G}''}{\omega} = \eta = \text{constant}$

 $\lim_{\omega \to 0} \frac{G'}{2\omega^2} = \text{constant}$

In Fig. 3.8 straight lines must be obtained at low frequencies for both moduli. In the case of the loss modulus this line must have a slope equal to 1 and in the case of the storage modulus the slope must be equal to 2. In fact, the validity of the first expectation was already demonstrated in Fig. 3.7, as the ordinate of Fig. 3.7 differs only by a factor D_1/E from Fig. 3.8. At high frequencies the curve describing the storage modulus shows a deviation from the straight line found at low frequencies. The slope of this line is equal to 2.016, the correlation coefficient being $\rho = 0.999$. At the lowest frequencies (log $\omega < 1$), where the measured values of log G" are still linearly dependent on log ω , the loss angle approaches 90° very closely. In this region the accuracy of G' is drastically reduced. At the lowest frequency, at which the storage modulus can still be measured with sufficient accuracy a value of tan $\delta \approx 100$ is obtained for the tangent of the loss angle.

3.5.3 A 10% PVC-solution in Reomol (7)

An example for the contrary, i.e. for a system with a very small loss angle in the considered frequency range, is a 10% solution of PVC (Solvic 239) in the plasticizer Reomol. This system was aged at 60° C during 1, 10 and 100 h. The pertinent results are shown in Fig. 3.9. We shall return to this subject in detail in Chapter 4. At the lowest frequencies the loss angle appears to deviate only very little from 0° : tan $\delta \approx 0.01$.

3.5.4 A polystyrene melt

For the benefit of the measurement of the dynamic moduli of polymer melts an adapted measuring cell has been constructed (see the end of Section 3.3.4). Thermostating of the sample is achieved by placing this measuring cell into a thermostat bath filled with silicon oil. A pressure

(3.12)

(3.13)



Fig. 3.9 Double logarithmic plot of the storage and loss moduli of a 10% (w/w) solution of PVC (Solvic 239) in Reomol (ATM) for several ageing times, as indicated in the figure, at 60° C.



Fig. 3.10 Double logarithmic plot of reduced storage modulus, $G'_{p} = G' \rho_{0}T_{0}/(\rho T)$ (open symbols) and loss modulus, $G''_{p} = G'' \rho_{0}T_{0}/(\rho T)$ (filled symbols) as a function of reduced frequency, $\omega_{a_{T}}$, for a technical Polystyrene (Lacqrene 1531) at a reference temperature of 170° C. Original measurements are (Δ) ... 139.6° C; (\Box) ... 150.0° C; (O) ... 159.6° C; (\Box) ... 194.0° C.

moulded bar of the polymer with the desired outer (cylindrical) dimensions is clamped on a lathe and bored to the right inner diameter. The tube obtained in this way is put on the inner cylinder. The combination of sample and inner cylinder is brought into the outer cylinder. With heating the sample expands and sticks to the cylinder walls. In Fig. 3.10 the results of measurements on polystyrene (Lacqrene 1531) (9,10) are shown. The measurements were taken at temperatures varying from 139.6° C up to 194.0° C and reduced to 170° C. In Fig. 3.10 the slopes 1 and 2 (for the loss resp. storage moduli at low frequencies) are indicated by dashed straight lines. It appears that these slopes are really attained at low frequencies.

3.6 CONCLUSIONS

With the described dynamic viscometer an apparatus has been constructed by which the dynamic moduli of a viscoelastic material can be measured very accurately, especially also in those regions where the loss angle deviates only a little from 0° or 90° .

One remark must be made, however. The described dynamic viscometer is only useful for the investigation of linear viscoelasticity, as the deformation of the sample between the cylinders depends on the frequency.

3.7 APPENDICES

3.7.1 Appendix I: Calculation of the amplitude from the measurements

3.7.1.1 Preamble

For the first it is assumed that the central photomultiplier is positioned exactly at the zero passage of the sine, whereas the other two are placed at equal distances, a, on either side of this zero passage. The width of the light spot is assumed to be zero (see Fig. 3.11).

The light spot moves according to a deflection varying sinusoidally with time. At time t_1 the left hand photomultiplier P_{ℓ} is activated and at time t_2 the central one, P_m . The measured time difference is $t_{\ell} = t_2 - t_1$. At time t_3 the right hand photomultiplier P_r is activated and at



Fig. 3.11 Ideal situation on the ε_c -scale: zero width of the light spot; the central photomultiplier is positioned exactly in the zero passage of the sinusoidal movement of the light spot.



Fig. 3.12 Real situation on the ε_c -scale: width γ of the light spot and distance δ of the central photomultiplier P_m to the zero passage of the sinusoidal movement of the light spot.

time t_4 the central one again. The measured time difference is $t_r = t_4 - t_3$. If the mentioned assumptions are satisfied, one obtains: $t_{\ell} = t_r$. Hence, from Fig. 3.11 it follows:

$$a = A \sin \omega t_o = A \sin \omega t_o$$

or

$$A = \frac{a}{\sin \omega t_{\ell}} = \frac{a}{\sin \omega t_{r}}$$

3.7.1.2 The reality

In practice the width of the light spot will have a finite value γ and the central photomultiplier will be positioned at a distance δ from the zero passage of the sine (see Fig. 3.12). The distance δ corresponds to an angle of ν rad and the width of the light spot in the neighbourhood of the zero passage and hence in the neighbourhood of P_m to an angle of ψ rad. It is assumed that $\psi_{g} = \psi_{r}$, because both δ and γ will be small with respect to the amplitude A.

The light spot moves again according to a sinusoidally varying deflection. At time t_1 the left flank of the spot reaches P_{ℓ} and at time t_2 the right flank of the spot reaches P_m . At time t_3 the right flank reaches P_r and at time t_4 the left flank reaches P_m again. The measured time differences are again $t_{\ell} = t_2 - t_1$ and $t_r = t_4 - t_3$. We now can write down the following equations:

$$\mathbf{a} + \delta = \mathbf{A} \sin \omega \mathbf{t}$$

$$\delta + \gamma = A \sin \omega t$$

or

 $a - \gamma = A(\sin \omega t_1 - \sin \omega t_2) \approx A \sin \omega t_{\ell}$ (3.14a)

and in the same way:

$$a - \gamma = A(\sin \omega t_A - \sin \omega t_B) \approx A \sin \omega t_B$$
 (3.14b)

Hence, for the amplitude now can be written:

$$A \approx \frac{2(a - \gamma)}{\sin \omega t_{\ell} + \sin \omega t_{r}}$$

This value of A is used as a starting value in an iterative calculation process.

For the instants t_2 and t_4 we can write:

$$\omega t_2 = \pi - \nu - \psi$$
$$\omega t_4 = 2\pi + \nu - \psi$$

so that:

$$\omega t_2 - \omega t_1 = \omega t_{\ell} = \pi - \nu - \psi - \omega t_1$$

$$\omega t_4 - \omega t_3 = \omega t_r = 2\pi + \nu - \psi - \omega t_3$$
(3.15b)

In order to calculate the amplitude use is made of the following iterative calculation process.

We rewrite Eq. (3.14a) in the following way:

a -
$$\gamma = A(\sin \omega t_1 - \sin \omega t_2)$$

= - 2A $\sin \frac{\omega (t_2 - t_1)}{2} \cos \frac{\omega (t_1 + t_2)}{2}$
= - 2A $\sin \frac{\omega t_{\ell}}{2} \cos \frac{\pi - \nu - \psi + \omega t_1}{2}$
= 2A $\sin \frac{\omega t_{\ell}}{2} \sin \frac{\omega t_1 - \nu - \psi}{2}$

We now substitute:

$$q_{l} = 2A \sin \frac{\omega t_{l}}{2}$$

Hence,

$$\frac{\omega t_1 - \nabla - \psi}{2} = \tan^{-1} \frac{a - \gamma}{[q_{\ell}^2 - (a - \gamma)^2]^{\frac{1}{2}}} = \tan^{-1} z_{\ell}$$

where

$$z_{\ell} = \frac{a - \gamma}{\left[q_{\ell}^2 - (a - \gamma)^2\right]^{\frac{1}{2}}}$$

In this way we find:

 $\omega t_1 = v + \psi + 2 \tan^{-1} z_{\ell}$

or, with the aid of Eq. (3.15a)

$$\omega t_{\varrho} = \pi - 2\nu - 2\psi - 2 \tan^{-1} z_{\varrho}$$

We now define:

$$\Delta t_{\ell} \equiv v + \psi = \frac{1}{2}\pi - \frac{1}{2}\omega t_{\ell} - \tan^{-1} z_{\ell}$$

(3.16a)

In an analogous way we find:

$$a - \gamma = -2A \sin \frac{\omega t_r}{2} \cos \frac{\omega t_3 + v - \psi}{2}$$

and with:

$$q_r = 2A \sin \frac{\omega t_r}{2}$$

subsequently:

$$\frac{\omega t_3 + \nu - \psi}{2} = \tan^{-1} \frac{a - \gamma}{\left[q_r^2 - (a - \gamma)^2\right]^{\frac{1}{2}}} + \frac{\pi}{2} = \tan^{-1} z_r + \frac{\pi}{2}$$

where

$$z_{r} = \frac{a - \gamma}{[q_{r}^{2} - (a - \gamma)^{2}]^{\frac{1}{2}}}$$

We define again:

$$\Delta \mathbf{t}_{\mathbf{r}} \equiv \mathbf{v} - \psi = -\frac{1}{2}\pi + \frac{1}{2}\omega \mathbf{t}_{\mathbf{r}} + \tan^{-1} \mathbf{z}_{\mathbf{r}}$$
(3.16b)

From the Eqs. (3.16) it follows:

 $2v = \Delta t_{\ell} + \Delta t_{r}$

Hence,

$$\delta = A \sin \frac{\Delta t_{\ell} + \Delta t_{r}}{2}$$

The new amplitude \mathbf{A}^{\star} now can be calculated in the following way:

$$a + \delta = A_{\ell}^{*} \sin \omega t_{1} = A_{\ell}^{*} \sin(\omega t_{2} - \omega t_{\ell})$$
$$= A_{\ell}^{*} \sin(\pi - \nu - \psi - \omega t_{\ell}) = A_{\ell}^{*} \sin(\nu + \psi + \omega t_{\ell})$$
$$= A_{\ell}^{*} \sin(\omega t_{\ell} + \Delta t_{\ell})$$
(3.17a)

In an analogous way we find:

$$-a + \delta = A_r^* \sin \omega t_3 = -A_r^* \sin(\omega t_r - \Delta t_r)$$
(3.17b)

The new amplitude now follows from:

$$A^{*} = \frac{1}{2} (A^{*}_{\ell} + A^{*}_{\mathbf{r}}) = \frac{\mathbf{a} + \delta}{2 \sin(\omega t_{\ell} + \Delta t_{\ell})} + \frac{\mathbf{a} - \delta}{2 \sin(\omega t_{\mathbf{r}} - \Delta t_{\mathbf{r}})}$$
(3.18)

With the aid of this value of the amplitude the consecutive calculation of q_{ℓ} and q_{r} , z_{ℓ} and z_{r} , Δt_{ℓ} and Δt_{r} and finally δ can be repeated. From this calculation a new amplitude value follows according to Eq. (3.18).

The calculation process is repeated until A is known accurately enough, e.g. $A_n - A_{n-1} < 0.001 A_n$.

3.7.2 Appendix II: Calculation of the phase angle from the measurements

3.7.2.1 Preamble

Preliminary, it is assumed that both photomultipliers, P_a on the ε_a -scale and P_m on the ε_c -scale (see Fig. 3.13), are positioned exactly at the zero passages of the respective sines. The width of the light spots is assumed to be zero. The light spots move as mentioned above. At time τ_1 photomultiplier P_a is activated, at time τ_2 photomultiplier P_m . The measured time difference is $\tau_{\ell} = \tau_2 - \tau_1$. In an analogous way $\tau_r = \tau_4 - \tau_3$. The phase angle ϕ now can be calculated as:

$$\phi = \omega \tau_{\ell} = \omega \tau_{r}$$

3.7.2.2 The reality

In practice the widths of the light spots will have finite values. That on the ϵ_a -scale is equal to γ_a , corresponding to $\Delta\mu$ rad and that on the ϵ_c -scale is equal to γ_c , corresponding to $\Delta\psi$ rad. P_a will generally be positioned at a distance corresponding to μ rad from the zero passage of the ϵ_a -sine and P_m at a distance corresponding to ψ rad from the zero passage of the ϵ_a -sine.

If the widths of both light spots and μ and ψ are small, we are allowed to write:



Fig. 3.13 Ideal situation on the ε_a - and ε_c -scales: zero width of both light spots; both photomultipliers P_a and P_m are positioned in the zero passages of the sinusoidal movements of the corresponding light spots.



Fig. 3.14 Real situation on the ε_a and ε_c -scales: widths γ_a and γ_c of the corresponding light spots; distances, corresponding with μ and ψ rad of the phpotomultipliers P_a and P_m , respectively, to the zero passages of of the sinusoidal movements of the corresponding light spots.

$$\Delta \mu = \gamma_{a} / \varepsilon_{ao} \qquad \Delta \psi = \gamma_{c} / \varepsilon_{co}$$

The phase angle φ can now be calculated in the following way:

$$\omega(\tau_{\alpha} - \tau_{1}) = \omega\tau_{\alpha} = \phi + \mu + \psi$$

$$\omega(\tau_{4} - \tau_{2}) = \omega\tau_{2} = \phi - (\mu + \Delta\mu) - (\psi + \Delta\psi)$$

From these three relations the phase angle follows:

$$\phi = \frac{1}{2}\omega(\tau_{\ell} + \tau_{r}) + \frac{1}{2}(\gamma_{c}/\varepsilon_{c0} - \gamma_{a}/\varepsilon_{a0})$$

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CHAPTER 4

PHENOMENOLGY OF THE AGEING PROCESS OF PVC/PLASTICIZER SYSTEMS

4.1 KINETICS OF THE AGEING PROCESS

4.1.1 PVC in DOP

After the measuring cell, containing the sample, was cooled very quickly from 150° C to the desired ageing temperature T_a, measurements were started immediately. At a small number of frequencies the moduli were meas-



Fig. 4.1 Schematic view of the history of an ageing process of a 10% (w/w) solution of PVC in a plasticizer.

ured as functions of the ageing time t_a . The ageing time is defined as the time elapsed after the quench of the sample to T_a (see Fig. 4.1). In Fig. 4.2 the storage modulus is plotted against the angular frequency on logarithmic scales, for an ageing temperature of 90° C. The parameters of these curves are the ageing times. Fig. 4.2 gives an example for the tremendous increase of the storage modulus during the ageing process. For a frequency of 1.25 rad/s e.g. the storage modulus increases by a factor 230 from 0.18 to 41 N/m², in a period from 12 minutes till 100 hours. In this figure also the gradual formation of a rubber plateau is shown: at a short ageing time (0.2 h) the system still behaves like a liquid, the storage modulus being strongly dependent on the frequency, whereas at proceeding ageing the (low frequency) storage modulus becomes nearly independent of the frequency: the system gradually becomes rubber-like.

In a system which ages so quickly, however, one does not get the chance to carry out measurements over the whole frequency range during such a short time interval that no appreciable changes in the structure of the system occur. So it will be clear that the indicated points in Fig. 4.2, especially those at short ageing times, represent values obtained by interpolation of curves of the storage modulus against the ageing time, with the angular frequencies as parameters. Examples of such plots are shown in Figs. 4.3 and 4.4. In these figures the storage modulus is plotted against the logarithm of the ageing time. From Fig. 4.3 it appears that, after a



Fig. 4.2 Storage modulus of PVC/DOP plotted against angular frequency for several ageing times. Ageing temperature 90° C.

certain time t_a^* , the storage modulus becomes a linear function of the logarithm of the ageing time. Roughly spoken, the behaviour of the system becomes rubbery at an ageing time t_a^* . This time t_a^* depends on the frequency as well as on the ageing temperature. At 109° C t_a^* appears to be longer than 140 h. This means that after 140 h of ageing at 109° C still no rubbery state has been formed. From Fig. 4.4 it appears that t_a^* is smaller than 0.1 h and thus can impossibly be measured at an ageing temperature of 37° C.



Fig. 4.3 Storage modulus of PVC/DOP plotted against ageing time for several angular frequencies. Ageing temperature 79 $^{\rm O}$ C.



Fig. 4.4 Storage modulus of PVC/DOP plotted against ageing time for several angular frequencies. Ageing temperature 37° C.

At the same time it is remarkable that after long ageing times the curves in Fig. 4.4 show a deflection concave with respect to the time axis. This form of the curve appears to occur within 140 h at ageing temperatures below 70° C. At temperatures below 20° C, however, the form of the curves is again analogous to that of the curves in Fig. 4.3.

The changes in the loss modulus during the ageing process are much less pronounced, as appears from Fig. 4.5. In the beginning of the ageing process the loss modulus slightly increases, whereas after a certain time, depending on the frequency, a slight decrease is shown. In Fig. 4.6 the loss modulus is plotted against the angular frequency on logarithmic scales, the ageing time being the parameter of the curves. In comparison with the storage modulus the changes in the loss modulus are only small.

As is shown by WALTER (1), an equilibrium value of the YOUNG's modulus is reached after ageing a 10%-solution of polyvinyl chloride (VYNW) in DOP during one month at room temperature. It is quite obvious that the speed of the ageing process will show a steady decrease, when this process approaches equilibrium. Such a behaviour is just shown in Fig. 4.4. However, in our system an equilibrium value was never reached. Even after 650 h of ageing at 69° C the value of the storage modulus still increases.

The slope dG'/d log t of the linear region in Figs. 4.3 and 4.4 appears to be nearly independent of the frequency. So we may assume:

$$dG'/d \log t_a \simeq dG_e/d \log t_a$$
(4.1)

where G_e is the low-frequency limit of G'. The quantity dG'/d log t_a , which is determined completely by the composition of the sample and by the ageing temperature, may be called "rate of ageing". This quantity is plotted as a function of the ageing temperature in Fig. 4.7. Subscript r indicates that the moduli, which were measured at the various ageing temperatures, are reduced to a single reference temperature T_o (25.7^o C) for the purpose of comparison (2):

$$G_{r} = G(T_{o}) = G(T) c_{o}T_{o}/(cT)$$
 (4.2)

where c is the concentration in grams/100 ml at temperature T. The curve in Fig. 4.7 shows a remarkable resemblance to a crystallization curve (3,4)



Fig. 4.5 Loss modulus of PVC/DOP plotted against ageing time for several angular frequencies. Ageing temperature 69 $^{\rm O}$ C.



Fig. 4.6 Loss modulus of PVC/DOP plotted against angular frequency for several ageing times. Ageing temperature 69° C.



Fig. 4.7 Reduced rate of ageing, $dG'_r/d \log t_a$, of PVC/DOP plotted against ageing temperature. Reference temperature 25.7° C.

(i.e. the rate of crystallization as a function of temperature). The rate of crystallization is zero for temperatures above the melting point and for temperatures below the glass-transition temperature. The melting temperature of the gel is about 125° C. As will be shown in Section 4.2.2, for the glass-transition temperature a value of -87° C can be estimated.

One remark should be made, however: even if ageing is caused by crystallization, this does not necessarily mean that the above defined rate of ageing will be proportional to the overall rate of crystallization. However, DORRESTIJN, KEIJZERS and TE NIJENHUIS (5) have shown that the amount of crystallinity increases linearly with the storage modulus during the ageing process. At the same time,MERCIER and coworkers (6) state that an increase in crystallinity, caused by secondary crystallization, is a linear function of the logarithm of time.

4.1.2 PVC in other plasticizers

If polyvinyl chloride is dissolved in other plasticizers, the course of the ageing process resembles that in DOP: curves are obtained analogous to those in Figs. 4.2-4.7. As an example, in Fig. 4.8 the storage moduli are shown (as functions of the ageing time at an ageing temperature of 80° C) for three PVC/plasticizer systems, viz. PVC/Reomol, PVC/DOP and PVC/DBP. As this figure does not bear sufficient evidence, it should be stated that after proper induction periods, the storage moduli become linear functions of the logarithm of the ageing time, corresponding slopes being independent of the frequency. The ageing process of PVC/Reomol is the quickest one and that of PVC/DBP the slowest one. So, in this respect Reomol is a worse plasticizer than DOP, whereas DBP is a better one. This is also evident from Fig. 4.9, in which the rate of ageing of the three systems is plotted against the ageing temperature, analogous to Fig. 4.7. Also in this figure the rate of ageing of PVC/DOP is shown to be intermediate. The maximum of the PVC/DBP curve is located at a somewhat lower temperature than that of



Fig. 4.8 Storage modulus of PVC in different plasticizers plotted against ageing time for two angular frequencies, open symbols $\omega = 0.39$ rad/s, filled symbols $\omega = 39$ rad/s. (O) ... PVC/Reomol; (O) ... PVC/DOP; (V) ... PVC/DDP. Ageing temperature 80° C.

PVC/DOP. This is in agreement with the lower value of the glass-transition temperature of PVC/DBP. As will be shown in Section 4.2.2, for this glass-transition temperature a value of -95° C can be estimated. For the PVC/ Reomol system a maximum value of the rate of ageing was not found: at temperatures below 20° C the ageing process of this system is so fast that,



Fig. 4.9 Reduced rate of ageing, $dG'_{r'}/d \log t_{a}$, of PVC in different plasticizers plotted against ageing temperature. (D) ... PVC/Reomol; (O) ... PVC/DDP; (V) ... PVC/DBP. Reference temperature 25.7° C.

as a consequence of the corresponding shrinkage, the gel is released from the walls of the measuring cell. As a consequence, measurements of the dynamic mechanical properties become impossible. Moreover, at temperatures below 60° C, dG'/d log t is no longer independent of the frequency for this system: the slope decreases if the frequency increases. In Fig. 4.9, for the lower temperatures, use was made of the values of dG'/d log t of PVC/Reomol as measured at a low frequency ($\omega = 0.39 \text{ rad/s}$), as the frequency dependence appears to be small at low frequencies. A possible explanation of this phenomenon is that, with decreasing temperature and increasing frequency, the (dynamic) glass-rubber-transition is approached. (This would mean, of course, that the glass-transition temperature of pure Reomol is considerably higher than that of the other plasticizers). In the glass-rubber-transition the dependence of the storage modulus on the structure of PVC/plasticizer systems is only small, so that the increase of the storage modulus will be small in this region during the ageing process. This also appears from Fig. 4.10, where the storage modulus of PVC/ Reomol at an ageing temperature of 110° C is plotted against the angular frequency on logarithmic scales. Although the value of the storage modulus of the rubber plateau is smaller after 100 hours of ageing than the corresponding value of the PVC/DOP system in Fig. 4.2 (aged at 90° C), the values at high frequencies are considerably higher than those in Fig. 4.2. In Fig. 4.10 the tail of a glass-rubber-transition occurring at still higher frequencies is clearly perceptible, although the temperature is 20° C higher than that in Fig. 4.2.



