

Series 07 Aerospace Materials 04

A New Method of Impregnating PEI Sheets for the *In-Situ* Foaming of Sandwiches

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I. Introduction

The sandwich panel, which combines a high bending stiffness with a low weight, is an important construction element. Applications of sandwich panels can be found not only in the aerospace industry but in any industry where structural weight is an important factor. A large percentage of these sandwiches consists of a honeycomb core and two aluminum or composite outer layers (facings). An improvement over the honeycomb sandwich is the use of a foam core which reduces the discontinuities.

During the last couple of years, sandwich panels with a foam core have been produced using an in-situ foaming technique that has been developed in the Structures and Materials Laboratory of Delft University of Technology¹. This is done by impregnating a polymer film with a solvent/blowing agent followed by heating. The thus obtained solvent impregnated film is allowed to expand under controlled conditions. The film is foamed and the bond between the core and the facings is created in one production step.

The aims of the present investigation were:

1. To develop practical impregnating and foaming procedures.
2. To describe the foaming process in terms of the process variables.
3. To predict the properties of the polymer foams.
4. To study the adhesion between the foam core and the facings.
5. To find an alternative blowing agent for polyetherimide (PEI).

Until now most experience has been gained using the thermoplastic PEI and the solvent/blowing agent methylene chloride (MC)². As MC is highly toxic, carcinogenic for animals³ and possibly carcinogenic for humans^{4,5}, the fifth aim is concentrated upon.

An attempt to find another chemical blowing agent, (i.e. a blowing agent that produces a gas as a result of a chemical reaction) has previously been made in the Structures and Materials Laboratory. The research as described in this report will concentrate on finding another physical blowing agent (i.e. a blowing agent that changes from liquid to gas phase). Although there are some physical blowing agents that can produce a sandwich with a high quality foam, they all have the drawback that they are flammable⁶.

One of the main problems for the production of a foam is the impregnation of the polymer film with the blowing agent. A new method has been developed to solve this problem. It consists of immersing the film in a swelling agent. When the film has swollen to the maximum volume, the film is immersed again in another liquid, thereby replacing the swelling agent by the other liquid. The film is then ready to be foamed between two facings, thus producing a sandwich.

In the second chapter the theoretical aspects of polymer solutions will be discussed. In the third chapter the experimental set-up will be described, followed by the results in the fourth chapter. Subsequently the results will be discussed. Finally, the conclusions will be drawn in chapter 6.

II. Theory of Polymer Solutions

A new method of impregnating a polymer film with a blowing agent consists of the following steps:

1. Swelling the polymer.

2. Replacing the swelling agent with a liquid blowing agent.

There are three processes involved: the swelling, the replacement of the swelling agent by the blowing agent and possibly the relaxation of the swelling. The first two processes are described below. If a relaxation of the swollen polymer takes place, it occurs on such a large time scale that it is of no practical interest. Therefore it will not be described.

Polymer-Liquid Interaction Parameter

An elaborate overview of the thermodynamics of polymer solutions has been given by Kamide⁷. Here some of the relevant aspects will be described.

P.J. Flory^{8,9} and M.L. Huggins¹⁰ developed a lattice model in which the mixing of a polymer and a solvent is described. They introduced the dimensionless interaction parameter χ which can be written as follows:

$$\chi = \frac{\mu_1 - \mu_2}{RT\phi_2^2} - \frac{\ln\phi_1 + (1 - \frac{1}{r})\phi_2}{\phi_2^2} \quad (1)$$

where μ (J $^{-1}$ mol⁻¹) is the chemical potential, R is the gas constant (=8.3144 J $^{-1}$ mol⁻¹ $^{-1}$ K⁻¹), T is the temperature (K), ϕ is the volume fraction and r is the number-average degree of polymerization. The subscripts refer to the solvent (1) and the polymer (2). The interaction parameter is composed of one term that describes the non-combinatorial free energy of interaction χ_H and one that describes the excess entropic interactions χ_S :