Fig. 4.10 Storage modulus of PVC/Reomol plotted against angular frequency for several ageing times. Ageing temperature 110° C.

4.2 TIME-TEMPERATURE SUPERPOSITION

4.2.1 Preamble

In general, the time-temperature superposition principle is used in order to obtain values of the moduli in frequency ranges not covered by
the frequency range of the apparatus used. For that purpose measurements are taken at various temperatures. The obtained values of the moduli are multiplied by a factor $c_{O}T_{O}/(cT)$ (see Eq.(4.2)), T_{O} being a reference temperature (in K), one of the measuring temperatures, and c the concentration of the polymer in the solution (in grams/100 ml) at temperature T. If these values are plotted against the corresponding frequency on logarithmic scales, curves are obtained which can be matched with the measurements at the reference temperature and with each other, by shifting the curves over the logarithmic frequency scale. The measurements at lower temperatures to lower frequencies. As a result a modulus curve is obtained over a much larger frequency scale and belonging to the reference temperature T_o.

The amount of shifting over the logarithmic frequency scale, which is necessary for the measurements taken at temperature T, is equal to log a_T , where a_T is the horizontal "shift factor", i.e. the factor by which the angular frequency ω has to be multiplied in order to obtain the corresponding frequency at T_o . Conditions for the application of this method are the following:

- a shape of the various measured curves must fit sufficiently well;
- the value of a_T has to be independent of the type of the viscoelastic function considered (in our case the values of a_T obtained by shifting the storage and the loss moduli must be equal);
- the temperature dependence of $a_{\rm T}$ has to satisfy the semi-empirical equation of WILLIAMS, LANDEL and FERRY (WLF-equation) (2,7):

$$\log a_{T} = -c_{1}^{o}(T - T_{o})/(c_{2}^{o} + T - T_{o})$$
(4.3)

where c_1^o and c_2^o are constants characteristic for the reference temperature and the polymer system. For the purpose of comparison between various polymers, c_1^o and c_2^o can be converted to values c_1^g and c_2^g which correspond to the respective glass-transition temperature T $_g$. This occurs with the aid of the equations:

$$c_2^g = c_2^o + T_g - T_o$$
 (4.4a)

$$c_1^g c_2^g = c_1^o c_2^o$$
 (4.4b)

The values of c_1^g and c_2^g appear to be rather similar for a great variety of polymers. Sometimes universal values are ascribed to c_1^g and c_2^g , viz. $c_1^g = 17.44$ and $c_2^g = 51.6$. However, these values must be considered as averages over values obtained for a number of polymers.

In deriving the WLF-equation the constants c_1^g and c_2^g were used as substitutes for other quantities, viz.:

$$c_1^g = B/(2.303 f_g)$$
 (4.5a)
 $c_2^g = f_g/\alpha_f$ (4.5b)

where

B = a constant, often put equal to 1.

With the aid of the mentioned "universal" values of c_1^g and c_2^g and with B = 1 we can calculate:

 $f_{g} = 0.025 \text{ and } \alpha_{f} = 4.8 \times 10^{-4} \text{ o}\text{C}^{-1}$ (4.6)

4.2.2 Application to ageing systems

The before mentioned conditions will not be satisfied, if the internal structure of the material is dependent on temperature. As the internal structure of PVC/plasticizer systems is dependent on temperature to a high extent (8,9), the time-temperature superposition principle cannot be applied without modification. In order to make the time-temperature reduction applicable also to these ageing systems, the following procedure was used.

After the system was aged during a certain time (t_a) at a certain temperature (T_a) , the moduli were measured over a frequency range as large as possible. If the ageing process has proceeded over a relatively long time, measurements can be taken at relatively low frequencies. In fact, the time needed to go through the frequency range must always be small with respect to the preceding ageing time. For long ageing times (e.g. 150

hours) the use of a frequency of 2 x 10^{-4} Hz appeared to be still possible. On the other hand, for short ageing times the available frequency range is very limited. In such a case the gel was cooled very quickly to a new temperature T (mostly 25.7° C, sometimes 1° C). The following "excess" ageing of the gel, as occurring at this lower temperature, was observed during 30 - 90 min.by measuring the moduli for several frequencies and noting each time the pertinent excess-ageing time, t_{ea}. These measurements were extrapolated back to the "moment" of the change in temperature. In this way, the values of the moduli of the gel, which still had the internal structure corresponding to the higher temperature T_{o} , were obtained at the lower temperature T. With these extrapolated values plots of log G'_{μ} and log G''_{μ} against log ω were constructed. These plots could be used for the application of the time-temperature reduction. In Fig. 4.11 a schematic view of this application of the time-temperature reduction is shown, whereas in Fig. 6.2 this extrapolation procedure is shown for one frequency (ω = 0.393 rad/s) and several ageing times. For the calculation of the reduction factor, $c_{T_o}/(cT)$, it was supposed that the thermal expansion of the systems could be described by means of the thermal expansion coefficient of the pure plasticizer: For DOP a value of $\alpha = 10 \times 10^{-4} \text{ o}\text{C}^{-1}$ (10), for DBP a value α = 8.3 x 10⁻⁴ °C⁻¹ (as determined in our laboratory) was used.



Fig. 4.11 Schematic view of the application of the time-temperature superposition principle. Left hand side: excess-ageing plotted against excess-ageing time. Right hand side: original reduced ageing curve $(T_a^{\circ}C)$ and the corresponding curve at the reference temperature $(T_o^{\circ}C)$ obtained by extrapolation of the excess-ageing to zero excess-ageing time.

An example of a mastercurve, as obtained with this procedure, is given in Fig. 4.12. From this figure it appears that this method gives good results.

It is clear that the described method can be applied only once to a gel of a certain degree of ageing. In fact, the speed of ageing is increased by a decrease in temperature and, as will become clear in Section 6.2, also the type of cross-links formed is changed. This means that the ageing process at the ageing temperature T_a cannot be investigated by regularly repeated probing at T_o , as it is not possible to continue the ageing process after an interlude at T_o by simply raising the temperature back to T_a . As a consequence, for the investigation of the consequences of each ageing time t_a (at temperature T_a) a new ageing process must be started. Before doing so the system must be completely "rejuvenated" (regenerated) for half an hour at 150° C. The same would hold for measurements which should be reduced to a new reference temperature. After rejuvenation the system should be aged for the same time t_{a1} and at the same temperature T_a as in the previous ageing process. Then the gel should be cooled quickly to the new reference temperature. After measurements of the excess ageing



Fig. 4.12 Mastercurve of the storage and loss moduli of PVC/DOP. Ageing temperature 49° C. Ageing time 3 h. (O) ... 49° C; (D) ... 25.7° C. Reference temperature 25.7° C.



Fig. 4.13 Schematic view of different ageing histories.

at this temperature the process should be repeated, starting with the rejuvenation at 150° C, in order to enable measurements at a following reference temperature. The scheme for such a procedure is shown in Fig. 4.13. It is clear, that this is a very time consuming method, especially for the long ageing times. For this reason per ageing temperature only one reduction temperature is chosen (or at most two: 25.7 and/or 1.0° C). The temperature dependence of the shift factor a_T is determined by reduction of the measurements at different ageing temperatures to the same reduction temperature. To be sure that thermal degradation of polyvinyl chloride would not affect our measurements, not more than five rejuvenations and subsequent ageing processes were applied per sample. After rejuvenation of an aged sample the values of the moduli of the same sample showed smaller differences than those of different samples, for which variations of about five per cent were obtained.

The following experimental results justify this unusual application of the superposition principle:

- a good matching of the curves after shifting;
- measurements of the storage modulus and the loss modulus furnished the same values of log $a_{\rm m};$

- the shift factor ${\bf a}_{_{\rm T}}$ was independent of the ageing time and, as a conse-



Fig. 4.14 WLF-equation of PVC/DOP over the temperature range from 1° C to 90° C. Reference temperature 1° C.

quence, of the amount of ageing at one ageing temperature; the maximum deviation of log $a_{\rm T}^{}$ being about 5% for ageing times varying from 1 - 150 h (see table 4-I);

- the temperature dependence of a_T could be represented by the WLF-equation: $(T_o - T)/\log a_T$ plotted against the temperature gave a straight line, as is shown in Fig. 4.14 for the PVC/DOP system.

For the PVC/Reomol system the procedure did not work so far. The reason is that the gel released the walls of the measuring cell owing to the before mentioned shrinkage, especially after cooling to the reduction temperature. Probably, for this system the temperature range from 50 to 100° C will be more appropriate. For the other systems the constants c_1° and c_2° were calculated using the least squares fit. In Fig. 4.14 the correlation coefficient of this fit is $\rho = 0.996$. For a reference temperature T_{\circ} of 1° C we found the following values:

PVC/DOP : $c_1^{o} = 6.98$ $c_2^{o} = 152.0$ °C PVC/DBP : $c_1^{o} = 5.58$ $c_2^{o} = 178.7$ °C

Table 4-I

Values of the horizontal shift factor for several ageing processes of PVC/ $\ensuremath{\texttt{DOP}}\xspace.$

ageing	ageing time (h)	log :	^a T
temperature (^O C)		$T_{0} = 25.7^{\circ} C$	$T_{0} = 1.0^{0} C$
90.0	140 48 3	-1.59 -1.68 -1.55	
79.3	144 23 1	$ \begin{array}{c} -1.38 \\ -1.36 \\ -1.34 \end{array} \right\} -1.36$	
68.8	647 146 23 1 0.27	$ \left. \begin{array}{c} -1.16 \\ -1.20 \\ -1.20 \\ -1.12 \\ -1.12 \\ -1.16 \end{array} \right) -1.17 $	
58.8	148 23 3 1	$ \left. \begin{array}{c} -0.92 \\ -0.92 \\ -0.95 \\ -0.94 \end{array} \right\} -0.93 $	
48.9	146 23 1	$ \begin{array}{c} -0.66 \\ -0.65 \\ -0.66 \end{array} \right\} -0.66 $	-1.69 -1.67 } -1.68
36.8	146 23 3 1	$ \begin{array}{c} -0.34 \\ -0.34 \\ -0.34 \\ -0.31 \end{array} $	$\begin{array}{c} -1.25 \\ -1.33 \\ -1.34 \\ -1.35 \end{array}\right) -1.32$
25.7	146 23 3 1		-0.96 -0.97 -1.01 -0.99

From these values c_1^g and c_2^g can be calculated, provided the glass-transition temperatures T_g of both systems are known. In order to estimate this temperatures, use is made of the following equation, which is valid for dilute to moderately concentrated solutions (11,12):

$$T_{\sigma}(\phi) = T_{\sigma 1} + (f_{\sigma 2}/\alpha_{f1}) \cdot [\phi/(1 - \phi)]$$
(4.7)

where ϕ is the volume fraction of polymer, and the subscripts 1 and 2 refer to solvent and solute, respectively. According to MORTON and FERRY (10), $c_1^{0} c_2^{0} = 495$ is found for pure DOP and, according to our measurements, $c_1^{0} c_2^{0} = 351$ is obtained for pure DBP. With the aid of the product formed from Eqs. (4.5a) and (4.5b) and with B = 1 we find for DOP $\alpha_{f1} = 8.8 \times 10^{-4}$ and for DBP $\alpha_{f1} = 12.3 \times 10^{-4}$. (These values for the pure plasticizers are not in agreement with the corresponding values of α mentioned before in the 2nd paragraph of Section 4.2.2, because we assume here B = 1). With T_{g1} = -89° C for DOP (13) and T_{g1} = -97° C for DBP (13) and f_{g2} = 0.025 (14) we find for the glass-transition temperature of the PVC/DOP system T_g = -87° C and of the PVC/DBP system T_g = -95° C.

Insertion of these values into Eqs. (4.4) and (4.5) furnishes the values which are quoted in Table 4-II. The results appear to be in good agreement with the "universal" values, especially if one takes into account the scattering of the known values of f and α_{f} (15), i.e. 0.016 < $f_{g} < 0.028$ and $10^{-4} < \alpha_{f} < 5 \times 10^{-4}$, respectively.

	PVC/DOP	PVC/DBP	"universal"
c ^g ₁	16.6	17.2	17.44
c ^g ₂ (°C)	64.0	58.0	51.6
т _д (^о С)	-87	-95	
α _f (°c ⁻¹)	4.1×10^{-4}	4.4×10^{-4}	4.8×10^{-4}
$f_g \text{ (with } B = 1\text{)}$	0.026	0.025	0.025

Table 4-II

WLF-parameters of PVC/DOP and PVC/DBP

From our measurements it appears, that the contribution of polyvinyl chloride to the shift factor is considerable and cannot be neglected, as has been done by MORTON and FERRY (10). These authors used for the shift factor values which were calculated from c_1^{o} and c_2^{o} -values for pure DOP in order to shift their results on PVC/plasticizer systems. In order to reduce the viscoelastic properties of our PVC/DOP system from 90° C to 25.7°C a value of log $a_T^{}$ = -1.07 can be calculated from c_1^{o} and c_2^{o} for pure DOP, as quoted in ref. (10). Experimentally, however, we found log $a_T^{}$ = -1.61.

An extra justification of this application of the time-temperature reduction follows from measurements on a PVC/DOP gel which was aged during 14 months at room temperature. On this gel measurements were taken at 20, 11, 0, -16 and -25° C respectively. This was possible because the gel was aged so strongly, that no measurable excess ageing at the lower temperatures occurred. The obtained values of the loss modulus are shown in Fig.



Fig. 4.15 Double logarithmic plot of the reduced loss moduli of the longly aged PVC/DOP gel, its ageing history being mentioned in the text, as a function of angular frequency, at different temperatures. (O) ... -24.8° C; (O) ... -16.5° C; (Δ) ... -8.3° C; (∇) ... 0° C; ($\overline{\Delta}$) ... 11.5° C; ($\underline{\Omega}$) ... 19.8° C. Reference temperature -24.8° C.



Fig. 4.16 Horizontal shift, log a_T , of PVC/DOP plotted against temperature. (O)... measurements corresponding with the extrapolation procedure; (Δ)... measurements corresponding with the normal application of the time-temperature superposition principle (see Fig. 4.15). The full line is calculated and corresponds with the WLF-equation in Fig. 4.14.

4.15. It appears that shifting in the usual way is possible for this gel. The values of log a_T obtained for $T_o = 1^o$ C can be compared with the formerly obtained values of log a_T . For that purpose the values of log a_T , obtained with the extrapolation procedure, were plotted against temperature in Fig. 4.16. The full line was calculated with the aid of the WLF-equation by substituting the values of c_1^o and c_2^o for $T_o = 1^o$ C. In this figure also the values of log a_T for the longly aged gel are shown. It appears that the agreement between both applications of the time-temperature superposition principle is quite good.

It may be concluded that the described extrapolation procedure, which enables us to extend the frequency range of the viscoelastic measurements on certain, aged gels, gives good results under the necessary precautions. One final remark should be made, however. The procedure requires a temperature change to a *lower* reduction temperature. In fact, a change to a higher temperature causes an immediate change in the values of both moduli, as will be shown in Section 6.3. This makes the extrapolation to the moment of the temperature change impossible.

4.3 MODULUS CURVES

4.3.1 PVC in DOP

By the application of the time-temperature reduction, as described in the previous section, moduli were obtained over a frequency range of about seven decades. An example for an ageing temperature of 49° C is shown in Fig. 4.17. From this figure the following can be concluded:

- the span of the rubber plateau is considerable;
- with proceeding ageing the height of the rubber plateau increases;
- the storage modulus becomes independent of the ageing time at high frequencies: the glass-rubber transition is not sensitive for the degree of ageing;
- the loss modulus goes through a minimum value at low frequencies;
- the curves for the loss moduli allow a clear distinction between varying degrees of ageing only at very low frequencies.

Measured values of G $_e$ vary from about 1 N/m 2 (3 h at 90 o C) to 3100 N/m 2 (146 h at 25.7 o C). At high ageing temperatures the speed of the age-



Fig. 4.17 Mastercurves of the storage and loss moduli of PVC/DOP for several ageing times. Ageing temperature 49° C. Reference temperature 25.7° C.



Fig. 4.18 Mastercurves of the storage and loss moduli of PVC/DOP for several ageing temperatures. Ageing time about 144 h. Full lines ... loss modulus; dashed lines ... storage modulus. Reference temperature 25.7° C.



Fig. 4.19 Dispersion region caused by slip in entanglements in PVC/DOP. Measurements after 313 h of excess-ageing at 49° C preceded by 23 h of ageing at 25.7° C. Reference temperature 25.7° C.

ing process is extremely low. This appears when observations at 109° C are considered: after 140 h of ageing no signs for the formation of a threedimensional network could be detected with the aid of dynamic mechanical measurements. The loss modulus shows a minimum for ageing temperatures below 60° C (see Fig. 4.18). The presence of this minimum in the loss modulus points to a relaxation mechanism at still lower frequencies. The presence of such a minimum in the loss modulus is shown for the PVC/DBP system in Fig. 4.20.

From Fig. 4.18 one can see that with decreasing ageing temperature ω_{\min} , the location of the minimum in the loss modulus G"min on the angular frequency scale, shifts to higher frequencies, whereas G"min itself increases. An increase of G"min together with an increase of ω_{\min} points to a decrease in the mean distance between the junctions between the molecules (16-20). Apparently, as suggested also by Fig. 4.7 for temperatures higher than 5° C, a decrease in ageing temperature should cause, at constant ageing time, an increase in the degree of ageing. From this point of view the results of Fig. 4.17 seem contradictory to those of Fig. 4.18. However, the differences in G" are small in Fig. 4.17. In this connection it should be kept in mind that the accuracy in the loss modulus is rather low in this region of frequencies (for 146 h tan $\delta_{\min} = 0.004$).

Returning to Fig. 4.18 we may conclude that, in view of the general course of the loss modulus, there should be another maximum at a still lower frequency, and a corresponding decrease in the storage modulus in the same frequency range. However, since it is hard to believe that the low frequency loss is caused by slip in permanent cross-links formed by crystallites, one is lead to the assumption that entanglements must play an important role in this relaxation process. But if, in the presence of permanent cross-links, this loss is really caused by slip of entanglements, a new plateau region must exist behind the maximum in the loss modulus and the corresponding decrease in the storage modulus at still lower frequencies. Such a situation is shown in Fig. 4.19, where results are plotted of measurements which were performed on a gel that had first been aged during 23 h at 25.7 $^{\circ}$ C and after a quick rise of temperature to 49 $^{\circ}$ C had been kept for another 313 h at this latter temperature. Obviously, this special ageing process causes such a structure in the gel, that entanglements clearly put their mark on the course of the moduli within the attainable frequency range. To this special behaviour we shall return in Section 6.2.

4.3.2 PVC in other plasticizers

In Fig. 4.20 both moduli of the PVC/DBP system, reduced to 25.7° C, are shown after 144 h of ageing at several ageing temperatures. This pict-



Fig. 4.20 Mastercurves of the storage and loss moduli of PVC/DBP for several ageing temperatures. Ageing time about 144 h. Full lines ... loss modulus; dashed line ... storage modulus. Reference temperature 25.7⁰ C.

ure is completely analogous to Fig. 4.18. G''_{min} and ω_{min} shift to higher values, when the ageing process proceeds. A closer inspection shows, in agreement with the expectation from Fig. 4.9, that the level of the curves is lower than that of the PVC/DOP system. This is emphasized once more in Fig. 4.21, where the moduli of both systems with the same thermal history, i.e. 140 h at 60[°] C, are shown.

For PVC in Reomol this temperature dependence cannot be shown in this way, as the application of the time-temperature reduction proved to be a complete failure. However, in Fig. 4.22 the effect of continuing ageing on the course of the moduli is shown. Besides the remark that the level is higher than the corresponding level of PVC/DOP, little new features can be mentioned. Marked differences between PVC/DOP and PVC/Reomol are shown in Fig. 4.23. In the foregoing it was already mentioned that at 110° C no three-dimensional network could be detected in the PVC/DOP system. In

contrast to this experience, the gradual formation of a three-dimensional network is clearly perceptible in this figure for the PVC/Reomol system. Finally, in Fig. 4.24 both moduli are shown for the three PVC/plasticizer systems after 144 h of ageing at 60° C. Again it appears, that the ageing process of the PVC/Reomol system is the fastest one and that of the PVC/DBP system is the slowest one.



Fig. 4.21 Mastercurves of the storage and loss moduli of PVC/DOP (full lines) and of PVC/DBP (dashed lines). Ageing temperature 60° C. Ageing time about 144 h. Reference temperature 25.7° C.



Fig. 4.22 Storage and loss moduli of PVC/Reomol plotted against angular frequency for several ageing times. Ageing temperature 60° C.



Fig. 4.23 Storage modulus of PVC/Reomol (full lines) and of PVC/DOP (dashed lines) plotted against angular frequency for several ageing times. Ageing temperature 110° C.



Fig. 4.24 Storage and loss moduli of the three PVC/plasticizer systems plotted against angular frequency. Ageing temperature 60° C. Ageing time 144 h. (---) ... PVC/Reomol; (----) ... PVC/DOP; (----) ... PVC/DBP.