$$\chi = \chi_H + \chi_S \quad (2)$$

The interaction parameter gives a measure of the specific interactions in a polymer-liquid system relative to the assumed lattice model. For values of χ below a certain critical value, the polymer and liquid are miscible in any proportion. To obtain this value, equation 1 can be rewritten as a function of $\mu_1 - \mu_1^0$ (where μ_1^0 is the chemical potential of the pure solvent) and differentiated. This results in the critical value for the interaction parameter:

$$\chi_c = \frac{1}{2} \sqrt{1 + \frac{1}{\sqrt{r}}} \quad (3)$$

For polymers with long chains χ_c is equal to 0.5. This means that a polymer is soluble in a liquid if χ is less than 0.5. If χ is somewhat larger than 0.5, swelling of the polymer will occur. For the equilibrium between a polymer and the vapor of a solvent, the following holds true:

$$\ln\left(\frac{p}{p_0}\right) = \ln(1-\phi_2) + \phi_2 + \chi\phi_2^2 \quad (4)$$

where p is the vapor pressure and p_0 is the saturated vapor pressure. This relationship is illustrated for a saturated vapor pressure in Figure 1.

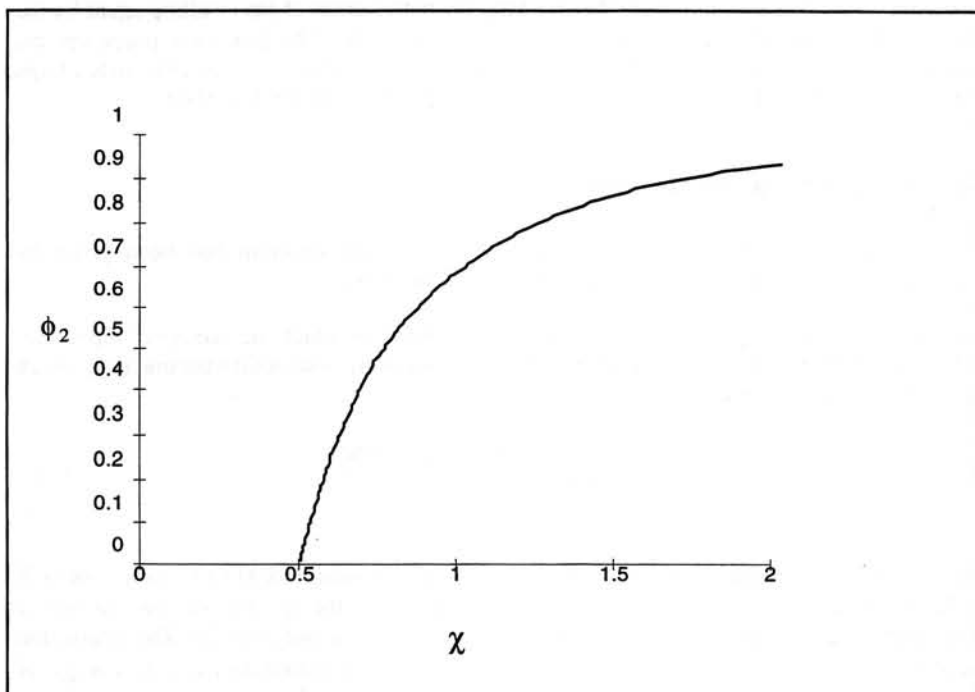


Figure 1 Polymer volume fraction as a function of the interaction parameter at saturated vapor pressure

The Solubility Parameter

J.H. Hildebrand and R.L. Scott¹¹ defined a cohesion parameter (the solubility parameter δ) that describes the interaction between two components. Later C. Hansen¹² proposed a three component parameter that consists of a dispersion component of the intermolecular forces, a polar component and a hydrogen-bonding component. Whereas χ has to be determined for each polymer-liquid pair, the interaction can be described using cohesion parameters that are specific for each component individually. For a given system there is a relationship between the enthalpic component of the interaction parameter and the solubility parameters:

$$\chi_H = \frac{V}{RT} (\delta_1 - \delta_2)^2 \quad (5)$$

where v ($\text{m}^3 \text{mol}^{-1}$) is the specific volume of the solvent. Using the literature values of δ ($\text{MPa}^{1/2}$), χ_H could be calculated.

According to the equation presented above, swelling of polymers (χ slightly larger than 0.5) could be predicted if χ_S were known. The value of χ_S is often considered to be 0.3, but can vary¹³ between 0 and 2.5. Furthermore, χ is not constant, but depends on polymer concentration and molecular weight¹⁴. This means that it is not possible to predict swelling agents using theoretically calculated values of the interaction parameters. Experiments should be performed to obtain accurate values of χ . If experiments must be performed anyhow, it would be less time consuming to test for swelling directly. Prior to these tests, values of δ can be used to indicate possible swelling agents.

Diffusion

The simplest mathematical model of diffusion is based on the assumption that the number of molecules diffusing through a surface is proportional to the concentration gradient perpendicular to that surface:

$$\Phi = -D \frac{\partial C}{\partial x} \quad (6)$$

where Φ ($\text{g m}^{-2} \text{s}^{-1}$) is the mass flux, D ($\text{m}^2 \text{s}^{-1}$) is the diffusion coefficient, C (g m^{-2}) is the concentration and x (m) is the space coordinate perpendicular to the surface. Together with the mass balance this leads to

$$\frac{\partial C}{\partial t} = D \frac{\partial^2 C}{\partial x^2} \quad (7)$$

where it was assumed that D is independent of the concentration. To calculate the concentration $C(x,t)$ in a semi-infinite medium with $C(x,0)=0$ for $x > 0$, bounded by a constant concentration $C(0,t)=C_0$ equation 7 can be solved¹⁵ which results in a weight increase proportional to \sqrt{t} . For a film with diffusion from both sides the \sqrt{t} proportionality holds true until the penetrant fronts meet, at which point the mass uptake will slow down until equilibrium has been reached. To calculate the diffusion out of a film, equation 7 can be solved with $C(0,t)=0$, $C(l,t)=0$ and $C(x,0)=C_0$ for $0 < x < l$ where l is the thickness of the film. The total concentration can then be written as

$$C = \frac{8C_0}{\pi^2} \sum_{n=0}^{\infty} \frac{1}{(2n+1)^2} e^{-\frac{D(2n+1)^2\pi^2 t}{4l^2}} \quad (8)$$

Case II Sorption

Often the diffusion coefficient is not independent of the concentration. An experimentally observed case, where the weight increase rate is constant until equilibrium has been reached, is called Case II Sorption¹⁶. The factor that determines the rate of diffusion is the mechanical viscous resistance to a change in volume. Once the volume of an element in the medium has been increased, the diffusion through it takes place immediately. The Case II Sorption process has been described extensively for methylene chloride and PEI¹⁷.

III. Materials and Methods

To investigate the possibility of using different blowing agents for the in-situ foaming process, PEI samples were swollen with acetone. The samples were then placed in a bath with another liquid. Two methods were used to determine if any diffusion had taken place: weighing and the radiotracer method. The impregnated PEI films were used for foaming and mechanical properties of the produced sandwich panels were tested.

Materials

The amorphous thermoplastic polyetherimide (PEI) is a polymer based on repeating ether and imide linkages as can be seen in Figure 2. Some relevant properties can be found in the following table¹⁸:

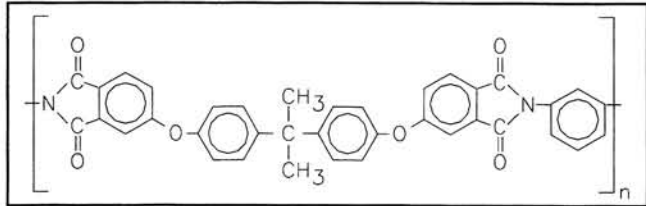


Figure 2 Structure formula of polyetherimide

Table 1 Polyetherimide properties

property	value	unit
glass transition temperature	219	°C
tensile strength, yield	105	MPa
compressive strength	140	MPa
water absorption at 22°C (equilibrium)	1.25	%
solubility parameter ¹⁹	21.5	MPa ^{1/2}

All PEI films used were based on Ultem 1000, a PEI produced by General Electric Plastics. The same company produced films with thicknesses of 50 and 250 µm. The 135 µm films (Litrex) were made by PCD in Austria.