4.4 THE RELAXATION SPECTRUM

The relaxation spectrum H(T) was calculated from the moduli with the aid of the method of NINOMIYA and FERRY (21). The results are inaccurate for relaxation times longer than one second, because in this region the course of the storage modulus is very flat and the loss modulus is not accurately enough known. Fig. 4.25 shows the relaxation spectrum of PVC/ DOP, reduced to 25.7° C, for an ageing time of about 144 h at several ageing temperatures. In the transition region (here for log $\tau < 0$) the spectrum is nearly independent of the amount of ageing. This is in agreement with Fig. 4.18, where the loss modulus is also nearly independent of the



Fig. 4.25 Reduced relaxation spectrum, $H_{p}(\tau) = H(\tau) c_{0}T_{0}/(cT)$, of PVC/DOP for several ageing temperatures. Ageing time about 144 h. Reference temperature 25.7⁰ C.

amount of ageing for $\omega a_T > 1 \text{ s}^{-1}$. This phenomenon is also in agreement with the well known assumption that contributions of mechanisms with relatively short relaxation times are not affected by the degree of cross-linking. Cross-links in PVC gels, however, do not belong to the normal class of tetrafunctional, chemical cross-links. It is quite possible, that with progressing ageing, crystallization takes place along the chain backbone. This would affect the transition zone of the relaxation spectrum, but the

accuracy of the spectrum is not high enough to evaluate this effect. Moreover this effect would possibly influence the spectrum only in the short time range of the transition region.

In Fig. 4.26 the relaxation spectra of the three PVC/plasticizer systems are shown, after ageing at 25.7° C. In the cases of DOP and DBP this ageing proceeded for 144 h, in the case of Reomol it took only 2 h. The comparison between the three spectra is still possible, since the glass-rubber transition is only litlle affected by the degree of ageing (as has been mentioned before). Also from this picture the sequence of the speed of the ageing process is clearly perceptible.



Fig. 4.26 Relaxation spectrum of the three PVC/plasticizer systems at 25.7° C. (---) ... PVC/Reomol, ageing time 2 h; (---) ... PVC/DOP, ageing time 144 h; (----) ... PVC/DBP, ageing time 144 h.

4.5 THE LOSS COMPLIANCE

For networks formed by cross-links as well as by entanglements, the loss compliance J" is an interesting function, because it shows a maximum in the low frequency range of the transition region. With the aid of molecular theories one can calculate molecular parameters from the magnitude and the location of this maximum (see Chapter 5).

The function $J^{\prime\prime}\left(\omega\right)$ can be calculated from the modulus functions with the aid of the relation:

$$J'' = G'' / [(G')^{2} + (G'')^{2}]$$
(4.8)

With progressing ageing the maximum in the loss compliance becomes smaller and shifts to higher frequencies. As an example in Fig. 4.27 the loss compliance is plotted vs log ωa_T at the ageing time of 144 h with various ageing temperatures as parameters. We get a similar picture if the



Fig. 4.27 Reduced loss compliance, $J_{p}'' = J'' cT/(c_{O}T_{O})$, of PVC/DOP plotted against reduced angular frequency for several ageing temperatures. Ageing time about 144 h. Reference temperature 25.7° C.

same quantities are plotted for different ageing times at one ageing temperature. Instead of J" in Fig. 4.28 the ratio $J''/J_e^{}$, where $J_e^{} = 1/G_e^{}$, is plotted vs log $\omega a_T^{}$ for an ageing temperature of 68.8° C and various ageing times. The height of the maximum of the loss compliance varies strongly with ageing: J" = $0.17 \text{ m}^2/\text{N}$ (3 h at 90° C) and J" = 0.67 x $10^{-4} \text{ m}^2/\text{N}$ (146 h at 25.7° C). The value of J" $_{\text{max}}/J_e^{}$ varies only between 0.17 and 0.34 (most values lie between 0.22 and 0.30), its mean value (27 values) being 0.263, with a standard deviation of 0.040. According to





BUECHE's theory (22) for an ideal network formed by cross-links one should expect $J''_{max}/J_e = 0.42$, whereas MARVIN (23) calculated for an entanglement network a value of 0.32. For most polymers values varying from 0.24 to 0.32 have been found (24). However, it has to be pointed out that both theories require a uniform chain length between junctions. Moreover, both authors started their calculations from ideal networks, without the presence of dangling ends and without the presence of a sol fraction. According to Chapter 5 our gels are far from ideal: the sol fraction is considerable in many cases and dangling ends are abundantly present.

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CHAPTER 5

CALCULATION OF SOME MOLECULAR PARAMETERS

5.1 THE MOLECULAR WEIGHT BETWEEN COUPLINGS

The theory for ideal networks gives the following result for the equilibrium shear modulus (1):

$$G = g c RT/M$$

where c is the concentration of the polymer (in g/m^3) and \overline{M}_c the average molecular weight between two cross-links; g is a numerical factor, often taken equal to one for GAUSSian networks. Using this value for g we find values of \overline{M}_c varying from 8 x 10⁴ (for $G_e = 3100 \text{ N/m}^2$) to 25 x 10⁷ (for $G_e = 1 \text{ N/m}^2$). The weight-average molecular weight being 240,000, we have, according to FREEMAN and MANNING (2), a number-average molecular weight of about 70,000. This value will be used in this thesis. A possible error in \overline{M}_n , however, does not affect the validity of the arguments used in this chapter.

With \overline{M}_n being 70,000 it follows from the values for \overline{M}_c , as calculated from Eq. (5.1), that the network is far from ideal, even after long ageing. A first difference between the gels and an ideal network is the functionality of the cross-links. One must expect the functionality of the crosslinks to be much higher than 4 in the case of the polyvinyl chloride gels. This phenomenon, however, does not affect the validity of Eq. (5.1). Another aspect of the non-ideality of the gel network is the fact that many chains may be only loosely attached to the network and therefore do not contribute to G_e . A correction for Eq. (5.1) for dangling ends has been given by FLORY (3):

 $G_{e} = g(cRT/\overline{M}_{e}) (1 - 2\overline{M}_{e}/\overline{M}_{e})$

(5.2)

(5.1)

where \overline{M}_n is the number-average molecular weight prior to cross-linking. Other modifications of Eq. (5.1) are a correction for a possible solfraction w_s, and a correction ε for the presence of entanglements. The equilibrium shear modulus is then given by the more general equation (4):

$$G_{e} = g(cRT/\bar{M}_{c}) (1 - 2\bar{M}_{c}/\bar{M}_{n}) (1 - w_{s}) (1 + \varepsilon)$$
 (5.3)

A noticeable contribution of entanglements may be present in some cases, as is demonstrated in Fig. 4.19.

Values of \overline{M}_c calculated from Eq. (5.3) are given in Table 5-I. Besides $\varepsilon = 0$ and g = 1 it is also assumed that $w_g = 0$. This assumption will obviously be disputable, in particular for low values of the equilibrium shear modulus. Table 5-I also gives the weight fraction of the polymer forming the ideal part of the network: $w_m = 1 - 2\overline{M}_c/\overline{M}_n$. Even for $G_e = 10000 \text{ N/m}^2$ this value is only 0.59; the remaining fraction consists of dangling ends.

Table 5-I

 \overline{M}_{c} and w_{m} as functions of G_{er} , assuming $w_{s} = 0$.

G _{er} (N/m ²)	M _c	w _m
30	34900	0.004
100	34600	0.014
300	33600	0.04
1000	30700	0.12
3000	24700	0.30
10000	14500	0.59

5.2 THE MONOMERIC FRICTION COEFFICIENT

5.2.1 ROUSE's theory

According to ROUSE's theory (5) the equation for the transition region of the relaxation spetcrum reads:

$$H(\tau) = (a c N_{A} / (2\pi M_{a})) (\zeta kT/6)^{\frac{1}{2}} \tau^{-\frac{1}{2}}$$
(5.4)

where a is a stiffness parameter which gives the root-mean-square end-toend distance of a molecular chain when multiplied by the square root of the number of monomeric units contained in that chain, M the molecular weight per monomer unit, N_{A} AVOGRADO's number and ζ_{O} the monomeric friction coefficient. From the region in the logarithmic spectrum where the slope is equal to $-\frac{1}{2}$ (cf. Fig. 4.26), the monomeric friction coefficient can be calculated. With $a = 6 \stackrel{0}{A}$ (6) and T = 298.8 K Eq. (5.4) gives:

$$\log \zeta_{-} = 2 \log H + \log \tau - 12.78$$
 (5.5)

the unit of ζ_{o} being Ns/m. In this way we find for different amounts of ageing (G varying from 1000 - 3000 N/m²) the values for log ζ_0 as given in Table 5-II. Assuming a bead diameter of 6 Å the monomeric friction co-

Table 5-II

 η_{s} of the plasticizers and log ζ_{o} calculated from ROUSE's theory and STOKES' law for the three PVC/plasticizer systems at 25.7°C.

plasticizer	$\sim (N - (\pi^2))$	$\log \zeta_{o}$ (Ns/m)	
	(NS/m)	ROUSE	STOKES
DOP	0.054	- 9.25	- 9.5
DBP	0.0159	- 10.1	- 10.0
Reomol	0.136	- 8.9	- 9.1

efficient can also be calculated from STOKES' law, provided the viscosity η_{s} of the solvent is known:

$$\zeta_{0} = 3 \pi \eta_{s} a \qquad (5.6)$$

The values of the solvent viscosity as well as the values of log ζ_0 calculated from Eq. (5.6) are also given in Table 5-II.

5.2.2 BUECHE's theory

According to BUECHE (7) ζ_0 can also be calculated from the height of the maximum in the loss compliance and its location on the frequency scale (see e.g. Fig. 4.27):

$$J''_{max} = 0.42 Z_{c} M_{o} / (cRT) = 0.42 J_{e}$$
 (5.7a)

$$ω_{\text{max}} = 3 \pi^2 \text{ kT} / (a_c^2 Z_c^2 \zeta_o)$$
 (5.7b)

where $\rm Z_{c}$ is the number of monomeric units between two cross-links. From the Eqs. (5.7a) and (5.7b) ζ_{c} can be calculated as:

$$\zeta_{o} = [(0.53 \pi^{2} M_{o}^{2})/(a^{2} c^{2} N_{A} RT)]/[\omega_{max} J''_{max}]$$
(5.8)

Results of these calculations for the PVC/DOP-system are given for some samples, as characterized by their equilibrium moduli, in Table 5-III together with ζ_0 values calculated from the relaxation spectrum according to the previous Section. The agreement between the values of the monomeric friction coefficient, as calculated with these two theories is only reasonable for the highest equilibrium moduli.

Table 5-III

Log ζ_{o} of the PVC/DOP-system at 25.7°C for different values of G_{or} .

$C = (N/r^2)$	log ζ _o (Ns/m)		
er (N/m)	BUECHE	ROUSE	
30	- 10.20	-	
100	- 9.80	-	
300	- 9.45	-	
1000	- 9.15	- 9.25	
3000	- 9.10	- 9.25	

Table 5-III shows that the monomeric friction coefficient increases strongly with increasing ageing. Such a strong increase is difficult to

understand, because the monomeric friction coefficient is a quantity which is determined by the immediate surroundings of a monomeric unit. During the ageing process these surroundings will not change strongly on the average. So it is unlikely that ζ_0 changes as strongly as given in Table 5-III during the ageing process. Also in contradiction with this strong increase is the phenomenon that the glass-rubber transition, as revealed by the loss modulus in Figs. 4.17 and 4.18, is nearly independent of the degree of ageing. In this respect it is interesting to note that lightly crosslinking of Hevea rubber also causes a strong increase in the friction coefficient (8). However, this increase may be caused mainly by chemical combination with sulfur. An increase is also clear from diffusion measurements of n-hexadecane through several polymers: the diffusion constant decreases with increasing cross-link density (9).

In order to correct log ζ_0 as calculated with BUECHE's theory we have to realise that the sol fraction in the system is neglected. In fact we assumed that w_s = 0 in Eq. (5.3). However, an existing sol fraction will also contribute to the loss compliance and thus will affect its maximum and its location on the frequency scale. In using BUECHE's theory for networks we properly have to calculate the actual contribution of the network to the loss compliance. This might be possible in the following way.

We assume that the loss modulus as well as the storage modulus is additively composed of the contributions of the sol fraction (subscript s) and of the gel fraction (subscript g):

$$G'' = (1 - w_s) G''_g + w_s G''_s$$
 (5.9a)

$$G' = (1 - w_s) G'_g + w_s G'_s$$
 (5.9b)

where G'_g , G'_s , G''_g and G''_s are the moduli of the pure gel (i.e. network) and sol fractions. From Eqs. (5.9a) and (5.9b) it follows that:

$$G''_{\sigma} = (G'' - w_{s} G''_{s})/1 - w_{s})$$
 (5.10a)

$$G'_{a} = (G' - w_{a}G'_{a})/(1 - w_{a})$$
 (5.10b)

As is shown in Fig. 4.18 by the dashed curve for 109°C and 140 h ageing,

the contribution of the sol fraction to the storage modulus is very small (the curve for $109^{\circ}C$ and 1 h ageing is still one decade lower than that for 140 h; the curve for the sol fraction will be still lower). This allows us to write:

$$G'_g = G'/(1 - w_g)$$
 (5.11)

On the other hand the contribution of the sol fraction to the loss modulus, as revealed again in Fig. 4.18 by the curve for the loss modulus for $109^{\circ}C$, cannot be neglected at all. In order to find this contribution we assume that the loss modulus G" of the pure sol fraction can be obtained by extrapolation of the experimental loss modulus to zero ageing time. However, it appears that this is possible in a proper way only with ageing processes at temperatures of $90^{\circ}C$ and higher, because at lower temperatures the initial rate of ageing is too fast to make extrapolation possible. In Fig. 5.1 the results of these extrapolations are shown: the values of the reduced loss moduli agree very well for the ageing temperatures.



Fig. 5.1 Results of extrapolation of the loss moduli to zero ageing time for ageing temperatures of 90° C (O) and 109° C (O). Reference temperature 25.7° C.

tures, 90°C and 109°C. The least squares fit gives us:

$$\log G''_{m} = 0.97 \log (\omega a_{m}) + 1.45$$
 (5.12)

with a correlation coefficient $\rho = 0.998$ (the subscripts "or" stand for extrapolation to zero ageing time and for reduction to the referencetemperature (i.e. 25.7° C)). The slope of this line resembles closely the slope of a newtonian fluid. Comparison of the result of Fig. 5.1 with the loss modulus for $T_a = 109^{\circ}$ C in Fig. 4.18 shows that G''_{or} is smaller than G''_{109} in the considered frequency range (-2.7 < log $\omega a_T < 0$). The difference becomes smaller with increasing frequency. At still higher frequencies G''_{or} , as calculated with Eq. (5.12) will be higher than the loss moduli in Fig. 4.18. As a matter of fact the loss modulus of the sol fraction will reach the loss moduli of the ageing material asymptotically at higher frequencies, as the glass-rubber-transition is hardly influenced by the degree of ageing. In the following we will identify G''_{or} with G''_{or} as long as $G''_{or} < G''$ and we will assume $G''_{s} = G''$ when $G''_{or} > G''$.

The values of the loss modulus of the sol fraction obtained in this way will be quite incorrect for a sol fraction at a finite degree of ageing, since in such a sol fraction many polymer molecules are also crosslinked. However, with increasing ageing, the maximum of J" shifts to higher frequencies, as is shown in Figs. 4.27 and 4.28, but at the same time w_s , the sol fraction, becomes gradually smaller, as will be shown below. As a consequence, the contribution of the sol fraction to the loss modulus becomes also smaller. The result is that at a higher degree of ageing the increasingly uncertain value of G''_s becomes only a minor correction to the loss modulus of the system.

From the theory described in the Appendix of this Chapter we can calculate the sol fraction w_s . For a monodisperse polymer the cross-linking index γ (i.e. the average number of cross-links per primary polymer molecule in the system as a whole) is given by (10):

$$\gamma = -\ln w_{g}/(1 - w_{g})$$
 (5.13)

whereas the molecular weight between the cross-links is given by:

$$\bar{M}_{n}/\bar{M}_{c} = \gamma(1 + w_{s}) = -(1 + w_{s})(\ln w_{s})/(1 - w_{s})$$
(5.14)

Insertion of w_s = 1 (i.e. no gelfraction) in Eq. 5.14 yields $\gamma = 1$ (i.e. the gel point) and $\overline{M}_n/\overline{M}_c = 2$, whereas insertion of w_s = 0 (i.e. only gel fraction) yields $\gamma \rightarrow \infty$ (i.e. an ideal network, without dangling ends) and $\overline{M}_n/\overline{M}_c \rightarrow \infty$. These two equations, combined with Eq. (5.3) (with $\varepsilon = 0$ and g = 1), lead us to:

$$G_{en}^{\tilde{M}}/(cRT) = -(1 + w_s) \ln w_s - 2(1 - w_s)$$
 (5.15)

From this equation the value of w can be calculated approximately, if the left-hand-side is known. The w $_{\rm m}$, the fraction of ideal network in the system as a whole, can be calculated as:

$$w_{\rm m} = (1 - w_{\rm s})(1 - 2\bar{M}_{\rm c}/\bar{M}_{\rm n})$$
 (5.16)

whereas $\mathbf{w}_{_{\mathbf{f}}},$ the fraction of dangling ends, is given by:

$$w_{f} = 1 - w_{s} - w_{m} = (1 - w_{s})(2\bar{M}_{c}/\bar{M}_{n})$$
 (5.17)

In Fig. 5.2 these quantities are plotted against G_{pr} for our systems, whereas in Table 5-IV the values of these magnitudes are given for different amounts of ageing. The sixth column shows the values of quantity w_{e}^{2} , which, according to FLORY (11) is approximately equal to the fraction of the total number of cross-links present in the sol. This quantity enables us to calculate the number of cross-links per primary polymer molecule in the sol fraction as well as in the network fraction in the following way. Let us suppose there are A primary polymer molecules in the whole system. Then, the total number of cross-links is $\gamma A.$ The number of cross-links in the sol fraction is equal to w_s^2 YA and in the network fraction equal to $(1 - w_s^2)$ YA. The number of primary polymer molecules in the sol fraction is w A and in the network fraction $(1 - w_s)A$. Hence, the number of crosslinks per primary polymer molecule in the sol fraction is $(w_s^2 \gamma A)/(w_s A) =$ $w_s \gamma$ and in the network fraction $[(1 - w_s)^2 \gamma A]/[(1 - w_s)\gamma A] = (1 + w_s)\gamma =$ $\bar{\mathbb{M}}_{n}/\bar{\mathbb{M}}_{c}$ (cf. Eq. (5.14)). In the last column w $_{S}\gamma,$ the average number of cross-links per primary polymer molecule in the sol fraction is shown.



Fig. 5.2 Some gel parameters for a 10% (w/w) solution of PVC (\overline{M}_n = 70000) in a plasticizer as functions of the equilibrium shear mofulus at 25.7° C.

These small numbers, especially at relatively large amounts of ageing, justify our previous simplifying assumption with respect to the contribution of the loss modulus of the sol fraction.

Table 5-IV

Some gel parameters at different amounts of ageing.

$G_{er}(N/m^2)$	ws	M _c	wm	w _f	ws ² s	w _s γ
30	0.67	34539	0.004	0.33	0.45	0.81
100	0.54	33933	0.014	0.45	0.27	0.72
300	0.40	32740	0.039	0.56	0.16	0.61
1000	0.22	29558	0.12	0.66	0.05	0.43
3000	0.085	23939	0.29	0.63	0.01	0.23
10000	0.0085	20621	0.58	0.41	0.00	0.03

We now can calculate the loss compliance of the network by:

$$J_{g}^{"} = \frac{G_{g}^{"}}{G_{g}^{'2} + G_{g}^{"2}} = \frac{(1 - w_{s})(G^{"} - w_{s}G_{s}^{"})}{G^{'2} + G^{"2} + w_{s}^{2}G_{s}^{"2} - 2w_{s}G^{"}G_{s}^{"}}$$
(5.18)

This leads us to new values of the maximum of the loss compliance and its location on the frequency scale. An example is given in Fig. 5.3. By



Fig. 5.3 Reduced loss compliance of PVC/DOP plotted against reduced frequency. Ageing time 148 h. Ageing temperature 59° C. (O) ... uncorrected; (O) ... corrected for sol fraction and for dangling ends in the network.

inserting in Eqs. (5.7a) and (5.7b) the corrected values J''_{max} (corr) and ω_{max} (corr) and replacing the factor 0.42, which equals to J''_{max}/J_e (cf. Eq. (5.7a)), by J''_{max} (corr)/ $[J_e(1 - w_s)]$, the monomeric friction coefficient is now calculated by:

$$\zeta_{o} = [3\pi^{2}M_{o}/(a^{2}c^{2}N_{A} RT)]/[\omega_{max}J_{e}^{2}(1-w_{s})^{2}]$$
(5.19)

The values of log ζ_o calculated in this way show no clear dependence on the degree of ageing. Its mean value of 26 different ageing processes $(23 \leq G_{er} \leq 3090 \text{ N/m}^2)$ is -9.04 with a standard deviation of 0.15. In Table 5-V the values of log ζ_o calculated in three different ways for the PVC/DOP system are given.

Table 5-V

Log ζ_0 calculated in different ways for the PVC/DOP system. $T_0 = 25.7^{\circ}C$.

	log ζ _o (Ns/m)	standard deviation
ROUSE	- 9.25	0.08
BUECHE (corr.)	- 9.04	0.15
STOKES	- 9.5	

We can conclude that the results of the three methods to calculate the monomeric friction coefficient are in reasonable agreement. Finally it has to be mentioned that MORTON and FERRY (6) calculated log $\zeta_0 = -8.9$ for a 10% PVC/DOP system at 25°C.

5.3 APPENDIX: CALCULATION OF THE RELATION BETWEEN THE CROSS-LINKING INDEX AND THE SOL FRACTION

5.3.1 Preamble

In this Chapter some molecular parameters of aged polyvinyl chloride gels were calculated. From Section 5.2.2 it becomes obvious that knowledge of the composition of the gel in terms of the sol fraction w_s and the network fraction w_g is needed. By MORTON and FERRY (6), TE NIJENHUIS and DIJKSTRA (12) as well as in this thesis use is made of the theory of FLORY (13), which describes network formation by tetrafunctional chemical crosslinking as occurs e.g. during copolymerization of styrene and divinyl benzene. From this theory it follows a relation between the cross-linking index γ (i.e. the number of junctions per primary polymer molecule) and the sol fraction of the network. This relation reads (13): $\gamma = - \ln w_{g} / (1 - w_{g})$

However, the question arises whether this theory is applicable to ageing PVC/plasticizer gels without modification. Admittedly, the result of the theory will not or hardly be affected by the fact that the cross-links in polyvinyl chloride gels are physical by nature instead of chemical. How-ever, the important question is, whether the polyfunctionality of the cross-links in the crystallites will affect the usefulness of the theory. In FLORY's theory a potential junction is only able to cooperate once in the formation of a tetrafunctional cross-link. In the network formation which is the consequence of crystallization, the cross-links can be extended continuously.

In this Appendix it is shown that the results of FLORY's theory, γ as a function of w_s, can be applied to our gels, too. A theory is presented, which follows FLORY's ideas, but takes care, in addition, of the polyfunctionality of the cross-links.

5.3.2 Theory

We start from a situation, in which a three-dimensional network is not yet formed: in this stage polymer molecules are only coupled by means of junctions to a giant, branched molecule. The following assumptions are made:

- in every junction (a crystallite) an equal number, α , of polymer molecules is involved (α = 20 e.g.); in other words the junctions are homofunctional;
- intramolecular junctions do not play a role;
- the original polymer is monodisperse, i.e. it consists of "primary" molecules of equal length;
- for every primary polymer molecule the number, v, of potential junctions (regular sequences) which are able to contribute to crystallite formation, is the same (v = 20 e.g.).

Out of the solution an arbitrary primary polymer molecule is considered. We shall calculate the probability that the giant polymer molecule, of which this primary molecule is a part, consists of z primary molecules. In other words, we calculate the weight fraction, w_{α} , of giant molecules con-

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(5.20)

sisting of z primary polymer molecules. Summation of w_z over all possible values of z yields the sol fraction w_s , i.e. the weight fraction of polymer molecules that are still in solution, hence, have not been bound on a three-dimensional network. As long as no three-dimensional network has been formed, the sol fraction is equal to 1:

$$\mathbf{w}_{\mathbf{s}} = \sum_{z=1}^{\infty} \mathbf{w}_{z} = 1$$

(5.21)

We now define ρ as the probability that in an arbitrary polymer molecule a real junction is present:

number of potential junctions bound to cross-links, in the whole $\rho = \frac{\text{system}}{\text{total number of ratential junctions of statential junctions}}$

total number of potential junctions, irrespective of their state of bonding, in the whole system (5.22)

The probability that α potential junctions out of ν potential junctions of an arbitrary primary molecule (Oth generation) are engaged in real junctions, is:

$$\mathbf{P}_{\alpha} = \frac{\nabla !}{(\nabla - \alpha)! \alpha!} \quad \rho^{\alpha} (1 - \rho)^{\nabla - \alpha} \tag{5.23}$$

Hence, in these a junctions (of the 1st generation) a polymer molecules of the 1st generation are bound, each with v potential junctions and thus with va potential junctions in total. These a polymer molecules are bound to a polymer molecules of the 2nd generation in the a junctions of the 1st generation and, moreover, to another A polymer molecules in A new junctions of the 2nd generation. Hence, the total number of polymer molecules of the 2nd generation is equal to b = a + A (see Fig. 5.4 as an illustration). The probability that the a molecules of the 1st generation are bound to b molecules of the 2nd generation in the described way (out of b molecules of the 2nd generation a molecules were attached to fixed places, the remaining A molecules were distributed randomly over the remaining va - a potential junctions) is:



Fig. 5.4 Schematic representation of the count down of a giant polymer molecule.

- A: primary polymer molecule (0th generation) with 5 potential junctions (v = 5);
- B: id. connected with two primary polymer molecules (1st generation) each with 5 potential junctions (a = 2);
- C: id. connected with two primary polymer molecules (2nd generation) on old junctions and with three primary polymer molecules (also second generation) on three new junctions (a = 2, A = 3, b = a + A = 5).

$$\mathbf{P}_{ab} = \begin{pmatrix} \forall a & -a \\ \mathbf{A} \end{pmatrix} \rho^{b} (\mathbf{1} - \rho)^{\forall a-b} = \begin{pmatrix} a\sigma \\ \mathbf{A} \end{pmatrix} \rho^{b} (\mathbf{1} - \rho)^{\forall a-b}$$
(5.24)

where $\sigma = v - 1$. As σ is reasonably large, we can write:

$$\begin{pmatrix} \alpha\sigma \\ A \end{pmatrix} = \frac{(\alpha\mu)^A}{A!} \quad \text{where } \sigma - 1 \le \mu \le \sigma$$
 (5.25)

Eq. (5.24) is now replaced by:

$$\mathbf{P}_{ab} = \frac{(a\mu)^{\mathbf{A}}}{\mathbf{A}!} \quad \boldsymbol{\rho}^{b} (\mathbf{1} - \boldsymbol{\rho})^{\mathbf{V} a - b}$$

These b molecules of the 2nd generation are bound in b junctions to b molecules of the 3rd generation and, moreover, with another B molecules in B new junctions of the 3rd generation. The total number of polymer molecules of the 3rd generation is equal to c = b + B = a + A + B. The probability that the b molecules of the 2nd generation are bound to c molecules of the 3rd generation in the described way is:

$$P_{bc} = \frac{(b\mu)^{B}}{B!} \rho^{C} (1 - \rho)^{\nu b - C}$$
(5.27)

In an analogous way it follows, that the probability, that the i molecules of the generation (α - 2) are bound in i junctions to i molecules of the next generation (α - 1) and with another I molecules in I new junctions, is equal to:

$$P_{ij} = \frac{(i\mu)^{I}}{I!} \rho^{j} (1 - \rho)^{\sqrt{i-j}}$$
(5.28)

with j = i + I = a + A + B + ... + I

In the generation $(\alpha - 1)$ there are j molecules bound to the giant molecule in j junctions. As we do not describe the growth of a giant polymer molecule, but are considering an existing situation (i.e. a giant polymer molecule, consisting of z primary polymer molecules) and as we have assumed that in each junction precisely α primary polymer molecules are involved, this means that for the a junctions of the first generation the count down procedure has come to an end. In the remaining j-a junctions j-a polymer molecules of the next generation (α) are bound. Moreover, another J molecules are bound to the giant molecule in J new junctions. The probability that this latest situation arises, is equal to:

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(5.26)
$$\mathbf{P}_{jk} = \begin{pmatrix} \forall j & -j \\ \mathbf{J} \end{pmatrix} \rho^{k} (1 - \rho)^{\forall j - k} = \frac{(j\mu)^{\mathbf{J}}}{\mathbf{J}!} \rho^{k} (1 - \rho)^{\forall j - k}$$
(5.29)

where k = j - a + J = A + B + ... + J

Hence, in the generation $(\alpha + 1)$ k polymer molecules are bound in k junctions. For A junctions out of these k junctions of the 2nd generation the count down procedure has come to an end. In the remaining k - A junctions k - A polymer molecules of the next generation $(\alpha + 2)$ are bound. Moreover, another K new polymer molecules are bound to the giant polymer molecule in K new junctions. Hence, in an analogous way, we can write:

$$P_{kl} = \frac{(k\mu)^{K}}{K!} \rho^{l} (1 - \rho)^{\nu k - l}$$
(5.30)

where l = k - A + K = B + C + ... + K.

In each of the succeeding generations successively B, C, ... K, ... new junctions are ruled out and L, M, ... molecules are bound to the giant polymer molecule in L, M, ... new junctions.

Of a certain generation $(\beta - 1)$ there are q polymer molecules bound to the giant polymer molecule in q junctions and of the next generation (β) p polymer molecules in p junctions. Suppose that the number of new junctions in the generation $(\beta - \alpha)$ is equal to G, then q - G junctions out of p junctions belong to the old generations. Another Q new polymer molecules are bound to the giant polymer molecule in Q new junctions of the generation $(\beta + 1)$. Hence, $p = q - G + Q = H + I + \ldots + P + Q$. The probability that q molecules of the generation $(\beta - 1)$ are bound to p molecules of the generation (β) in the decsribed way, is:

$$P_{qp} = \frac{(p\mu)^{Q}}{Q!} \rho^{p} (1 - \rho)^{\sqrt{q-p}}$$
(5.31)

We now assume that in the counting down procedure in the next generation $(\beta + 1)$ no molecules are bound to the giant polymer molecule in new junc-

tions; in other words new polymer molecules are bound to the giant polymer molecule only in old junctions. The total number of multifunctional, i.e. 2α -functional, junctions in the giant polymer molecule is equal to:

$$N = \alpha + A + B + ... + P + Q$$
 (5.32)

The new generation (β + 1) consists of s = I + J + ... + P + Q polymer molecules. The probability of this situation is given by:

$$P_{\gamma\beta} = \rho^{\beta} (1 - \rho)^{\nu p - \beta}$$
(5.33)

In the same way, with $t = J + \ldots + P + Q$, we can write:

$$\mathbf{P}_{st} = \rho^{t} (1 - \rho)^{\forall s - t}$$
(5.34)

In the generation $(\beta + \alpha - 1)$ the *x* molecules are still bound to the giant polymer molecule in P + Q junctions. Of these junctions the oldest P junctions are ruled out for connection to the next generation $(\beta + \alpha)$. In the remaining Q junctions now *y* polymer molecules are bound to the giant polymer molecule (so y = Q). For the probability of this situation we can write:

$$\mathbf{P}_{xy} = \rho^{\mathcal{Y}} (\mathbf{1} - \rho)^{\forall x - \mathcal{Y}}$$
(5.35)

The probability that the y polymer molecules are not bound again with a next generation is equal to:

 $P_{\mathcal{Y}} = (1 - \rho)^{\mathcal{V}\mathcal{Y}}$ (5.36)

In this way we have now a giant polymer molecule consisting of z polymer molecules with:

$$z = 1 + a + b + \dots + x + y$$
(5.37)

We can also write for Z:

$$z = 1 + (\alpha - 1)(\alpha + A + ... + P + Q) = 1 + (\alpha - 1)N$$
(5.38)

The overall probability that a *z*-polymer has been built up in the described way, is now given by:

$$\mathbf{R}_{a,b,\ldots,y} = \mathbf{P}_{a} \mathbf{P}_{ab} \ldots \mathbf{P}_{ij} \ldots \mathbf{P}_{is} \ldots \mathbf{P}_{xy} \mathbf{P}_{y}$$
(5.39)

Insertion of the Eqs. (5.22) - (5.36) yields:

$$\mathbf{R}_{a,\bar{b},\ldots,y} = \frac{(\mu + 1)^{a}}{a!} \frac{(a\mu)^{A}}{A!} \dots (q\mu)^{Q}}{a!} * \rho^{a+\bar{b}+\ldots+y} *$$

$$* (1 - \rho)^{\nu-a} + \nu a-\bar{b} + \dots \nu i-\bar{j} + \dots \nu x-y + \nu y$$
(5.40)

For a simplification we replace $\mu + 1$ by μ .(The error made in this way is not large. One may assume: $\mu \approx \sigma - 0.5 = \nu - 1.5 = 18.5$. Usually one finds $\alpha \leq 3$, cf. Table 5-IV). If we use Eqs. (5.32) and (5.37), Eq. (5.40) becomes:

$$\mathbf{R}_{a,b,\ldots,y} = \mu^{\mathbf{N}} \frac{\mathbf{1}^{\alpha} a^{\mathbf{A}} b^{\mathbf{B}} \ldots q^{\mathbf{Q}}}{a! \mathbf{A}! \ldots \mathbf{Q}!} \rho^{z-1} (1-\rho)^{z\nu-\nu+1}$$
(5.41)

A z-polymer may be built up in many ways. In order to calculate the weight fraction of z-polymers Eq. (5.41) has to be summed over all combinations that satisfy Eq. (5.32), taking into account that all terms have to be ≥ 0 . We thus can write for the weight fraction of z-polymers:

$$w_{z} = \Sigma R_{\alpha,b,\ldots,y} = \mu^{N} \rho^{z-1} (1 - \rho)^{\forall z-z+1} \sum_{z=1}^{\infty} \frac{1^{\alpha} a^{A} b^{B} \ldots q^{Q}}{a! A! \ldots Q!}$$
$$= \mu^{N} \rho^{z-1} (1 - \rho)^{\forall z-z+1} S_{N}$$
(5.42)

where the sum is replaced by ${\rm S}_{\rm N}^{}.$ We now make the following simplifications, almost analogous to those in ref. (13):

$$ρμ ≈ ρν = γ$$

 $(1 - \rho)/(\rho\mu) \approx 1/\gamma$

$$\rho\mu (1 - \rho)^{\vee} \approx \gamma \exp(-\gamma)$$

and we define:

$$\beta = \gamma \exp(1 - \gamma)$$

Insertion into Eq. (5.42) yields:

$$w_{Z} = \frac{S_{N}}{N(\alpha-2)} - \frac{1}{\gamma} - \left(\frac{\beta}{e}\right)^{Z}$$
(5.44)

From Fig. 5.5, where β is shown as a function of γ , it appears that β has a maximum value equal to 1, for $\gamma = 1$, the gel point. For every value $\beta \neq 1$ two solutions for γ exist, one smaller than 1, the other larger than 1. For values of γ , for which the gel point is not yet reached (0 < γ < 1), Eq. (5.20) must hold, so that:



Fig. 5.5 $\beta = \gamma e^{1-\gamma}$ as a function of the cross-linking index γ .

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(5.43)

$$\sum_{z=1}^{\infty} \frac{S_{N}}{\mu^{N}(\alpha-2)} \left(\frac{\beta}{e}\right)^{z} = \gamma'$$
(5.45)

where γ' is the smaller root of β . For values of $\gamma > 1$, thus beyond the gel point, we can write for the sol fraction:

$$w_{s} = \sum_{z=1}^{\infty} w_{z} = \gamma' / \gamma$$
(5.46)

where γ' and γ are the roots of Eq. (5.43) for the same value of $\beta.$ In a simple way the relation between both roots and the sol fraction can be derived:

$$\beta = \gamma \exp (1 - \gamma) = \gamma' \exp (1 - \gamma');$$

$$\gamma/\gamma' = \exp (\gamma - \gamma');$$

$$(\ln \gamma - \ln \gamma')/(\gamma - \gamma') = 1;$$

$$\gamma = (\ln \gamma - \ln \gamma')/(1 - \gamma'/\gamma) = \ln(\gamma/\gamma')/(1 - \gamma'/\gamma)$$

so that

$$\gamma = -\ln w_{g} / (1 - w_{g})$$
(5.47)

$$\gamma' = - w_{c} \ln w_{c} / (1 - w_{c})$$
 (5.48)

In Section 5.2.2 we have already shown that, γ being the cross-linking index, $\gamma' = \gamma \underset{S}{\text{w}}$ is equal to the mean number of cross-links per primary molecule in the sol fraction. According to Table 5-IV this number decreases with increasing cross-linking index.

5.3.3 Conclusions

The Eqs. (5.47) and (5.48) are equal to the results of FLORY's theory (13). Obviously, the functionality of the cross-links is of no importance. However, the question remains, as to how far the assumed homofunctionality of the junctions influences the results. For the counting down procedure the heterofunctionality of the cross-links is of minor importance. In the Eqs. (5.38), (5.44) and (5.45) α might be replaced by a mean value $\overline{\alpha}$. Just as in FLORY's theory, also here in particular the assumption that intra-molecular junctions do not play a role, is liable to objections.

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CHAPTER 6

CLOSER EXAMINATION OF THE NETWORK GROWTH IN PVC-GELS

6.1 KINETICS OF AGEING

In Section 4.1 it appeared that a plot of the storage modulus vs the logarithm of the ageing time t_a yields a straight line in a certain ageing period. The slope of this line is nearly independent of the frequency, hence, dG'/d ln t_a = A = constant (see e.g. Fig. 4.3). From this it can be derived in a simple way that $ln(dG'/dt_a)$ plotted vs the storage modulus must also yield a straight line, with a slope B = -1/A. According to Fig. 6.1 this result appears to be in agreement with the reality. In this figure



Fig. 6.1 $Log(dG'/dt_a)$ of PVC/DOP plotted against the storage modulus for two angular frequencies. Ageing temperature 79° C.

the results of Fig. 4.3 have been converted. We found A = 42.8 N/m² and $-1/B = 43.6 \text{ N/m}^2$. Closer examination of both figures teaches us that a linear relationship already exists in Fig. 6.1 at those low values of the storage modulus, where in Fig. 4.3 at low frequencies the relationship is still non-linear (for $\omega = 0.39 \text{ s}^{-1}$ a linear relationship can only be ascertained for G' > 100 N/m²).

The equations for these lines are respectively:

$$G' = A \ln t + C \tag{6.1}$$

and

$$\ln(dG'/dt) = -G'/A + \ln A + C/A$$
(6.2)

Integration of Eq. (6.2) with G' = 0 for t = 0 yields:

$$G' = A \ln[t_a \exp(C/A) + 1]$$
 (6.3)

For t exp(C/A) >> 1 Eq. (6.3) reduces to Eq. (6.1). Obviously, Eq. (6.3) is a more general one than Eq. (6.1). From Eq. (6.2) one can derive:

$$(dG'/dt) = (dG'/dt)_{t=0} \exp(-G'/A)$$
 (6.4)

where t is replaced by t. For small values of G' (e.g. G'/A < 0.1, or G' < 43 N/m $^2)$ Eq. (6.4) can be simplified to:

$$dG'/dt = (dG'/dt)_{t=0} (1 - G'/A)$$
(6.5)

If, according to this equation, G' is considered as the product of a chemical reaction, the ageing process might be seen as a reaction of first order -at least in the initial state. In crystallization processes the fraction α of crystalline mass increases with time t according to the AVRAMI-equation (see e.g. refs. 1-3):

$$\alpha = 1 - \exp(-kt^{''})$$

where k is a temperature dependent constant and n an integer, mostly quoted as varying from 1 to 4. In the special case of a one-dimensional growth of nuclei, where nuclei are formed only in the initial stage of the crystallization process, the value of n is equal to 1 (see e.g. ref. 2). Under these circumstances the crystallization process is a first order process. From the SAXS-investigation of the ageing processes of systems like 10% PVC/DOP and 10% PVC/Reomol at 28° C it has been established that the number of growing crystallites does not increase during the ageing process (4). Hence, the number of growing crystallites is constant. In that case a onedimensional growth of nuclei is possible. On this account, and regarding Eq. (6.5), we might conclude that the crystllites have the form of a ruler and grow in the longitudinal direction. Also OHTA and coworkers (5) arrive to this conclusion. They examined the kinetics of the crystallization process of PVC melts with the aid of differential scanning calorimetry and they found that the exponent n in the AVRAMI-equation is equal to 1, provided the undercooling is not too large ($\Delta T < 40^{\circ}$ C). They consider their results as being in agreement with those of ASAHINA and OKADA (6). From the measurements of these authors it might be concluded that one-dimensional growth predominates during crystallization of polyvinyl chloride.

If the AVRAMI-equation would hold for the whole crystallization process, the storage modulus should increase from 5% to 95% of its final value within two decades of the time. However, this is not the case with the described ageing processes. According to MANDELKERN (7) a large number of possibilities can be responsible for the delay of a crystallization process. These are:

- In the case of moderately concentrated and concentrated solutions the crystallization temperature will decrease during the crystallization process. This is caused by the continuous dilution of the solution. As a consequence, also the undercooling will become less;
- In the case of copolymers consisting of crystallizable and non-crystallizable chain units the same holds (Polyvinyl chloride is considered to be built up of these units);
- With continued crystallization amorphous regions containing sequences of

finite length are trapped between consecutive crystalline regions. Some of these isolated sequences are no longer able to participate in the crystallization process. Hence, the effective decrease of concentration is more pronounced than it is expected from the progress of the crystallization;

- The concentration of useful amorphous material decreases to such a low level that the diffusion of polymer molecules becomes rate determining in the crystallization process.

Each of the mentioned possibilities may play a role in the retardation of the crystallization process of the ageing systems described here.

6.2 KINETICS OF THE EXCESS-AGEING PROCESS OCCURRING AFTER PRECEDING AGE-ING AT A HIGHER TEMPERATURE

By means of the procedure which was developed for the application of the time-temperature reduction, the excess-ageing is followed with time at one temperature (normally 25.7° C) after pre-ageing at some other, higher temperature. The excess-ageing at 25.7° C appears to be strongly dependent on the pre-ageing time at the higher temperature. Apparently, any ageing process will depend on the thermal history. Such a dependency is shown in Fig. 6.2, where for one frequency ($\omega = 0.393$ rad/s) the excess-ageing is given as a function of time t_{ea} elapsed at 25.7° C after previous ageing at 69° C during respectively 647, 146, 23, 1, 0.27 and 0 h. If previous ageing is extended over a long time, the excess-ageing process is very

slow and for 647 h of pre-ageing even imperceptible. Obviously, after extended pre-ageing the network density is so high that the mobility of the chains which potentially are still able to contribute to a further growth of existing crystallites, has become too small. As a consequence, the process of excess-ageing practically stagnates. On the other hand, at short pre-ageing times, the network density is still very low. In this case the mobility of chains dangling at the network and of those still in the sol fraction is high enough to enable rapid excess growth of crystallites. These considerations are helpful in the understanding of the differences in the rate observed at the beginning of the excess-ageing processes. However, these considerations do not furnish an explanation for the phenomenon that



Fig. 6.2 Excess-ageing of PVC/DOP at 25.7° C,as indicated by the storage modulus, after previous ageing at 69° C for several pre-ageing times. Angular frequency 0.393 rad/s.

curves belonging to short pre-ageing times, cross those belonging to long pre-ageing times. At first sight one would expect that the curves should approach each other asymptotically. In order to explain this unexpected behaviour, we shall have a further look on the kinetics of the excess-ageing process.