The prepreg consisting of an E-glass 8H-satin weave impregnated with PEI was supplied by Nijverdal-Ten Cate.

The following liquids were used: Ultima Gold scintillation liquid, methylene chloride (CH₂Cl₂), 1,1,1-trichloroethane (CH₃CCl₃), ethanol (C₂H₅OH), N-methyl pyrrolidone (C₅H₉NO) and acetone (CH₃COCH₃) including acetone-2-¹⁴C, 1.85 MBq, 2.4 · 10⁸ Bq/mmol supplied by Sigma Chemical Company.

Methods

Weighing

The weighing procedure was as follows: PEI films with dimensions between 25 and 100 cm² were taken out of the bath and were dried on the outside with a Kleenex towel. They were then placed on a balance and exactly 30 seconds after they were taken out, the weight was determined. Samples taken out of the bath were not used again.

Spot Test

To determine if any acetone was transferred from the PEI to a bath containing another liquid, spot tests were performed. The method used to detect acetone with salicylaldehyde and sodium hydroxide is described in Spot Tests in Organic Analysis²⁰.

Acetone ¹⁴C tests

To determine the amount of acetone present in PEI films, the films were swollen with acetone containing ¹⁴C labeled acetone as radiotracer. This radionuclide ¹⁴C has a half-life of 5730 years and emits β^- -radiation with a maximum energy of 156 keV. The long half-life guarantees a constant activity during the experiments.

Acetone-2-¹⁴C with an activity of 1.85 MBq was diluted with acetone to 20 ml. Several 5

μ l samples were taken and transferred to a counting vial containing 2 ml Ultima Gold and a PEI film dissolved in N-methyl pyrrolidone (NMP). The 50 μ m PEI films (1.5 x 3.5 cm²) were dissolved in 2 ml of NMP, the others in 6 ml. After waiting several hours to rule out chemical luminescence, the activity of the content of the vials was determined by liquid scintillation counting, providing a calibration for the amount of acetone.

The setup that was used consisted of two vessels with a volume of 20 ml, of which one was kept at a constant temperature of 20°C by circulating water around it, connected by two closable tubes. The whole setup could be rotated about a horizontal axis in order to let the liquid flow from one container to the other. The PEI samples were weighed and placed in the empty container while the labeled acetone remained in the reservoir. After closing the vessel, the valves were opened and the system was rotated to allow the acetone to flow from the reservoir. The samples were then kept in the acetone bath for a period that was longer than was needed to reach equilibrium absorption of acetone. The acetone could then be transported back to the reservoir and after closing the valves a sample could quickly be moved to a bath containing the second liquid. This bath, which was renewed after one to four samples, was also kept at 20°C. For the measurements where the second bath contained water of 80°C, the films were taken directly out of the acetone. After taking a film out of the second bath, it was put in a bottle containing NMP. When the film had dissolved 2 ml Ultima Gold was added. After several hours the activity of the content of the bottle was determined by liquid scintillation counting and subtracting the background.

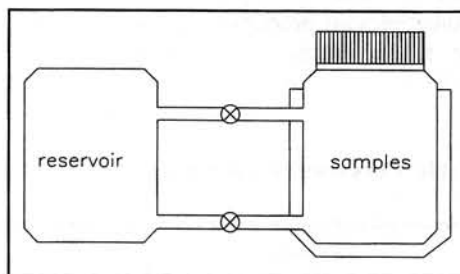


Figure 3 Experimental setup.

The fact that some points in Figure 6 suggest a higher concentration of acetone than can be expected from the other measurements can be explained by the following. When a film of PEI is taken out of the second bath it is quickly transferred to a bottle with solvent for liquid scintillation counting. Care is taken to ensure that no drops remain attached to the film. However, it is not always possible to do so, as the acetone evaporates quickly and the film must be transferred as rapidly as possible.