After the moment of the temperature quench (from -say- 69° C to 25.7° C) the crystallites formed at the previous temperature (of 69° C) will grow with the rate belonging to the new temperature (of 25.7° C). As a consequence of the formation of new nuclei, the rate of the excess-ageing process will be determined in the following by the growth of old as well as of new crystals. In order to be able to compare the rates at 69° C and 25.7° C, we have to determine the values of dG'/dt, as obtained immediately after the temperature decrease, from Fig. 6.2. In other words we have to find lim (dG'/dt). This quantity is plotted in Fig. 6.3 against $t_{es} \rightarrow 0$



Fig. 6.3 $\log(dG'_r/dt_a)$ of PVC/DOP plotted against the reduced storage modulus. The lower line is obtained during the ageing process at 69° C ($\omega = 5.8 \text{ rad/s}; \omega a_T = 0.393 \text{ rad/s}$). The upper line shows the same quantity at the same reduced frequency ($\omega a_T = \omega = 0.393 \text{ rad/s}$), immediately after the temperature quench to 25.7° C; these points correspond to <u>different</u> ageing processes of varying duration at 69° C. Reference temperature 25.7° C.

the corresponding value of lim $\,$ G'. In accordance with Fig. 6.1, a $t_{ea}^{\to 0}$

straight line is drawn through the obtained points. This line appears to be nearly parallel to the one constructed from measurements of the normal ageing process at 69° C at the same reduced frequency ($\omega = 5.8 \text{ rad/s}$, $\omega a_T = 0.393 \text{ rad/s}$, cf. Section 4.2.2), which is also shown in Fig. 6.3. The slope is equal to $-5.37 \times 10^{-3} \text{ m}^2/\text{N}$ at 25.7° C and $-5.61 \times 10^{-3} \text{ m}^2/\text{N}$ at 69° C. Hence, a constant ratio, independent of the degree of ageing, exists between the values of dG'/dt as found at these two temperatures, the one at 25.7° C being 8.3 times as large as that at 69° C. From this consideration it may be concluded that, at a certain state of ageing, the ageing process at 25.7° C is 8.3 times as fast as that at 69°C.

For the various excess-ageing processes as such (see Fig. 6.2) values of $log(dG'/dt_a)$ are plotted as functions of the storage modulus in Fig. 6.4. In this figure the curve for 25.7⁰ C, as obtained without pre-ageing at



Fig. 6.4 $\log(dG'/dt_{ea})$ of PVC/DOP plotted against the storage modulus at 25.7° C, after pre-ageing at 69° C during several times: (\Box) ... 146 h; (\bigcirc) ... 23 h; (\bigcirc) ... 1 h; (\bigcirc) ... 0.27 h; (\triangle) ... 0 h. The filled symbols are the values obtained by extrapolation as shown in Fig. 6.3.

 69° C, is shown as well. It appears that also these curves are nearly parallel. Hence, at every value of the storage modulus a constant ratio exist between the corresponding rates of increase of the storage modulus. This figure demonstrates clearly that the excess-ageing process can certainly not be only the consequence of the growth of crystals formed at 69° C. In fact, this latter process would yield the line for the initial excess-ageing, as indicated by the filled symbols (this is the line shown also in Fig. 6.3). Obviously, new nuclei are formed immediately after the quench from 69° C to 25.7° C, which will also grow. Both processes together yield the curves in Fig. 6.4.

With the aid of the linear relationships between $\log(dG'/dt_a)$ and G' the contributions of the two processes can be separated in the following way. For the excess-ageing process at 25.7° C, due to the crystals originally formed at 69° C and reflected by G'_1 , the following equation holds (see Fig. 6.3):

$$\ln(dG'_{1}/dt) = A - BG'$$
 (6.7)

where G'_1 can be determined from the relations for the total excess-ageing process at 25.7° C:

$$\ln(dG'/dt) = C - DG'$$
 (6.8)

From Eq. (6.8) it follows:

$$\int_{G'_{O}}^{G'} e^{DG'} dG' = \int_{O}^{t} e^{C} dt$$
(6.9)

where $G'_{O} = \lim_{\substack{t \to 0 \\ ea}} G'$. Hence, it follows: $t_{ea} \rightarrow 0$ $G' = (1/D) \ln[\exp(DG'_{O}) + Dt \exp(C)]$ (6.10)

Insertion of Eq. (6.10) into Eq. (6.7) yields:

$$\ln(dG'_{1}/dt) = A - (B/D) \ln[\exp(dG'_{2}) + Dt \exp(C)]$$
(6.11)

or

$$G'_{1} = G'_{0} + \exp(A) \int_{0}^{t} \left[\exp(dG'_{0}) + Dt \exp(C) \right]^{-B/D} dt$$
$$= G'_{0} + \left\{ \left[\exp(A - C) \right] / (D - B) \right\} \left\{ \left[\exp(DG'_{0}) + Dt \exp(C) \right]^{1-(B/D)} - \frac{1}{2} \left[\exp(DG'_{0}) + Dt \exp(C) \right]^{1-(B/D)} \right\} \right\}$$

$$- \exp[G'(D - B)]$$
 (6.12)

Equation (6.12) furnishes the relation between the excess-ageing due to the crystals formed at 69° C and the excess-ageing time. The following values were found for the various constants:

A = 4.422 (G' in N/m², t in min)
B = 12.37 x
$$10^{-3}$$
 m²/N
D = 2.874 x 10^{-3} m²/N



Fig. 6.5 Excess-ageing of PVC/DOP at 25.7° C , as indicated by the storage modulus, after previous ageing at 69° C for several ageing times, splitted in two contributions: (----) ... 0.27 h; (-----) ... 1 h;

(----) ... 23 h; (\cdots) ... 146 h.

Curves I are the experimental curves of Fig. 6.2.

Curves II are calculated with the aid of Eq. (6.12).

Curves III are obtained by subtracting curves II from corresponding curves I.

Angular frequency 0.393 rad/s.

Constants C and G' depend on the degree of pre-ageing:

t _a (h)	$C(G' \text{ in } N/m^2, \text{ t in min})$	G'_{o} (N/m ²)
0.27	3.80	55
1	3.25	146
23	0.91	357

We assume that the contributions to the moduli are additive. Then, the storage modulus which is the consequence of the newly formed crystallites, is obtained by subtracting the curves constructed with the aid of Eq. (6.12) from the experimental curves. In this way, in Fig. 6.5 curves III are obtained by subtracting curves.II from the corresponding curves I.

increase of the storage moduli at 25.7° C appear to become quickly very small. The contribution to the moduli by the growth of the crystallites newly formed at 25.7° C is very large after short pre-ageing at 69° C and becomes very small after long pre-ageing at 69° C.

The contributions of the growth of crystallites formed at 69° C to the

6.3 CONSEQUENCES OF A SUDDEN TEMPERATURE CHANGE, IN PARTICULAR A TEMPERA-TURE RISE, ON THE NETWORK GROWTH

In Fig. 6.6 the effects of sudden temperature changes on the course of the storage modulus are shown for one reduced frequency, $\omega a_T = 8.5 \text{ s}^{-1}$. In this figure curves B show the consequence of a change from 49 to 25.7°C, curves A those for the reverse change. The curves obtained at the original unchanged temperatures are represented by $A_1(25.7^{\circ} \text{ C})$ and $B_1(49^{\circ} \text{ C})$, both with unfilled symbols. After rejuvenation new experiments were run at the same temperatures for 3.25 h, whereupon in both cases the temperature was changed suddenly. Curve B_2 shows the effect of a sudden temperature fall and curve A_2 that of a sudden temperature rise.

In accordance with the continued ageing processes in the Figs. 6.2 and 6.5, the sudden temperature fall from 49° C to 25.7° C has no clearly perceptible effect on the ageing process: the number of new crystallites seems to be small and growth of the old ones is as little perceptible as



Fig. 6.6 The effect of a sudden temperature change on a prolonged excess-ageing process of PVC/DOP.

Curves A: previous ageing temperature 25.7° C, excess-ageing temperature 49° C. Curves B belong to the reverse treatment of that of curves A. Unfilled symbols: pre-ageing process; filled symbols: excess-ageing process. Curve A₁: plain ageing at 25.7° C; curve A₂: 3.25 h pre-ageing at 25.7° C, followed by excess-ageing at 49° C; curve A₃: 23 h pre-ageing at 25.7° C,

Curve B_1 : plain ageing at 49° C; curve B_2 : 3.25 h pre-ageing at 49° C, followed by excess-ageing at 25.7° C.

Reference temperature 25.7° C. Reduced angular frequency 8.5 rad/s.

in the mentioned cases of Figs. 6.2 and 6.5. Only after several hours the difference in ageing becomes clear, the one at 25.7° C being faster than that at 49° C.

On the other hand, a sudden rise in temperature causes an immediate fall in the storage modulus (and also an immediate rise of the loss modulus, which is not shown here). This may be the consequence of melting of crystallites that are stable at 25.7° C but unstable at 49° C. In fact, the critical number of molecules needed for the formation of a crystallite

will be higher at 49° C than at 25.7° C. This effect shows that many crystallites are far from ideal. After a sudden fall in the storage modulus a quick rise occurs as a consequence of the provision of new crystallization possibilities created by the previous melting of the unstable crystallites. In this way the larger crystallites can grow. When the extra possibilities are exhausted the crystallization rate becomes smaller again. The curve A_3 corresponds to a sudden temperature rise to 49° C after previous ageing during 23 h at 25.7° C. The same effect is obtained, but the fall in the storage modulus (and the not shown corresponding rise in the loss modulus) is much more pronounced because the effect is easier to be measured, due to the prolonged time scale.

After some time the crystallization rate at 49° C (curves A_2 and A_3) is lower than at 25.7° C. This will be the consequence first of the lower number of crystallites and secondly of the tendency to approach an equilibrium value, as is shown by the curve B_1 , and is mentioned already in Section 4.1 (Fig. 4.4). In respect of this tendency it is very surprising that the ageing processes as indicated by the curves A_2 and A_3 , which belong to the same temperature as curve B_1 , are still continuing at such high levels of the storage modulus.

In Fig. 6.7 the dynamic moduli are shown as functions of frequency after ageing during 23 h at 25.7° C (dotted curves). In the same figure these moduli are shown at different times after the sudden rise to $49^{\rm O}$ C. These measurements correspond to curves A3. All measurements are reduced to 25.7° C. On the logarithmic scale of this figure the initial decrease in the storage modulus as described above for $\omega a_{_{T\!T}}$ = 8.5 rad/s, is not very spectacular, however. In this figure is also visible the before mentioned initial increase of the loss modulus after the sudden rise of the temperature. At low frequencies the changes in the loss modulus are much more pronounced than at high frequencies, where after a quick rise, which is in contrast to the fall in the storage modulus, a slow decrease is observed. However, for the first all values of the loss modulus remain much higher than those for the simple ageing process at 25.7° C. At low frequencies the loss modulus rises again after some time. This means that its maximum shifts to higher frequencies. At the same time, the storage modulus rises continuously.

After 313 h excess-ageing at 49° C measurements were taken over a



Fig. 6.7 Reduced storage and loss moduli of PVC/DOP plotted against reduced angular frequency for several times after the sudden temperature rise from 25.7° C to 49° C, which took place after 23 h of pre-ageing at 25.7° C: (Δ) ... 10 min. at 49° C; (\bigcirc) ... 1 h at 49° C; (∇) ... 3 h at 49° C; (\Box) ... 47 h at 49° C; (\bigcirc) ... 313 h at 49° C. Dashed lines: plain ageing at 25.7° C during 23 h. Reference temperature 25.7° C.

larger frequency range, as was mentioned before in Section 4.3.1 (see Fig. 4.19). A maximum in the loss modulus is accompanied by a fall in the storage modulus, whereupon a new rubbery region is reached at still lower frequencies. It appears that this rubbery region has a lower value than that for 25.7° C. This indicates that the number of effective chains is still smaller at 49° C. The obtained loss curves point to slip in entanglements.

The following mechanism may probably describe the process. After initial melting of unstable crystallites the remaining ones will grow. This seems to be evident from the slow decrease in the loss modulus and from the slow increase in the storage modulus, which both follow on the initial changes of the moduli. After some time also a slow recrystallization process may take place, by which the larger crystallites grow at the expense of the less stable smaller ones. In principle this process should not affect the storage modulus, as the number of effective chains remains constant. However, during the recrystallization process entanglements are formed, which is very evident from the renewed increase in the loss modulus and the shift of its minimum to higher frequencies. As a matter of fact, during the migration of molecules or parts of molecules to the larger crystallites, the movement of these molecules is sometimes hampered by other molecules already fixed in the loose network. In this way entrapped entanglements are formed (cf. Fig. 6.8). This formation obviously causes an increase of the



Fig. 6.8 Schematic view of the formation of an entrapped entanglement during the recrystallization process.

storage modulus in the higher frequency region. In contrast, only permanent cross-links will affect the storage modulus in the lower frequency range. In other words, when going from high to low frequencies, one will find a stepwise decrease in the storage modulus from a higher to a lower rubber plateau. Just this behaviour is revealed by the Figs. 4.19 and 6.7. From Fig. 6.7 it is also seen that the low frequency rubber plateau of the

sample which was only aged for 23 h at 25.7° C, is still higher than that of the sample, which underwent an additional excess-ageing for 313 h at 49° C. This means that, in the excess-ageing process, (almost) only recrystallization takes place. At the same time this fact obviates our before mentioned surprise at the continuing ageing process: the increase of the storage modulus, as demonstrated by the curves A_2 and A_3 in Fig. 6.6, is not an increase due to continuing crystallization but a consequence of the formation of entanglements.

We can conclude that after ageing at a certain temperature a sudden rise in the temperature causes melting of small crystallites. This is followed by a fast recrystallization which brings about the formation of entrapped entanglements. As a consequence of the momentary melting of small crystallites at a sudden temperature rise, the extrapolation method needed for the application of the time-temperature reduction (see Section 4.2.2) can only be used in combination with a temperature decrease.

For the gel (already mentioned in Section 4.2.2), which was aged at -10° C during 23 h, subsequently at 24° C during one week and finally 15 months at room temperature, we find an analogous picture after excessageing at 48° C during 238 h. The corresponding moduli are shown in Fig. 6.9 together with those measured at room temperature on the 15 months old gel, which was not excess-aged at 48° C. All curves have been reduced to 25.7° C. The large drop of the modulus of about one decade from the one to the other rubber plateau is remarkable. This drop is much larger than that in Fig. 6.7, where the drop amounts only to 0.2 decades. In contrast to what is shown in Fig. 6.7, the curve for the original storage modulus lies on a higher level than the one for the storage modulus measured after the excess-ageing. This holds for the whole frequency range. Obviously, during ageing at -10° C this special ageing history yielded so many crystallites that are unstable at 48° C, that the prolonged ageing at room temperature (15 months) was not able to change this number considerably. However, the rate of ageing at room temperature is, according to Fig. 4.7, nearly equal to that at -10° C. This again shows that the initial stage of the ageing process is of primary influence for the continued ageing process. As to how far in Fig. 6.9 the ripple in the curve for the loss modulus is a real one and can be considered as a consequence of the special ageing history,



Fig. 6.9 Mastercurves of the storage and loss moduli of PVC/DOP with the following ageing process: 23 h at -10° C, one week at 24° C, 15 months at room temperature and eventually 238 h at 48° C. (O) ... storage modulus; (Δ) ... loss modulus. The dashed lines , without indicated points: the same gel just before the temperature rise to 48 ° C. Reference temperature 25.7° C.

cannot be checked with reasonable reliability by duplication. However, it has to be mentioned that the rubber plateau is also less horizontal than is usual for this kind of gels. This is really an indication for some relaxation. For the rest it has to be mentioned that the ripple in the course of the loss modulus has been measured at all temperatures mentioned in Section 4.2.2: the ripple was shiftable over the frequency range in using the time-temperature reduction.

We shall compare these results with those of Fig. 6.7. For that purpose both excess-ageing curves are shown in Fig. 6.10. The agreement of the course of both curves is remarkable. The maxima of the loss moduli are located at the same frequency and are accompanied by the decrease of the storage modulus from one rubber plateau to the other. According to MARVIN (8), G'_{max} of entanglement networks increases if M_e , the molecular weight between entanglements, decreases. This points to the presence of a much larger number of entanglements in the gel obtained by prolonged ageing, when compared with the other gel. Also according to MARVIN and coworkers



Fig. 6.10 Mastercurves of the storage and loss moduli of PVC/DOP with different temperature histories. (O) ... the gel mentioned in Figs. 4.19 and 6.7; (Δ) ... the gel mentioned in Fig. 6.9. Reference temperature 25.7^o C.

(8-10), the frequency of the maximum decreases if more entanglements per molecule are created. This is the case with polymer melts, where ω_{\max} shifts to lower frequencies with increasing molecular weight. However, this is the consequence of the increase of the length of the molecules and ω_{\max} is the frequency at which the molecules have the opportunity to move with respect to each other. In a polymer melt M is independent of the molecular weight: the number of entanglements per molecule is proportional to the molecular weight. With the aid of a trick we are able to vary the number of entanglements in polyvinyl chloride gels without changing the longest relaxation time (of the molecule itself). Due to this trick the height of the maximum changes, but its location on the frequency scale is not affected.

From the mathematical equations in MARVIN's theory (8-12) it can be derived that both G''_min and ω_{min} shift to higher values at a decrease of M_e . This relationship between G''_min and ω_{min} is shown with logarithmic scales in Fig. 6.11 by the filled symbols. In this figure also the experimental points from the Figs. 4.18, 4.19 and 6.10 are shown as unfilled symbols. Both groups of points lie on straight lines, but far from each other and with different slopes. However, the differences in network build up are great. In MARVIN's entanglement theory $M/(2M_e)$ varies from 3 to 40, where-as in the polyvinyl chloride gels, which are built up of an intertwined combination of crystallites and entanglements, $M/(2M_c)$ varies only from 1.12 to 1.60. Moreover, in the beginning of the network formation the increase in G''_min will proceed faster. In fact, the percentage of non-ideal structure elements in the network decreases fastly with increasing ageing (cf. Chapter 5).



Fig. 6.11 The minimum of the loss modulus in the rubbery region of PVC/DOP plotted against its location on the angular frequency scale. Unfilled symbols: experimental points; filled symbols: calculated from the theory of MARVIN with parameters of the PVC/DOP system.

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CHAPTER 7

PHENOMENOLOGY OF THE AGEING PROCESS OF AQUEOUS GELATIN SOLUTIONS

7.1 INTRODUCTION

Gelatin solutions, varying in concentration from 1 to 5% (w/w), were brought into the dynamic viscometer at 60° C. This temperature was maintained for 20 min. (1). Then the measuring cell was quickly cooled to the desired ageing temperature. This temperature must be below the concentration dependent maximum gelation temperature (approximately $26-30^{\circ}$ C, according to Chapter 8), but above -2° C in order to prevent freezing of the sample. Measurements were started immediately in the same way as described in Chapter 4 for polyvinyl chloride/plasticizer systems.

7.2 MEASUREMENTS ON A 1.95% (w/w) SOLUTION

In Fig. 7.1 the reduced storage modulus G'_r of a 1.95% (w/w) solution is plotted vs the ageing time t_a . G'_r is again defined as (2): $G'_r =$ $G' c_0^T c_0'(cT)$, where c_0 resp. c are the (w/v) concentrations of the dissolved gelatin at the reference temperature T_0 (i.e. -1.2° C) resp. at the ageing temperature T_a . The ageing history is analogous to the one in Fig. 4.1, on the understanding that instead of 150° C one has to read 60° C. The parameters at the various curves are the ageing temperatures T_a , varying from -1.2° C to 20.6° C. The angular frequency ω is equal to 0.393 rad/s in all cases. From this figure it appears that the rate of the ageing process increases strongly if the temperature is lower. It also appears that an induction period exists, where the storage modulus has no measurable values yet. In Fig. 7.2 the logarithm of this induction period, log t_{ind} , is plotted vs the ageing temperature varying from 2.6° C to 25.2° C. (In fact log t_{ind} is determined in a more accurate way from Fig. 7.5). The induction period appears to increase quickly with the ageing temperature.



Fig. 7.1 Storage modulus of 1.95% (w/w) gelatin/water plotted against ageing time for several ageing temperatures. Angular frequency 0.393 rad/s.



Fig. 7.2 Induction period of 1.95% (w/w) gelatin/water plotted against ageing temperature. Angular frequency 0.393 rad/s.

This could be expected, because at the maximum gelation temperature, i.e. the temperature above which no gelation occurs, the induction period should become infinite. In Fig. 7.2 this maximum gelation temperature is shown as a asymptote by the dashed line. In Section 8.1.2 it will be explained in which way the maximum gelation temperature might be determined from these measurements.

In Fig. 7.3 the storage modulus, as found at an ageing temperature of 14.8° C, is shown against the angular frequency on a double logarithmic plot. The parameters at the curves are the ageing times in h. Already after very short times the course of the storage modulus is almost horizontal: after 6 min. of ageing a small increase of G' with the frequency is still perceptible, whereas after 1 h G' is almost independent of the frequency. It has to be mentioned that after 5 min. of ageing the storage modulus just starts to increase; however, already then, at a level of 0.3 N/m², the





course of the storage modulus with the frequency is almost horizontal: a liquidlike course of the storage modulus, as is shown for the PVC/DOP system in Fig. 4.2, was never observed by us for gelatin solutions.

In Fig. 7.4 the reduced storage modulus is plotted vs the angular frequency on logarithmic scales for ageing processes of 120 to 170 h at several temperatures. The frequency range runs from 0.001 to 100 rad/s. The increase of the storage modulus appears to be very small. The increase is most pronounced at 20.5° C, where it covers 0.06 decades in the modulus



Fig. 7.4 Reduced storage modulus of 1.95% (w/w) gelatin/water plotted against angular frequency for several amounts of ageing. Reference temperature -1.2° C. (() ... 120 h at -1.2° C; (() ... 145 h at 10.6° C; (() ... 146 h at 17.3° C; (() ... 170 h at 20.5° C.

over 5 decades in the frequency. This is an increase of 2.6% per frequency decade. For an ageing temperature of -1.2° C this increase amounts only to 1.9% per frequency decade. From the Figs. 7.3 and 7.4 it appears that the storage modulus, certainly after long ageing times, is nearly independent of the frequency. For this reason in Fig. 7.5 only one frequency ($\omega = 0.393 \text{ rad/s}$) is used for the comparison of the ageing processes at different temperatures. In this figure the storage modulus is plotted vs the logarithm of the ageing time, the ageing temperature varying from -1.2° C to 25.2° C. Except for the curve for -1.2° C, the curves are nearly parallel after the mentioned induction period. Hence, the slope dG'/d log t_a is nearly independent of the ageing temperature and amounts approximately 155 N/m² per decade. Another remarkable feature in this figure is that, at



Fig. 7.5 Reduced storage modulus of 1.95% (w/w) gelatin/water plotted against ageing time for several ageing temperatures. Angular frequency 0.393 rad/s. Reference temperature -1.2° C.

low values of log t_a , the curves are concave with respect to the log time axis, thereupon they become convex and finally linear at high values of log t_a . The position on the time scale of the transition from the convex to the linear region shifts to longer times if the temperature decreases. At the highest temperature a convex region is not perceptible. According to MERCIER and coworkers (3) this behaviour reflects a transition from primary to secondary crystallization. In their publication they show a figure in which ΔH^0 , the heat of melting of a gelatin gel, determined with the aid of differential scanning calorimetry, is plotted vs the logarithm of the ageing time. This curve is an image with respect to the axis of the log time scale, of the curves for the storage modulus in Fig. 7.5. This means that ΔH^0 has negative values. This comparison leads to the fact, revealed by Fig. 7.5, that secondary crystallization starts earlier if the temperature is higher or, in other words, that the primary crystallization is exhausted earlier if the ageing temperature is higher.

In Fig. 7.6 the reproducibility of the measurements is demonstrated. At a temperature of 17.4° C the storage modulus is shown as a function of the logarithm of the ageing time for three different 1.95%-solutions. The reproducibility appears to be good enough: in the region where the ageing



Fig. 7.6 Storage modulus of several samples, as indicated by different symbols, of 1.95% (w/w) gelatin/water plotted against ageing time. Ageing temperature 17.4[°] C. Angular frequency 0.393 rad/s.

process starts to be perceptible, the differences are biggest. For the linear region (0.3 to 3 h) the correlation coeffcient of the straight line amounts to ρ = 0.998.

The influence of a temperature decrease after pre-ageing at a higher temperature is demonstrated in Fig. 7.7. Here the storage modulus is plotted vs the excess-ageing time t_{ea} at -1.2° C, after pre-ageing at 17.4° C during several times, varying from 0.125 h to 146 h. In Fig. 7.7 the results of ageing at unvaried temperatures of 17.4° C and -1.2° C, respectively, are shown too. The curves for 3 h pre-ageing and longer are close together and far beyond the ageing curves for 17.4° C and -1.2° C. Between 0 and 3 h pre-ageing a gradual increase of the distance from the curve of -1.2° C is perceptible. This is also shown in Fig. 7.8, where the storage modulus, as found after 2.5 h excess-ageing at -1.2° C. The shape of the curve suggests a subdivision into two linear portions, in accordance with Fig. 7.7, with a point of intersection at approximately 3 h. This means that pre-ageing at 17.4° C has a considerable effect only in the first three hours. After that period pre-ageing has only little effect.



Fig. 7.7 Reduced storage modulus of 1.95% (w/w) gelatin/water plotted against excess-ageing time elapsed at -1.2° C after previous ageing at 17.4° C during several pre-ageing times. The ageing curves of -1.2° C and 17.4° C are also shown. Angular frequency 0.393 rad/s. Reference temperature -1.2° C.



Fig. 7.8 Storage modulus of 1.95% (w/w) gelatin/water after 2.5 h of excess-ageing at -1.2° C plotted against the pre-ageing time at 17.4° C. Angular frequency 0.393 rad/s. The influence of a temperature rise imposed after pre-ageing at a lower temperature is demonstrated in Fig. 7.9. The temperature of a sample which was aged at -1.2° during 120 h, was increased to 10.4° C. Initially,



Fig. 7.9 Storage modulus of 1.95% (w/w) gelatin/water plotted against ageing time at 10.4° C, whether (\bullet) or not (O) aged at -1.2° C during 120 h. Angular frequency 0.393 rad/s.

the storage modulus decreases rather quickly. After 5 to 10 h excess-ageing it passes through a minimum. Finally, it increases slowly and approaches the ageing curve for plain ageing at 10.4° C asymptotically. Total duration of this process: 70 h. The described course of the curve might lead to the almost generally accepted statement of FERRY (4) that short pre-ageing at low temperature, followed by excess-ageing at a higher temperature, faster leads to an equilibrium value of the shear modulus than direct ageing at the higher temperature. However, this is only deceptive appearance: in reality the ageing process is continuously proceeding. In this way, also from Fig. 7.1 it might be deduced that ageing leads quickly to an equilibrium value. However, comparison with Fig. 7.5 where the ageing time scale is logarithmic instead of linear, demonstrates that the ageing process is still continuing after long times.

7.3 INFLUENCE OF THE CONCENTRATION

Besides measurements on a solution of 1.95% (w/w), as mentioned in the previous section, measurements were taken also on solutions of other concentrations. In Fig. 7.10 the storage moduli of four different solutions, viz. 1.95, 3, 4 and 5% (w/w), are shown as functions of the ageing time at an ageing temperature of 17.4° C and an angular frequency of 0.393 rad/s. The ageing process is faster if the concentration is higher. Also the induction period, where the storage modulus shows no measurable increase, is concentration dependent, being smaller if the concentration is higher. The influence of the frequency is not checked anymore, however.



Fig. 7.10 Storage modulus of gelatin/water of several concentrations plotted against ageing time. Ageing temperature $17.4^{\circ}C$. Angular frequency 0.393 rad/s.

In Fig. 7.11 the loss moduli of the four solutions are plotted vs the logarithm of the ageing time at an ageing temperature of 10.6° C. The loss moduli, which appear to be higher for higher concentrations, start to increase very fast in the early beginning of the ageing process, go through a maximum value and subsequently decrease slowly. The maximum is reached earlier if the concentration is higher, i.e. after 3 min. of ageing for 5% and after 20 min. for 1.95%. An analogous picture is obtained, if the age-

ing of a 5%-solution is investigated at different temperatures, as is shown in Fig. 7.12 for ageing temperatures of -1.2 to 25.2° C. A maximum is obtained, which is higher and shifted to shorter ageing times, if the temperature is lower. Obviously, the maximum at -1.2° C occurs at such short



Fig. 7.11 Loss modulus of gelatin/water of several concentrations plotted against ageing time. Ageing temperature $10.6^{\circ}C$. Angular frequency 0.393 rad/s.



Fig. 7.12 Reduced loss modulus of 5.00% (w/w) gelatin/water plotted against ageing time for several ageing temperatures. Angular frequency 0.393 rad/s. Reference temperature $-1.2^{\circ}C$.

times, that it escaped observation. In fact, the first measurement could not be carried out earlier than two minutes after the start of the ageing process. Inspection of the position of the maximum on the time scale shows that it is reached just after the induction period, thus at the moment the network is still very far from ideal.

Admittedly, the measurements of the loss modulus are not very accurate. In this connection it should be mentioned that $\tan \delta = G''/G'$ has values that approach the lower limit of reliability of the apparatus. In fact, after 1 h ageing at -1.2° C e.g. the measured time differences, from which the phase angles are calculated, are of the order of only 3 ms, if a period of oscillation as large as 16 s is chosen.

In Figs. 7.13 and 7.14 the storage moduli of the four solutions are plotted against the logarithm of the ageing time as obtained at ageing temperatures of 25.2° C and -1.2° C. In both cases an angular frequency of 0.393 rad/s was chosen. In these figures the differences between the induction periods of the four solutions is better perceptible than in Fig. 7.10. The course of the curves in Fig. 7.13 is simpler than that in Fig.



Fig. 7.13 Storage modulus of gelatin/water of several concentrations plotted against ageing time. Ageing temperature 25.2^oC. Angular frequency 0.393 rad/s.


Fig. 7.14 Storage modulus of gelatin/water of several concentrations plotted against ageing time. Ageing temperature -1.2° C. Angular frequency 0.393 rad/s.

7.14. The position on the time scale of the transition from convex to linear behaviour seems to be independent of the concentration. In other words, the moment of transition from primary to secondary crystallization is independent of the concentration, according to the statement of MERCIER and coworkers (3), who arrived at this conclusion after studying a publication of VIDOTTO and KOVACS (5). The slope of the linear region increases with the concentration: at -1.2° C dG'/d log t is 180 N/m² per decade of time at 1.95% and 1067 N/m² per decade of time at 5%.

In Fig. 7.15 the reduced storage modulus of the 5%-solution is plotted vs the logarithm of the ageing time at ageing temperatures varying from -1.2° C to 25.2° C. The slope of the linear region appears to be temperature dependent (1067 N/m² per decade of time at -1.2° C and 467 N/m² per decade of time at 25.2° C), in contrast with Fig. 7.5 where the slope is almost independent of the temperature.



Fig. 7.15 Reduced storage modulus of 5.00% (w/w) gelatin/water plotted against ageing time for several ageing temperatures. Angular frequency 0.393 rad/s. Reference temperature $-1.2^{\circ}C$.

Finally, some remarks have to be made about the special application of the time-temperature reduction which was so successful for PVC/plasticizer systems. As is shown in Fig. 7.7, the extrapolation of the excessageing to the moment of the change in temperature is very difficult and inaccurate. In fact, it might be possible to use smaller temperature differences in order to make the extrapolation procedure feasible. However, two other circumstances cause the method to be less applicable. First, the storage modulus is nearly independent of the frequency, which makes the shifting of the curves very inaccurate. Secondly, in most cases the loss modulus is rather inaccurate, especially at times longer than three times the induction period. These circumstances make the application of the reduction a risky undertaking.

7.4 REFERENCES

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CHAPTER 8

CLOSER EXAMINATION OF THE NETWORK GROWTH IN AQUEOUS GELATIN SOLUTIONS

8.1 DETERMINATION OF THE MAXIMUM GELATION TEMPERATURE AND THE HEAT OF RE-ACTION OF THE AGEING PROCESS

8.1.1 Preamble

According to ELDRIDGE and FERRY (1) the relationship between the melting temperature ${\rm T}_{\rm m}$ of gelatin gels and the concentration is given by:

$$(d \ln c/dT_m)_{\tilde{M}_w} = -\Delta H^0 / (RT_m^2)$$
(8.1)

where:

R = the gas constant (= 8.316 J/(mol K)).

The following assumptions were made by the authors in deriving this relationship:

- The fraction of the total number of junctions in the gel that contribute to the elasticity, hence the fraction of the number of elastically effective cross-links, is a function of the concentration, but not of the temperature. This assumption is questionable since the degree of intramolecular cross-linking will depend on the rate of the ageing process, being smaller if the ageing temperature is higher. This conclusion follows also from Chapter 6 for polyvinyl chloride gels. However, in the following it will appear that the variation in T_m is small, so that the question about the strict validity if this assumption is rather irrele-

vant;

- The number of potential junctions per unit of volume of the gel is proportional to the concentration. However, this is only true if the number of junctions already coupled in cross-links, is small with respect to the original number of potential junctions. In other words, this holds if the ageing process has not proceeded very far. In view of the method of determination of T_m , at least of T_{gel} (i.e. the maximum gelation temperature), this demand will certainly be satisfied;
- The number of potential junctions still available is not a function of the temperature. Also in this case the argumentation, mentioned in the previous point, is valid;

ELDRIDGE and FERRY, in deriving Eq. (8.1), started their calculation from the following equilibrium:

2 potential junctions $\stackrel{?}{\leftarrow}$ 1 cross-link - $\triangle H^{O}$

with the equilibrium constant:

$$K = m_{c\ell} / (m_{\ell}^{2})$$
(8.2)

where:

 m_{ϱ} = the concentration of potential junctions;

 m_{c0} = the concentration of cross-links.

Hence, the cross-links they consider are tetra-functional. Extension of the treatment to a functionality f > 4, where the following equilibrium is envisaged:

 $\frac{1}{2}$ f potential junctions $\stackrel{\scriptstyle \neq}{\leftarrow}$ 1 f-functional cross-link - $\triangle H^{O}$

yields as an equilibrium constant:

$$K = m_{c\ell} / (m_{\ell})^{\frac{1}{2}f}$$
(8.3)

In working out this relationship, in the way it was shown by ELDRIDGE and FERRY for tetra-functional cross-links, one obtains the following equation:

$$(d \ln c/dT_m)_{\tilde{m}} = \Delta H^0 / [RT_m^2 (1 - \frac{1}{2}f)]$$
 (8.4)

$$\left[d \log c/d(1/T_m)\right]_{\overline{M}} = -\Delta H^0 / \left[2.303 R(1 - \frac{1}{2}f)\right]$$
(8.5)

where ΔH^{O} is the heat of reaction for breaking 1 cross-link in $\frac{1}{2}$ f potential junctions. A plot of log c vs $1/T_{m}$ yields a straight line with a slope equal to $\Delta H^{O}/[2.303 \text{ R}(\frac{1}{2}\text{f} - 1)]$, provided both ΔH^{O} and the functionality do not depend on the melting temperature and, as a consequence, also not on the concentration (in reality, T_{m} appears to be dependent on the concentration).

8.1.2 Determination of the maximum gelation temperature

It appears from Fig. 7.2 that the induction period, i.e. the time needed for the development of a measurable increase of the storage modulus, increases strongly with the ageing temperature. At the maximum gelation



Fig. 8.1 Reciprocal square root of the induction period of 1.95% (w/w) gelatin/water plotted against ageing temperature.

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or

temperature, T_{gel} , the induction period becomes infinite and hence, its reciprocal value goes to zero. In an empirical way it is found that, if the square root of the reciprocal induction period is plotted vs the ageing temperature, a straight line is obtained. This is shown in Fig. 8.1 for a 1.95% (w/w) solution of gelatin. In fact, one does not need much phantasy to draw a straight line through the experimental points (the correlation coefficient amounts to $\rho = -0.998$). Extrapolation to $t_{ind} \rightarrow \infty$ yields $T_{gel} =$ 26.3° C. Why the relation between $t_{ind}^{-\frac{1}{2}}$ and T_{a} is linear, is still unclear to the author. In an analogous way the maximum gelation temperatures of the other gelatin solutions were determined. The results are mentioned in Table 8-I. It appears that the maximum gelatin temperature increases with the concentration.

Table 8-I

The maximum gelation temperature, ${\rm T}_{\mbox{gel}}$, of aqueous gelatin solutions as a function of the concentration.

c%(w/w)	5.00	4.00	3.00	1.95
T _{gel} ^O C	29.6	28.4	27.4	26.3

8.1.3 Calculation of the heat of reaction of the cross-linking process

In Fig. 8.2 log c is plotted vs the reciprocal maximum gelation temperature. The slope of the straight line (correlation coefficient ρ = -0.991) yields:

 ${\rm \Delta H}^0/(\frac{1}{2}f$ - 1) = -221 kJ per mol of potential junction regions.

Measurements of the melting temperature of gelatin gels, as reported by ELDRIDGE and FERRY (1), yield values for this quantity varying from -206 to -924 kJ/mol, depending on the molecular weight and on the melting temperature. Analogous measurements taken by TAR (2) yield -252 to -317 kJ/mol. From measurements by FLORY and GARRETT (3) one can derive a value of -150 kJ/mol.





Since the cross-linking in gelatin gels consists of the formation of triple-helices the functionality f of the resulting cross-links is equal to 6, so that $\Delta H^{0} = -442$ kJ/mol. HARRINGTON and RAO (4) report values varying from -170 to -340 kJ/mol.

From their measurements of the temperature dependence of the optical rotation of very dilute α -gelatin solutions EAGLAND c.s.(5) conclude that ΔH^{O} of a folding process has a value of -18.8 kJ/mol. OTH and coworkers (6) conclude to a value of -17.6 kJ/mol and FLORY and GARRETT (3) to a value of -18.8 kJ/mol. In fact, measurements of the optical rotation yield a value of ΔH^{O} corresponding to the formation of a repeating unit of three windings for the formation of a triple helix. With the aid of the mean value, i.e. -18.3 kJ/mol, the mean number of windings per helix in a cross-link may be calculated to be 442/18.3 = 24. HARRINGTON and RAO (4,7) state that for the formation of a stable helix at low temperature 7 to 11 wind-ings are needed, whereas at higher temperatures this number will be consi-

derably higher. Hence, a mean value of 24 in the temperature region of $26-30^{\circ}$ C is not unreasonable. We shall return to this subject in Sections 8.1.3 and 8.3.3.

8.2 CONCENTRATION DEPENDENCE

In many publications (8-16) it is demonstrated that the quotient G'/c^2 (or G/c^2) has a constant value in a certain concentration region, or at least that G' (or G) is a linear function of c^2 . For the value of G' the equilibrium value (whatever it may be!) should be used. However, in Chapter 7 it is demonstrated that even after 150 h of ageing the storage modulus still linearly increases with log t_a. Hence, it is not surprising that the values of G'/c^2 reported show a rather large scattering. SAUNDERS and WARD (17) report that for concentrations lower than 2% the storage modulus is a linear function of the concentration; above this concentration no linear



Fig. 8.3 $G'_{\mu'}c^2$ of gelatin/water of several concentrations plotted against ageing time. Ageing temperature 17.4° C. Angular frequency 0.393 rad/s. $(\Box) \ldots 1.00\% (w/w); (\bigtriangledown) \ldots 1.95\% (w/w); (\bigtriangleup) \ldots 3.00\% (w/w);$ $(\bigcirc) \ldots 4.00\% (w/w); (\bigcirc) \ldots 5.00\% (w/w).$

relationship between the storage modulus and any power of the concentration could be detected. However, they do not report measurements in the concentration region of 2 to 5%. Also SHEPPARD and SWEET (18) did not find a quadratic relationship at high concentrations (10-45%).

In Fig. 8.3 G'_r/c^2 of the four gelatin solutions is plotted vs the logarithm of the ageing time. Measurements were carried out at an ageing temperature of 17.4° C and at one frequency ($\omega = 0.393$ rad/s). Only after 50 h of ageing G'_r/c^2 obtains a reasonably concentration independent value, whereas with increasing ageing time this value still increases: in the time interval from 50 h to 200 h with approximately 15%.

Besides for the usual concentrations of 2 to 5% the ageing curve is also shown for a 1% (w/w) solution. This curve has a considerably lower course and does not match the set of ageing curves of the other solutions. Obviously, the lower limit for a concentration independent value of G_r'/c^2 lies between a concentration of 1 and 2%. This conclusion is in agreement with measurements of FERRY and ELDRIDGE (13), who state that a deviation from the c^2 -rule really starts at a concentration of 2%. Obviously, intramolecular helix formation starts to play an important role at concentrations below 2%.

By FERRY and ELDRIDGE (13) the shear modulus is determined as a function of temperature, weight average molecular weight and concentration for a series of low molecular weight gelatins, prepared by hydrolytic degradation of a high molecular weight alkali-precursor ossein gelatin. They arrive at the following empirical relationship:

$$G_r^{\frac{1}{2}}/c = 0.00386 \left[\bar{M}_w - 3.1 \times 10^{10} \exp(-3980/T) \right]$$
 (8.6)

where G_r is expressed in N/m², c in kg/m³ and T in K. Inserting in Eq. (8.6) the results of our measurements on the four mentioned gelatin solutions (after 100 h of ageing at the four different temperatures -1.2, 10.6, 17.4 and 25.2° C), we find for our gelatin a weight average molecular weight of \overline{M}_w = 62 200, with a standard deviation of 270 (= 0.4%). Insertion of the storage modulus as obtained after 30 h of ageing yields a value for \overline{M}_w , which is 2.7% lower. We may conclude that the weight average molecular weight of the gelatin of investigation is approximately 60 000, provided Eq. (8.6) can be applied. This value must be compared with \overline{M}_w as it

is found by means of light scattering: $\bar{M}_{_{\rm W}}$ = 70000 (see Section 1.3.2).

Our measurements show also much agreement with those of SAUNDERS and WARD (17, 19-21): their measurements of the shear modulus of a solution of a certain gelatin after 17 h of ageing at 10° C agree almost exactly with our measurements after 17 h of ageing at 10.6° C. Unfortunately, in none of their publications the molecular weight of the investigated gelatin is reported. However, they do mention the Bloom-jelly strength ^{*)} to be 209, whereas this value for our gelatin is approximately 220 (22).



Fig.8.4 Storage modulus of gelatin/water plotted against the square of the concentration for several ageing times. Ageing temperature 17.4[°] C. Angular frequency 0.393 rad/s.

In Fig. 8.4 the storage modulus is plotted vs the square concentration for the gelatin solutions aged at 17.4° C. The ageing times vary from 0.3 to 100 h. The relationships between G' and c² appear to be linear (the correlation coefficients vary from 0.999 to 0.99995). The straight lines

^{*)} The Bloom-test is described in the British standards methods of sampling and testing gelatins (23). For that purpose 7.5 g gelatin is dissolved in 105 ml water under standard conditions in a special jar. In this way a concentration of 6 2/3% is obtained. The jar is placed in a thermostat bath of 10° C, during one night. Then a stamp of defined dimensions is pressed in the gel to a depth of 4 mm with the aid of a Bloomgelometer. The force needed to cause this impact, expressed in grams, is called the Bloom-jelly strength. Usually its values run from 50 to 250 grams.



Fig. 8.5 Concentration of critical ageing plotted against corresponding ageing time. Ageing temperature 17.4 $^{\rm O}$ C.

do not pass through the origin, whereas the deviation is larger if the ageing time is shorter. If extrapolation to G' = 0 is justified, those concentrations are obtained, at which the indicated ageing times are just in the phase of critical gel formation. In other words: the times indicated at the straight lines are the induction periods for the gel formation of solutions which possess the concentration found by the extrapolation. In Fig. 8.5 the logarithm of this induction period is plotted vs the concentration. The relation between log t_{ind} and c, which appears to be linear according to Fig. 8.5, is given by:

 $\log t_{ind} = -1.512 c + 2.129$

with a correlation coefficient $\rho = -0.997$, where t_{ind} is given in hours and c in % (w/w). From Fig. 8.5 one can derive e.g. that for a concentra-





tion of 1.95% the induction period amounts to 0.15 h. In Section 7.2 the same value was obtained in a completely different way. However, the extrapolation as shown in Fig. 8.4, is yet a risky one: in Fig. 8.6 t ind, as measured at 17.4° C for different concentrations, is plotted vs the concentration, together with the values obtained with the extrapolation method. Below a concentration of 2% the agreement is reasonably good. It is clear, that extrapolation of the straight line to higher concentrations certainly does not give satisfactory results. It has to be mentioned, however, that for such short induction periods (shorter than 0.1 h) the cooling rate of 60° C to the ageing temperature plays an important role. If the cooling rate is not high enough, the induction period will be too long. This will, of course, affect the values of T as mentioned in Section 8.1. These values would be too high, especially for the higher concentrations. The consequence will be that the line in Fig. 8.2 is not steep enough: the negative slope will be too small. Hence, we have to conclude that the value of $-\Delta H^0$ (i.e. 442 kJ/mol) is too small. In accordance with this conclusion also the mean number of windings in a helix, for which we calculated 24, will be too low.