Foaming

The apparatus that was used to foam the samples consisted of two press plates (25 cm x 25 cm) that were built into a computer controlled hydraulic fatigue machine (Figure 3). The plates could be heated to a set temperature and cooled by manually opening two valves allowing tap water to flow through the plates. Parameters like pressure, opening rate and opening distance were controlled by computer.

The method used for fabricating a sandwich by in-situ foaming of a polymer consists of the following steps:

- Several impregnated films were put between two layers (facings) of consolidated prepreg of glass/PEI.
- The package was put in a preheated press and pressure was applied quickly.
- When the temperature is constant and homogeneous, the press was opened at a constant speed.
- After reaching the final distance, the press plates were cooled to room temperature, while they were left opened to the final distance.
- The sandwich was dried in an oven.

Mechanical Properties

The tensile and compression tests were performed according to ASTM C 297-61 and ASTM C 365-57 (method A) respectively on a Zwick 2T machine. The tests were performed on samples of about 2500 mm² with a test speed of 1 mm/min.

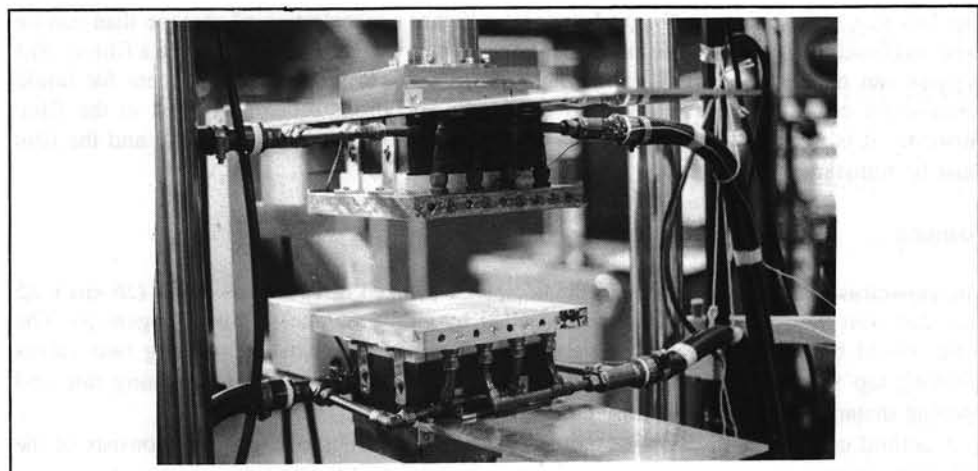


Figure 4 The press in which the foaming took place.

IV. Results and Discussion

The Swelling Agent

By performing weighing measurements, several liquids were found to be swelling agents for PEI. An overview is given in the following table:

Table 2 Swelling agents

swelling agent	solubility parameter (MPa ^{1/2}) ²¹	equilibrium weight fraction (%)
acetone	20.3	20
methyl ethyl ketone	19.0	22
methyl acetate	19.6	25
methyl propionate	18.2	23
nitroethane	22.7	30

When immersed in acetone, PEI absorbs it at a constant rate until an equilibrium is reached, as can be seen in Figure 4 for room temperature. The rate at which the weight in the films increases is independent of the sheet thickness and the final weight fraction increase is always