In Fig. 8.7 the rate of ageing, dG'/d log t_a , is plotted against c^2 for an ageing temperature of 17.4° C. It appears that not only the storage modulus is a linear function of the square concentration, but also the rate of ageing (the correlation coefficient is 0.99235).



Fig. 8.7 Rate of ageing of gelatin/water plotted against the square of the concentration. Ageing temperature 17.4° C. Angular frequency 0.393 rad/s.

8.3 THE INFLUENCE OF THE TEMPERATURE HISTORY

8.3.1 The effect of a temperature decrease

In Fig. 7.7 the effect is demonstrated of a temperature decrease to -1.2° C, as imposed to solutions of 1.95% after pre-ageing at 17.4° C during various time intervals. At that occasion it has already been shown, that pre-ageing has a tremendous influence on the continued ageing at lower temperatures. In Fig. 8.8 the effect of the excess-ageing at -1.2° C is shown again, but now in the overall ageing curves (G'_r plotted vs log t_a). The influence of pre-ageing has proceeded for a longer time: the effect of excess-ageing after short times of pre-ageing is quickly overruled by that



Fig. 8.8 Reduced storage modulus of 1.95% (w/w) gelatin/water of several ageing histories (see text) plotted against ageing time. Angular frequency 0.393 rad/s. Reference temperature -1.2° C.

of excess-ageing after longer pre-ageing! Hence, in the same time a stiffer gel is obtained, if the pre-ageing at higher temperature has occurred during a longer time.

In Fig. 8.9 the results of Fig. 7.7 are plotted in another way: the storage modulus is plotted vs the logarithm of the excess-ageing time. In this way lines are obtained, which are almost parallel to that for -1.2° C. This parallel course is approached at a later time, if the pre-ageing has lasted for a longer time. The parallel course persists even to times, where the normal ageing curve for -1.2° C already tends to level off.

In Fig. 8.10 two ageing processes are compared. Both processes occur at -1.2° C after 1.5 h of pre-ageing at various temperatures. One is pre-aged only at 17.4° C, the other is pre-aged at 17.4° C during half an hour and, subsequently, at 8.6° C during one hour. From the results it appears that the intermediate ageing process at 8.6° C has a retarding effect on the excess-ageing process at -1.2° C.

In Fig. 8.11 the influence of various pre-ageing processes, as carried



Fig. 8.9 Storage modulus of 1.95% (w/w) gelatin/water after several periods of pre-ageing at 17.4° C plotted against excess-ageing time at -1.2° C. Angular frequency 0.393 rad/s.



Fig. 8.10 Reduced storage modulus of 1.95% (w/w) gelatin/water with several ageing histories, as indicated, plotted against ageing time. Angular frequency 0.393 rad/s. Reference temperature -1.2° C.



Fig. 8.11 Reduced storage modulus of 1.95% (w/w) gelatin/water plotted against ageing time for several ageing temperatures, on the one hand, and at -1.2° C after 1.5 h of ageing at the mentioned ageing temperatures, on the other hand.

Angular frequency 0.393 rad/s. Reference temperature -1.2° C.

out during 1.5 hat temperatures varying from 6.5° C to 22.4° C, on the excess-ageing at -1.2° C is demonstrated for a 1.95% solution. On the overall ageing pre-ageing at 17.4° C has the largest and pre-ageing at 6.5° C has the smallest effect. The storage modulus after 5 h of excess-ageing at -1.2° C is plotted vs the pre-ageing temperature T_{pa} in Fig. 6.12. According to this figure the maximum effect of pre-ageing may be expected at 16.2° C. In this figure also $\Delta G'_r$ is plotted vs the pre-ageing temperature, where $\Delta G'_r$ is defined as the difference between the storage modulus obtained after 1.5 h of ageing at T_{pa} and 5 h of subsequent ageing at -1.2° C, and the storage modulus obtained after 6.5 h plain ageing at the pre-ageing temperature. A monotonous increase of $\Delta G'_r$ with pre-ageing temperature is perceptible. The curve seems to go to a maximum value at approximately 24° C. It is conceivable that also in this case a maximum has to occur: the overall storage modulus decreases for pre-ageing temperat tures higher than 16.2 $^{\rm O}$ C, whereas the storage modulus for an unchanged ageing temperature T _{pa} becomes very small at high temperatures T _{pa}.





STAINSBY (24) reports for the position of this maximum on the temperature scale a value of 24.2° C. Unfortunately, the concentration of the gelatin solution was not mentioned; the excess-ageing temperature is probably 10° C.

In Fig. 8.13 the storage modulus is plotted vs the logarithm of the excess-ageing time for the experiments shown in Fig. 8.11. With increasing excess-ageing time all lines attain the same slope, equal to that for -1.2° C, as is the case also in Fig. 8.9. It should be noticed that the measurements on the sample with a pre-ageing temperature of 6.5° C, starting at a relatively high level, still deviate from the parallel course after 6 h of excess-ageing.



Fig. 8.13 Storage modulus of 1.95% (w/w) gelatin/water at -1.2° C, after 1.5 h of ageing at several pre-ageing temperatures, plotted against excess-ageing time. Angular frequency 0.393 rad/s.

8.3.2 The effect of a temperature increase

It has already been observed that a temperature increase causes a quick decrease of the storage modulus to the value it should have at that higher temperature (see Fig. 7.13). In Fig. 8.14 this is again demonstrated for a 1.95% solution, that was aged consecutively at 17.4° C (1.5 h), at -1.2° C (5 h) and, again, at 17.4° C. The pre-ageing process at 17.4° C causes a strong increase of the modulus during the excess-ageing at -1.2° C. The subsequent temperature increase to 17.4° C causes an initially very rapid decrease of the storage modulus, whereas, with proceeding time, another increase becomes observable, by which the curve for plain ageing at 17.4° C is approached gradually. This is shown in another way in Fig. 8.15. In this figure the plain ageing process at 17.4° C is shown, together with the excess-ageing at 17.4° C. As zero time of the excess-ageing process the



Fig. 8.14 Reduced storage modulus of 1.95% (w/w) gelatin/water with a special ageing history plotted against ageing time. (O) and (仓) ... 17.4° C; (仓) ... -1.2°C. Angular frequency 0.393 rad/s. Reference temperature -1.2° C.



Fig. 8.15 Storage modulus of 1.95% (w/w) gelatin/water at 17.4° C (\bullet) and with a special ageing history (see text) (O), plotted against (excess-) ageing time. Angular frequency 0.393 rad/s.

instant is chosen, at which the temperature is increased from -1.2° C to 17.4° C (hence, after 6.5 h of ageing). The storage modulus decreases to a minimum value after approximately 2 h. Subsequently, a gradual increase, by which the curve gradually approaches the curve for 17.4° C. From these measurements it appears clearly that an intermediate ageing at a lower temperature does not affect the final ageing at the higher temperature: the influence of the intermediate ageing fades away within approximately 40 h.

In this latter experiment the final ageing temperature was equal to the initial one. In this case a kind of memory for the old situation may exist, by which the original state is finally reached again. However, the process is more complicated, as is revealed by Fig. 8.16. In this figure,



Fig. 8.16 Reduced storage modulus of 5.00% (w/w) gelatin/water with different ageing histories (as indicated) plotted against ageing time. Angular frequency 0.393 rad/s. Reference temperature -1.2° C.

the result of ageing of a 5% gelatin solution is shown. This solution was originally aged at 17.4° C, subsequently during 5 h at -1.2° C, and finally at 25.2° C. In this figure the ageing curves for 17.4° C and 25.2° C are also shown. Apparently, the excess-ageing at 25.2° C causes the storage modulus to drop to the level of the plain ageing process at these latter temperature, though at this temperature no pre-ageing occurred.

From this figure it appears also that the relative effect of pre-ageing at 17.4° C on the ageing process at -1.2° C is smaller for the 5% solution than for the 1.95% solution: for the 5% solution the storage modulus increases during 5 h from 1800 to 6600 N/m² (i.e. 270% increase) and for the 1.95% solution from 170 to 1000 N/m² (i.e. 490% increase). For a 3% solution an increase of 380% was found.

It should be remarked, however, as also appears from Fig. 8.17, that for a concentration of 5% a pre-ageing at 17.4° C, strictly speaking, has only little effect on the overall ageing at -1.2° C: after 6.5 h of ageing the storage modulus of the pre-aged sample is only 4% higher than that of the sample which was plainly aged at -1.2° C. For 3% and 2% solutions this percentage is 31 resp. 71. It may be concluded that pre-ageing at high temperature is of great influence on the overall ageing at low temperature if the concentration is low (e.g. 2%), whereas this influence becomes smaller if the gelatin concentration becomes higher. It almost disappears at a concentration of 5%.



Fig. 8.17 Reduced storage modulus of 5.00% (w/w) gelatin/water with different ageing histories (as indicated) plotted against ageing time. Angular frequency 0.393 rad/s. Reference temperature -1.2° C.

8.3.3 Discussion of the results

Pre-ageing of a 2% gelatin solution at a higher temperature has an accelerating effect on the excess-ageing at -1.2° C. This is revealed by the Figs. 7.7, 8.8, 8.10 and 8.11. From this fact we might suppose that two processes are involved: a nucleation process, which takes place quickly at high temperatures, followed by a growth of structures (crystals, helices) which is fast at -1.2° C. An optimum effect is obtained by pre-ageing at 16.2° C (cf. Fig. 8.12).

Comparison of the mentioned figures with Fig. 8.17, however, falsifies this conclusion: pre-ageing of a 5% solution at 17.4° C has a negligible influence on the overall ageing at -1.2° C. There rather seems to exist a temperature dependent dynamic equilibrium, which, however, is never completely approached in the course of the (ageing) time. This is supported by the Figs. 7.13 and 8.14 to 8.16. From these figures it appears that heating up gels with different ageing histories quickly leads to a state of ageing, or at least to a storage modulus, which is also reached without pre-ageing at low temperatures.

From the Figs. 8.9 and 8.13, where the excess-ageing at -1.2° C is plotted vs the logarithm of the excess-ageing time, it appears that the rate of ageing dG'/d log t_{ea} is, within certain limits, independent of preageing. Hence, we may conclude that excess-ageing is a superposition of ageing on a network already formed at high temperature. However, if the sample has been pre-aged during a longer time or at a lower temperature, and a denser network has already been formed, the rate of ageing becomes constant only after a longer time (cf. t_{pa} = 147 h in Fig. 8.9 and T_{pa} = 6.5° C in Fig. 8.13).

According to STAINSBY (24) a gel network is formed during cooling of a gelatin solution, due to the rearrangement of disordered gelatin molecules into collagenlike structures. The structures which are formed, are far from perfect: at a certain temperature T_a only those structures are obtained which are stable in the temperature range T_a < T < T_{gel}. If this gel network is cooled to a lower temperature T_{ea} < T_a, first the structures already formed will grow and structures will be formed that are stable in the temperature suil be formed that are stable in the temperature region T_{ea} < T < T_a. The latter mentioned structures will be less stable than the first mentioned ones. On heating to the temperature T, they will melt again. The first mentioned structures will persist. This appears from Fig. 8.14 e.g., where an intermediate lowering of the temperature causes the storage modulus to increase strongly: structures, that are stable in the temperature region -1.2° C < T <17.4°C, will be superposed on the network that is stable in the temperature region 17.4° C < T < T_{gel}. On heating to 17.4° C these structures, formed in second instance, will melt again, causing a strong decrease of the storage modulus. Since also during the time interval at -1.2° C structures, which are stable at 17.4° C are formed and extended, the storage modulus is nevertheless higher than at the moment, when the temperature was lowered to -1.2° C. Heating a gel, that has been formed at T_o, whether or not followed by excess-ageing at a lower temperature ${\rm T}_{\rm ea}$, to a temperature T_{c} between T_{a} and T_{gel} will cause a melting of those structures that are stable in the temperature region $T < T_c$. The structures that are stable in the temperature region, will remain existing. This appears from Fig. 8.16 e.g. (and also from Fig. 7.9): heating a gel, that has originally been formed at 17.4° C and subsequently has been excess-aged at -1.2° C, to 25.2° C, causes melting of structures that are stable below 25.2° C. Only those structures that are stable in the temperature region 25.2° C < T < T_{gel}, remain existing.

It is remarkable that intermediate ageing at -1.2° C (cf. Fig. 8.14) as well as pre-ageing at 17.4° C followed by excess-ageing at -1.2° C (cf. Fig. 8.16), has no effect on the growth of the structures at 17.4° C resp. 25.2° C: the formation and growth of the structures that are stable at the respective temperatures, was started and continued at the lower temperatures with the same rate as would have been the case at the higher temperatures. Hence, we have to conclude that formation and growth of certain structures is almost independent of temperature. This means that the heat of activation of the rate determining step in the ageing process is rather small, e.g. smaller than 3 kJ/mol. This is in complete agreement with the conclusions of EAGLAND and coworkers (5). On the basis of their measurements of optical rotation and viscosity at 5 to 15° C on very dilute gelatin solutions, these authors conclude that the reaction rate constant of the rate determining step in the ageing process of gelatin is almost independent of temperature.

Hence, the difference in degree of ageing at the various temperatures

is not caused by a difference in reaction rate constant, but by increasing stability of small structures with decreasing temperature.

The foregoing explains also the measurements of ARISZ (21) in 1915, who was very surprised about his own findings. A 10% solution of gelatin in glycerine e.g. was shortly aged at 35° C and after gelation had taken place, the gel was heated to 44° C. By this heating the gel was melted, while after some time gelation took place again. Heating to 44° C did not cause melting, if the solution was aged at 35° C during a long time. The explanation is as follows: the time the solution was aged at 35° C in the first experiment, was shorter than the induction period at 44° C. In fact, we have learned that an intermediate ageing at a lower temperature has no influence on the final ageing process at a higher temperature. The gel formed at 35° C, had to melt, since not enough structures for an infinite network, which are stable at 44° C, had been formed. In ARISZ's second experiment the time of ageing at 35° C was longer than the induction period at 44° C, so that a network, which was stable at 44° C, had already been formed. On heating to 44° C this network persisted.

The phenomenon that the curve for pre-ageing at 6.5° C, as shown in Fig. 8.13, crosses the other curves, is not yet elucidated. It is remarkable that also the curve for 11.8° C tends to cross that for 17.4° C. In other words, the question arises why in Fig. 8.12 a maximum occurs. In contrast to what has been said before, nucleation may play an important role at higher temperatures. It is clear that, for the understanding of the curves in the Figs. 8.12 and 8.13, a systematic investigation of this possibility is necessary. A gelatin concentration of 5% will be more appropriate for this investigation than a concentration of 2% as, with higher concentrations, the ideality of the network will be better.

Finally, some remarks will be made about the results of the calculation of the heat of cross-linking in Section 8.1.3. In the foregoing it was advocated that, with decreasing temperatures, smaller structures will become stable. In determining the heat of reaction use has been made of the change of the maximum gelation temperature with the concentration. However, with the maximum gelation temperature also the extensiveness of the structures will change. Moreover, above the maximum gelation temperature also structures will be present. Their dimensions will be larger than those of the structures that are stable at and below the maximum gelation

temperature. However, their number is too small to enable gelation. Hence, the melting point of a gel to a sol is not the temperature where all structures will disappear. ΔH^{O} is the heat of formation of those structures, that are stable at the maximum gelation temperature (see also refs. 26-28). POURADIER (29) calculated ΔH , which corresponds to our $\Delta H^{0}/(\frac{1}{2}f - 1)$, with the aid of the temperature dependence of the shear modulus, as was shown by ELDRIDGE and FERRY (1). He found values varying from -20 kJ/mol at low temperatures to -250 kJ/mol at high temperatures. The phenomenon, that at low concentrations intramolecular cross-linking plays an important role, has also to be taken into account. As a consequence of intramolecular cross-linking, the maximum gelation temperature (and also the melting temperature) will have lower values than those to be expected from the total cross-link density (if this quantity would be known). Hence, the results in Table 8-I will be too low. This inaccuracy will become more important with lower concentrations. As a consequence, the value of $-\Delta H^{O}$ will be larger than 442 kJ/mol and, as a consequence, the number of windings will be larger than 24. Accurate measurements of the maximum gelation temperature and/or the melting temperature, which are useful for the determination of the heat of reaction, have therefore to be taken at concentrations of at least 5%.

From the Figs. 8.14 and 8.15 it becomes obvious that, after a temperature increase, approximately 150 h will elapse before all non-stable crystallites have disappeared: in fact, the difference between the storage modulus measured after an increase of the temperature to a certain value and the storage modulus obtained with plain ageing at this value of the temperature, only disappears after 150 h. This means that the real metling temperature of a gelatin gel can only be measured, if each of many samples, which are aged in the same way, is heated to a constant specific temperature and kept at this temperature during a long time (e.g. 150 h). In this way the melting temperature can probably be encircled. The usual methods of heating, -say- with 10° C per h or even slower, will yield too high values for the real melting temperature of the gel (not for all structures present in the system). What the consequence of this wrong determination of the melting temperature is on the value of ΔH° is difficult to anticipate.

One final remark has to be made, however: it is difficult to understand that a melting process takes 150 h, especially if the liquid phase

is present. We have to conclude that also a reorganization takes place, which causes a decrease of the number of elastically effective cross-links. It is probably not possible to distinguish between the two processes only with the aid of dynamic mechanical measurements. For this purpose other techniques will have to be used, like optical rotation, light scattering etc.

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GENERAL CONCLUSIONS

Ageing of gels can be studied in a very accurate way by the determination of the changing viscoelastic properties. In fact, the viscoelastic behaviour of these gels depends strongly on the degree of ageing. As a consequence, small differences in the ageing process can be determined.

For the purpose of the determination of the viscoelastic properties the measurement of the dynamic moduli is very appropriate, as for this measurement only small and continuously oscillating deformations are needed. Hence, the process of building up of the network will be hardly affected by this way of determination of the viscoelastic properties. Moreover, the measurement can be very fast, so that the network structure is hardly changed during the duration of the experiment.

Stress relaxation and creep experiments do not furnish these advantages. These techniques are not appropriate for the study of an ageing process, in particular since during a measurement the response on a constraint will be determined strongly by the continuous building up of the network structure.

It can be concluded from the study described in this thesis that much information on the kinetics of the ageing process and the structure of PVCand gelatin gels is obtained, merely by the measurement of the viscoelastic properties. However, in order to go into detail, additional measurements with other techniques have to be taken. In our laboratory SAXS (small angle X-ray scattering) measurements on PVC-gels were taken. In this way valuable information is obtained, by which the understanding of the ageing process can be deepened considerably. In our laboratory additional measurements on gelatin gels have not yet been made, but SAXS and ORD (optical rotation dispersion) are taken into consideration.

From the described investigations similarities between the ageing processes of PVC-gels and gelatin gels appear to exist: the storage modulus becomes, after a starting period, a linear function of the logarithm of the ageing time. This phenomenon points to a secondary crystallization process, in other words, to a growth of crystallites that are formed during the starting period.

On the other hand, also considerable differences in the ageing

behaviour are found: for PVC-gels, pre-ageing at a higher temperature has a retarding effect on the excess-ageing at a lower temperature, whereas, for gelatin gels, the same treatment has an accelerating effect on the excessageing at a lower temperature. As a consequence, plasticized polyvinyl chloride can be processed in such a way, that it is more durable, i.e. less liable to ageing. This means that it must be possible to make use of a cheaper, but less efficient plasticizer. For that purpose the extruded or calendered product has to be conditioned during a certain time at a temperature well above the temperature of the maximum rate of ageing, before it is cooled to room temperature. No further argument is needed that for this purpose the optimum processing conditions must separately be determined for each PVC/plasticizer system. Also advantages may be taken from the accelerating influence of pre-ageing at a higher temperature on the excess-ageing process of gelatin gels at lower temperatures. These gels can be stiffened more quickly by conditioning the gelatin solutions at room temperature before cooling them to a lower temperature. Admittedly, subsequent heating to room temperature will produce a gel of lower stiffness. However, the previous stiffening process can be made irreversible by chemical crosslinking or by evaporation of the solvent.

SUMMARY

In this thesis a description is given of an investigation into the physical ageing of gel forming polymer solutions. In the course of this investigation their time dependent viscoelastic properties were measured at various, sometimes changing, temperature levels. In this study 10%-solutions of polyvinyl chloride (Solvic 239; $\overline{M}_w = 240000$) in the plasticizers DPB (i.e. di(n-butyl)phthalate), DOP (i.e. di(2-ethylhexyl)phthalate) and Reomol (i.e. the trimellitic ester of a mixture of branched alcohols) and 1-5% aqueous gelatin (Gelatine Delft NV; $\overline{M}_w = 70000$) solutions were investigated.

In Chapter 1 after a short introduction a review is given of the history and of the properties of polyvinyl chloride and gelatin as far as they are relevant to this thesis. The chapter is concluded by a survey of the used materials and the preparation of the solutions.

In Chapter 2 a short review of linear viscoelasticity is given.

In Chapter 3 the dynamic viscometer is described. This apparatus is designed particularly for the purpose of the investigation of the ageing process of gels. However, it is also useful for the determination of the viscoelastic properties of polymer melts. With this apparatus the dynamic moduli can be determined very accurately in a range of about 8 decades $(-2 \leq \log G' \leq 5.7 \text{ and } -3 \leq \log G'' \leq 5.8; \text{ G'} \text{ and G''} \text{ in N/m}^2)$ and in a frequency range of 6 decades $(-3.3 \leq \log \omega \leq 2.7; \omega \text{ in rad/s})$. Results are shown of measurements on a silicon oil (with loss angles which deviate only little from 90°), on a gel of polyvinyl chloride in Reomol (with loss angles deviating only little from 0°) and on a polystyrene melt for which, at low frequencies, the dependencies of the storage and loss moduli on the frequency are guadratic and linear, respectively.