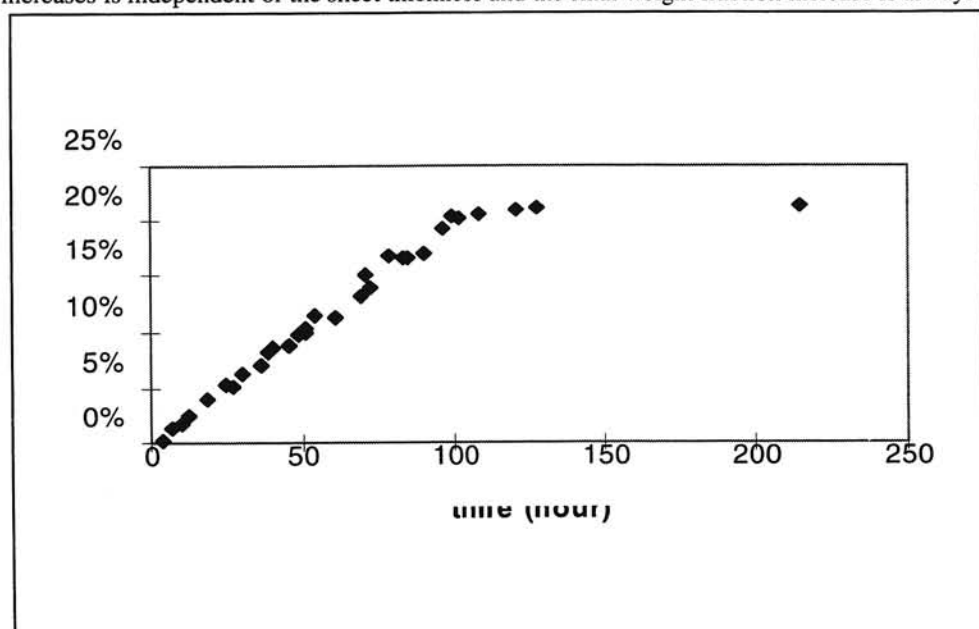


Figure 5 Weight fraction increase of a 250 μm film of PEI in acetone by weighing.

about 20%. When a PEI film is taken out of the acetone bath its weight decreases. However, when it is placed back into the bath after 2 minutes, the equilibrium weight is reached within 3 minutes. These properties, together with the fact that acetone has a relatively high maximum allowable concentration (750 ppm in air²²) in the Netherlands and that PEI does not become brittle after swelling, make it an ideal swelling agent.

The Blowing Agent

Once a film of PEI has been swollen with acetone, an attempt can be made to replace the acetone with another liquid. All of the liquids mentioned in Table 1 are absorbed by PEI at such a rate that if a high percentage could be reached, this would take months or even years. The first liquid that was tested at room temperature was water. However, not more than a 5% weight increase compared to the dry weight was observed, which was not

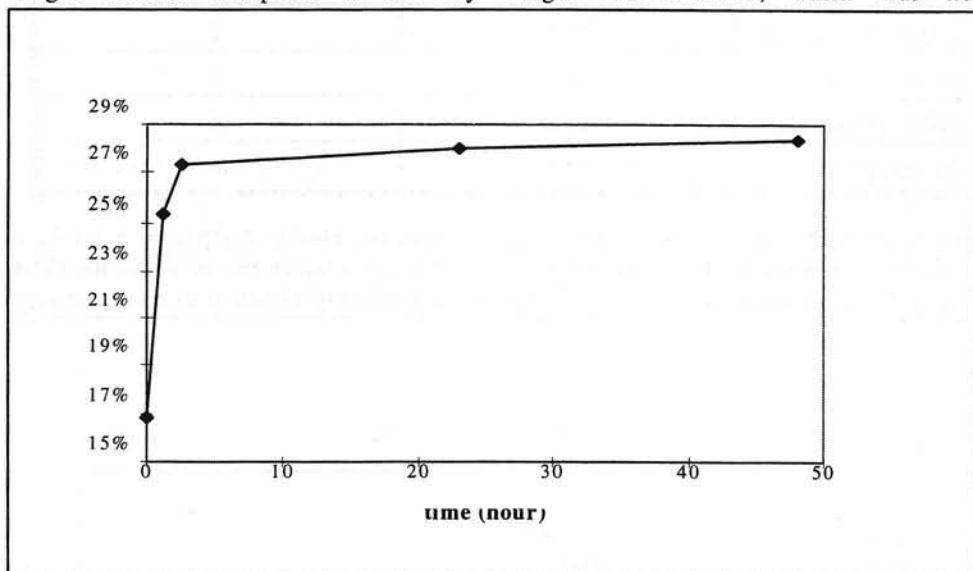


Figure 6 Weight fraction of liquid in PEI film swollen with acetone in a bath of 1,1,1-trichloroethane.

enough for foaming. Another liquid that was tested was 1,1,1-trichloroethane (CH_3CCl_3). It was chosen because it is hardly flammable and has a reasonable maximum allowable concentration (200 ppm in air or 500 ppm for short exposures).