In Chapter 4 the phenomenology of the ageing process of 10%-solutions of PVC in the three plasticizers is described. In these plasticizers the ageing rate of PVC increases in the sequence DBP, DOP, Reomol. If the storage modulus G' is plotted against the logarithm of the ageing time,

 t_a , a curve is obtained which becomes, after a starting period, a straight line. The slope of this linear region, dG'/d log t_a , which is independent of the frequency but strongly dependent on the temperature, is called "rate of ageing". The rate of ageing plotted against the ageing temperature yields a curve which closely resembles a crystallization curve of crystallizable polymers with a maximum rate half-way between the glass transition temperature and the melting temperature. In the course of time the character of the curve describing the storage modulus as a function of the frequency changes from liquidlike to rubberlike. The loss modulus shows a minimum in the rubbery region, which points to a maximum at lower frequency. However, this maximum could only be measured after the application of a special ageing technique, by which this maximum was shifted to a higher frequency, within the frequency range of the dynamic viscometer. The maximum in the loss modulus is accompanied by a decrease of the storage modulus from one rubber plateau to another rubber plateau.

By a special extrapolation method the time-temperature superposition principle could be applied also to these fast ageing systems. The calculated values of the constants c_1^g , c_2^g , α_f and f_g are well in agreement with the values which are known for polymers.

Calculation of the loss compliance from the dynamic moduli yields a curve with a maximum value in the low frequency region of the glass-rubber transition. This maximum points to the presence of an infinite network. It decreases with increasing degree of ageing and, at the same time, shifts to higher frequencies.

The reduced logarithmic spectrum of relaxation times shows a slope $-\frac{1}{2}$ in the glass-rubber transition and is, in this region, independent of the degree of ageing. Distinctions are only obtained for relaxation times longer than 1 sec., i.e. in the rubbery region of these systems.

In Chapter 5 some molecular parameters are calculated: \bar{M}_c , the number average molecular weight between cross-links, and ζ_o , the monomeric friction coefficient. ζ_o is calculated from the relaxation spectrum, according to ROUSE's theory, as well as from the maximum of the loss compliance and its location on the frequency scale, according to BUECHE's theory, as modified for the gels described in this thesis. The values of ζ_o calculated in both ways are in agreement within their standard deviations.

In the Appendix of this chapter it is shown that the relationship

between the cross-linking index (i.e. the mean number of cross-links per primary polymer molecule) and the solfraction of the gel, as derived by FLORY for tetrafunctional cross-links, can be applied also to gels in which multifunctional cross-links are formed by crystallites.

In this way it was also possible to calculate the solfraction, the fraction of dangling ends and the fraction of ideal network as a function of the degree of ageing.

In Chapter 6 the network growth in PVC/plasticizer systems is examined more in detail. The kinetics of ageing are examined more closely. It can be concluded that crystallites which are mainly formed in the beginning of the ageing process, grow in one dimension.

Also the kinetics of the excess-ageing which occurs after pre-ageing at a higher temperature, are described. It appears that this pre-ageing causes a retardation of the excess-ageing at lower temperatures. It is possible to separate the effect of an ageing process which is started at a higher temperature and continues at a lower temperature, from the contribution of an ageing process started by renewed nucleation at the lower temperature level.

Excess-ageing at higher temperature after pre-ageing at lower temperature causes an immediate melting of those crystallites that are unstable at the higher temperature. This becomes apparent from a quick initial decrease of the storage modulus. After the melting of unstable crystallites a recrystallization process takes place, by which entrapped entanglements are formed. This recrystallization process is the origin of a second rubber plateau.

In Chapter 7 the phenomenology of the ageing process of 2-5% aqueous gelatin solutions is described. The rate of ageing, dG'/d log t_a , of a 2%-solution appears to be almost independent of the temperature. The frequency dependence of the storage modulus is negligibly small: already in the beginning of the ageing process, immediately after the induction period, the course of the storage modulus with frequency is nearly horizontal. The loss angle is very small, so that the measurements of the loss modulus are not very accurate in most cases.

Pre-ageing at a higher temperature has a strongly accelerating influence on the excess-ageing at lower temperatures.

In Chapter 8 the network growth of aqueous gelatin gels is examined more closely. The maximum gelation temperature, the gel temperature, increases with increasing concentration. The method of ELDRIDGE and FERRY for the determination of the heat of reaction of the ageing process as caused by tetrafunctional cross-linking, is applied in a modified way to the hexafunctional cross-linking in gelatin gels. For the heat of renaturation a value of $\Delta H = -442$ kJ per mol of cross-links was found.

The concentration dependencies of the storage modulus as well as of the rate of ageing appear to be quadratic.

The influence of the thermal history on the excess-ageing of gelatin gels is considerable. Analysis of the measuring results shows that the energy of activation of the rate determining step in the ageing process is small. The temperature dependence of the degree of ageing is not caused by temperature variation of the reaction rate constant, but by the increase in stability of small structures which accompanies a decrease in temperature.

As a general conclusion it can be mentioned that the determination of the viscoelastic behaviour is a proper way in order to investigate the ageing process of gels. In fact, small differences in the system can be of considerable influence on the viscoelastic behaviour. For the purpose of the determination of the viscoelastic properties the dynamic mechanical method is most useful. In fact, small oscillatory deformations do not interfere with the growth of the network structure. Even rather fast changes of viscoelastic properties can be followed adequately by this technique.

SAMENVATTING

In dit proefschrift wordt beschreven het onderzoek naar de verandering met de tijd en de temperatuur van de visco-elastische eigenschappen van fysisch verouderende, gelvormende polymeeroplossingen. Onderzocht zijn 10%-oplossingen van PVC (Solvic 239, \overline{M}_{W} = 240000) in de weekmakers di-(n-butyl)ftalaat (DBP), di-(2-ethylhexyl)ftalaat (DOP) en de trimellietzure ester van een mengsel van vertakte alcoholen (Reomol) en 1-5%-oplossingen van gelatine (Gelatine Delft NV, \overline{M}_{W} = 70000) in water.

In Hoofdstuk 1 wordt na een korte inleiding een overzicht gegeven van de historie en de voor dit proefschrift relevante eigenschappen van polyvinylchloride en gelatine. Het hoofdstuk wordt afgesloten met een overzicht van de gebruikte stoffen en de bereiding van de oplossingen.

Hoofdstuk 2 geeft een kort overzicht van lineaire viscoelasticiteit.

In Hoofdstuk 3 wordt de dynamische viscosimeter beschreven. Dit apparaat is speciaal ontworpen voor het verouderingsonderzoek van gelen, maar is ook geschikt voor het onderzoek van gesmolten polymeren. De dynamische moduli kunnen met dit apparaat zeer nauwkeurig worden gemeten in een gebied van ca. 8 decaden (-2 \leq log G' \leq 5.7 en -3 \leq log G" \leq 5.8; G' en G" in N/m²) in een frequentiegebied van 6 decaden (-3.3 \leq log $\omega \leq$ 2.7; ω in rad/s). Gepresenteerd worden resultaten van metingen aan een siliconenolie (met verlieshoeken die maar weinig afwijken van 90°), aan een gel van PVC in Reomol (met verlieshoeken die maar weinig afwijken van 0°) en aan een gesmolten polystyreen, waarvoor bij lage frequenties de opslagmodulus resp. de verliesmodulus een functie is van de tweede resp. eerste macht van de frequentie.

In Hoofdstuk 4 wordt de fenomenologie van de veroudering van 10%-oplossingen van PVC in de drie weekmakers beschreven. Gebleken is dat de verouderingssnelheid van PVC-gelen in de weekmakers DBP, DOP, Reomol toeneemt in de volgorde, waarin de weekmakers vermeld staan. De verouderingssnelheid, gedefiniëerd als dG'/d log t_a, uitgezet tegen de verouderingstemperatuur, levert een curve, die sterke overeenkomst vertoont met kristallisatiesnelheidscurve van polymeren. Naarmate de tijd vordert, verandert het verloop van de opslagmodulus met de frequentie van vloeistofachtig in rubberachtig. De verliesmodulus vertoont in het rubbergebied een minimum, hetgeen wijst op een bij nog lagere frequenties voorkomend maximum. Dit maximum kan met de gebruikte apparatuur worden gemeten door een speciale verouderingstechniek toe te passen, waarbij het maximum in de verliesmodulus naar hogere frequenties verschuift. Ter plaatse van dit maximum daalt de opslagmodulus van het ene rubberplateau naar een ander rubberplateau.

Met een speciale extrapolatie-methode blijkt het mogelijk het tijdtemperatuur-superpositiebeginsel ook op deze snel verouderende systemen toe te passen. De berekende waarden van c_1^g , c_2^g , α_f en f zijn goed in overeenstemming met de voor polymeren bekende waarden.

Berekening van de verliescompliantie uit beide dynamische moduli levert een maximum op in het laagfrequente gedeelte van de glas-rubberovergang, hetgeen op de aanwezigheid van een netwerk wijst. Dit maximum neemt met toenemende veroudering af en verschuift daarbij naar hogere frequenties.

Het uit de beide moduli berekende logarithmische relaxatietijdenspectrum vertoont in het glas-rubberovergangsgebied een helling $-\frac{1}{2}$ en is in dit gebied vrijwel onafhankelijk van de mate van veroudering. Verschillen worden pas verkregen bij relaxatietijden groter dan 1 sec.

In Hoofdstuk 5 worden enkele moleculaire parameters berekend: \overline{M}_{c} , de aantal gemiddelde moleculaire massa tussen knooppunten, en ζ_{o} , de monomere wrijvingscoëfficiënt. Deze laatste grootheid is berekend uit het relaxatie-spectrum volgens de theorie van ROUSE en ook volgens de, voor de in dit proefschrift beschreven gelen gewijzigde, theorie van BUECHE, waarvoor gebruik gemaakt wordt van de hoogte van het maximum in de verliescompliantie en van de frequentie, waarbij dit maximum optreedt. Beide waarden zijn binnen de standaarddeviaties met elkaar in overeenstemming.

In de Appendix van dit hoofdstuk wordt aangetoond dat het door FLORY voor tetrafunctionele knooppunten afgeleide verband tussen de knooppuntenindex en de solfractie van gelen ook van toepassing is op gelen waarin de knooppunten gevormd worden door multifunctionele kristallieten. Op deze wijze is het ook mogelijk de solfractie, de fractie aan het netwerk bungelende uiteinden en de fractie ideaal netwerk te berekenen als functie van

de verouderingsgraad.

In Hoofdstuk 6 wordt nader ingegaan op de netwerkgroei in PVC/weekmaker-gelen. De kinetica van de veroudering wordt nader bestudeerd. Geconcludeerd wordt dat de - voornamelijk in het begin van het verouderingsproces gevormde - kristallieten eendimensionaal uitgroeien.

Ook wordt de kinetica van de veroudering na voorafgaande veroudering bij hogere temperatuur beschreven. Het blijkt dat de voorveroudering vertragend werkt op de naveroudering. Op het verouderingsproces, dat bij hoge temperatuur gestart is en bij lagere temperatuur wordt voortgezet, wordt een verouderingsproces, dat het gevolg is van de door de afkoeling nieuw gevormde kiemen, gesuperponeerd. Het is mogelijk de gevolgen van beide verouderingsprocessen door middel van een berekening van elkaar te scheiden.

Naveroudering bij hogere temperatuur na voorafgaande veroudering bij lagere temperatuur doet eerst die kristallieten smelten, die instabiel zijn bij de hogere temperatuur. Dit uit zich in een snelle afname van de opslagmodulus. Daarna vindt er een rekristallisatieproces plaats, waarbij ingesloten warpunten gevormd worden. Dit rekristallisatieproces is de oorzaak van een tweede rubberplateau.

In Hoofdstuk 7 wordt de fenomenologie van de veroudering van 2-5%-gelatineoplossingen in water beschreven. De verouderingssnelheid, dG'/d log t_a, van een 2%-oplossing blijkt nagenoeg onafhankelijk te zijn van de temperatuur. De frequentie-afhankelijkheid van de opslagmodulus is verwaarloosbaar klein: reeds in het begin van de veroudering, direct na de inductieperiode, is het verloop van de opslagmodulus met de frequentie vrijwel horizontaal.

Voorveroudering bij een hogere temperatuur heeft een sterk versnellend effect op de naveroudering bij lagere temperatuur.

In Hoofdstuk 8 wordt de netwerkgroei van de gelatinegelen nader bestudeerd. De maximale temperatuur, waarbij nog gelering optreedt, blijkt toe te nemen met de concentratie. De methode van ELDRIDGE en FERRY voor de bepaling van de reactiewarmte van de veroudering door tetrafunctionele verknoping wordt in gewijzigde vorm toegepast voor de hexafunctionele verknoping in gelatinegelen. Gevonden wordt $\Delta H = -442 \text{ kJ/mol.}$

De concentratie-afhankelijkheid van zowel de opslagmodulus als de verouderingssnelheid blijkt kwadratisch te zijn.
Het effect van de thermische voorgeschiedenis van de gelatinegelen op de veroudering is zeer groot. Analyse van de meetresultaten toont aan dat de activeringsenergie van de snelheidsbepalende stap in het verouderingsproces klein is. Het verschil in mate van veroudering bij verschillende temperaturen wordt niet veroorzaakt door verschillen in de reactiesnelheidskonstante, maar door een toenemende mate van stabiliteit van kleine structuren,met afnemende temperatuur.

Als algemene conclusie kan genoemd worden dat voor het onderzoek van de veroudering van gelen de bepaling van de visco-elastische eigenschappen zeer geschikt is, omdat kleine veranderingen in het systeem van grote invloed kunnen zijn op het visco-elastisch gedrag. Voor de bepaling van de visco-elastische eigenschappen is de dynamisch mechanische methode de meest aangewezene omdat kleine oscillerende deformaties de opbouw van de netwerkstructuren niet zullen beïnvloeden. Bovendien kunnen ook relatief snelle veranderingen van de visco-elastische eigenschappen met deze techniek gevolgd worden.

LIST OF SYMBOLS

a ~	stiffness parameter		
a _T	horizontal shift factor		
с	concentration		
co	concentration at reference temperature		
c_1^0, c_2^0	constants in the WLF-equation at temperature T		
c_1^g, c_2^g	constants in the WLF-equation at temperature T_{g}		
f	functionality of cross-links		
fg	fractional free volume at T		
g	numerical factor		
h	length of inner cylinder		
k	Boltzmann's constant		
	or constant in Avrami's equation		
m c 2	concentration of cross-links		
m	concentration of potential junctions		
n	constant in Avrami's equation		
t	time		
ta	ageing time		
tea	excess-ageing time		
tpa	pre-ageing time		
t	induction period		
wf	weight fraction of dangling ends in gel		
Wg	weight fraction of network in gel		
wm	weight fraction of ideal network in gel		
ws	weight fraction of sol in gel		
wz	weight fraction of giant polymer molecules consisting of		
	z primary polymer molecules		
В	numerical factor		
D ₁	torsion constant of the upper torsion wire		
D2	torsion constant of the lower torsion wire		
Е	apparatus constant, equal to $4 \pi h R_i^2 R_o^2 / (R_i^2 - R_o^2)$		
G	shear modulus		
G	equilibrium shear modulus		
G'	shear storage modulus		

G'r	reduced shear storage modulus	
G''	shear loss modulus	
G''	reduced shear loss modulus	
G*	complex dynamic shear modulus	
G(t)	shear relaxation modulus	
Η(τ)	shear relaxation time spectrum	
$\triangle H^{O}$	heat of reaction for breaking a cross-link in potential junctions	
I	moment of inertia	
M _c	number average molecular weight between two cross-links	
м _е	number average molecular weight between two entanglements	
Mo	molecular weight of a monomer unit	
M _n	number average molecular weight	
M _w	weight average molecular weight	
NA	Avogadro's number	
Р	probability	
R	gas constant	
R	radius of the inner cylinder	
R	radius of the outer cylinder	
Т	absolute temperature	
То	reference temperature	
Tg	glass-transition temperature	
Tm	melting temperature	
а	ageing temperature	
т ра	pre-ageing temperature	
Tea	excess-ageing temperature	
Z	number of monomer units between two cross-links	
C		
α	thermal expansion coefficient or	
	mass fraction of crystallites in Avrami's equation or	
	number of polymer molecules in a junction	
α _f	thermal expansion coefficient of free volume	
γ	shear deformation or	
	width of light spot or	
	cross-linking index	
Υ _o	constant shear deformation or	
	amplitude of sinusoidally varying shear deformation	

8	loss angle			
ε	angle of shear deformation or			
	correction term for the presence of entanglements			
Eao	angular amplitude of the driving shaft			
ε _{co}	angular amplitude of the inner cylinder			
ζ.	monomeric friction coefficient			
η	shear viscosity			
η _s	solvent shear viscosity			
λ	wave length of shear wave in a viscoelastic medium			
ν	frequency or			
	number of potential junctions in a primary polymer molecule or			
	number of elastically effective network chains			
ρ	density or			
	probability that in an arbitrary polymer molecule a junction			
	is present			
σ	shear stress			
σ	constant shear stress or			
0	amplitude of sinusoidally varying shear stress			
τ	relaxation time			
φ	phase angle or			
	volume fraction of polymer			
ω	angular frequency			
ω	angular eigenfrequency			

Curriculum Vitae van Klaas te Nijenhuis

1939			geboren te 's-Gravenhage
1956			eindexamen HBS-B, Chr. Lyceum "De Populier"
			te 's-Gravenhage
1956	-	1962	analist Chemisch Laboratorium RVO-TNO, te Rijswijk Z.H.
1959	-	1961	militaire dienst
1962	-	1966	scheikundestudie TH Delft
1966	-	heden	wetenschappelijk medewerker TH Delft

STELLINGEN

- De bepaling van adsorptie/desorptieisothermen van poreuze adsorbentia met behulp van een adsorptiebalans, zoals bijvoorbeeld door Okkerse beschreven, kan slechts dan nauwkeurige resultaten opleveren als de stappen in de relatieve dampdruk klein genoeg zijn.
 C. Okkerse, proefschrift Delft, 1961
- 2 Bij zijn berekening van de kristalliniteit van polyvinylchloride heeft Juijn ten onrechte geen rekening gehouden met de massa van de regelmatige sequenties. Een verbeterde berekening voert voor polyvinylchloride met 55% syndiotactische sequenties tot een drie maal hogere kristalliniteit.

J.A. Juijn, proefschrift Delft, 1972

3 De onbevredigende resultaten van de berekening van het relaxatiespectrum van polymeren, zoals uitgevoerd door Chömpff, zijn een gevolg van een onjuiste toepassing van de reeks van Sturm. Aanpassing van het door hem gebruikte rekenprogramma aan de lage δ waarden voert tot een spectrum dat meer overeenkomt met de werkelijkheid.

A.J. Chömpff, proefschrift Delft, 1965

4 De alkalisch gekatalyseerde methanolische omestering van polyvinylacetaat in polyvinylalcohol is een veel snellere reactie dan de resultaten van Joshi en Pritchard doen vermoeden.

D.P. Joshi, J.G. Pritchard, Polymer 19, 427 (1978).

Resultaten onderzoek in het project 23 "Polymeren" in het 2e-jaars practicum in de opleiding voor Scheikundig Ingenieur aan de Technische Hogeschool Delft. Ten behoeve van de functionalisering van onoplosbaar polystyreen dient bij de bereiding ervan door copolymerisatie niet meer dan 4% divinylbenzeen aan styreen te worden toegevoegd.

Resultaten onderzoek in het project 41 "Functionalisering van Polymeren" in het 2e-jaars practicum in de opleiding voor Scheikundig Ingenieur aan de Technische Hogeschool Delft.

Door een warmtebehandeling van het reactieprodukt van $Al(C_{2}H_{5})_{3}$ en 6 TiCl_{A} wordt de β -modificatie van het ontstane kristallijne geëthyleerde TiCl, omgezet in de actievere α -modificatie. Deze modificatie voert tot een hogere stereospecificiteit van het polymerisatieproduct van propeen. De opbrengst aan polypropeen is echter dermate laag dat een dergelijke warmtebehandeling niet is aan te bevelen.

F.W. Breuer, L.E. Geipel, A.B. Loebel, Hoofdstuk 3 in R.A.V. Raff, K.W. Doak, Eds., Crystalline Olefin Polymers, Part I, Vol. XX van H. Mark, P.J. Flory, C.S. Marvel, H.W. Melville, Eds., High Polymers, Interscience Publishers, New York (1965).

Resultaten onderzoek in het project 44 "Isotactisch Polypropeen" in het 2e-jaars practicum in de opleiding voor Scheikundig Ingenieur aan de Technische Hogeschool Delft.

- In het visco-elastisch onderzoek van oplossingen van gelatine in water 7 wordt doorgaans te snel geconcludeerd tot een evenwichtswaarde van de relaxatiemodulus, met name in die gevallen waar de halfwaardetijd van de evenwichtsinstelling wordt bepaald. Dit proefschrift
- In tegenstelling tot wat gebruikelijk is bij de bereiding van gelatine-8 puddingen dient men de warme gelatine-oplossing (60°C) niet direct na de bereiding in de koelkast te plaatsen, doch pas als de oplossing enigszins is opgestijfd bij kamertemperatuur. Dit proefschrift

5

- 9 Teneinde de snelheid van de fysische veroudering bij kamertemperatuur van weekgemaakt polyvinylchloride sterk te verminderen, dient het door extrusie of kalanderen verkregen produkt een voorveroudering bij een temperatuur van bijvoorbeeld 100°C te ondergaan alvorens het tot kamertemperatuur af te koelen. Dit proefschrift
- 10 Het examen in de bijzondere onderwerpen in de opleiding voor Hogere Kunststoffentechnicus, uitgaande van de Stichting Opleiding Rubbers en Kunststoffen (SORK), dient mondeling te worden afgenomen.
- 11 Het uitdrukken van elasticiteitsmoduli in Pa in plaats van in N/m² is een oneigenlijk gebruik van het SI-stelsel.
- 12 In de Nederlandse Samenleving in het algemeen en aan de Technische Hogeschool Delft in het bijzonder is de daadwerkelijke belangstelling voor het studiowerk van de Nederlandse Blindenbibliotheek verontrustend gering.
- 13 Het onderwijs in en onderzoek aan kunststoffen is aan de Technische Hogeschool Delft van te geringe omvang en dient derhalve uitgebreid te worden.
- 14 De wijze waarop in de Gereformeerde Kerk in Nederland de viering van het Heilig Avondmaal heden ten dage veelal plaats vindt, noopt tot een spoedige beslissing tot de toelating van niet-belijdende doopleden.

28 augustus 1979

K. te Nijenhuis



The dynamic viscometer, as constructed by RODEM Instrumentenfabriek, Bilthoven, The Netherlands, after the prototype described in this thesis.