Tests were performed to see whether PEI swollen with acetone, dried on the surface and immersed in 1,1,1-trichloroethane would show a change in weight. The results can be seen in Figure 5 for films with a thickness of 50 μm at a temperature of 19°C. Here $t=0$ is the moment of immersion in the 1,1,1-trichloroethane bath. It must be noted that the weight was measured 30 seconds after taking the film out of the bath. At small values for t , where the film still contains mainly acetone, the weight decreases fairly rapidly during weighing. When the equilibrium is approached, and the film contains more 1,1,1-trichloroethane, the weight

decreases rather slowly during weighing due to the fact that 1,1,1-trichloroethane is less volatile than acetone. This implies that the points on the left side of Figure 5 should be moved up more than those on the right side to obtain the weight of the film at the moment of taking it out of the bath. As this is a surface effect, this difference is expected to be smaller with thicker films.

It must be noted that the final weight percentage varied, depending on the thickness and the producer of the PEI film. From the change in weight, however, we could not conclude unambiguously that the acetone had been replaced. Spot tests were done to determine if acetone had been transferred from the PEI film to the bath of 1,1,1-trichloroethane, which proved to be the case. Subsequently experiments with radioactive acetone were performed to determine the rate the process. The procedure is described in the next paragraph.

The experiments described above were also done with a bath of ethanol. For swollen PEI no significant change in weight could be observed.

Determining the Transport Rate

After being swollen, the films were placed in a bath with a second liquid. At certain intervals a film was taken out of the bath and the concentration of acetone was determined using liquid scintillation counting. In the following figures, the concentration of acetone is shown as a function of time after the films were immersed in 1,1,1-trichloroethane and ethanol respectively.

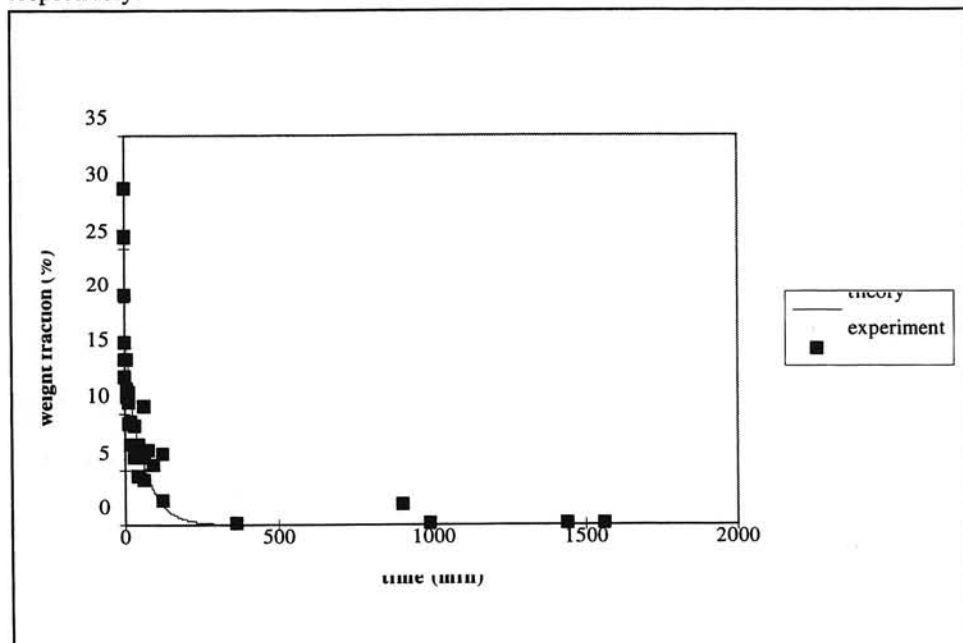


Figure 7 Acetone weight fraction in PEI in a bath of 1,1,1-trichloroethane. The theoretical line was calculated with $D=3 \cdot 10^{-13} \text{ m}^2 \cdot \text{s}^{-1}$.

As can be seen, the diffusion of acetone out of the PEI film occurs much quicker in a bath of ethanol than of 1,1,1-trichloroethane. However, in both cases the acetone is replaced almost completely until an equilibrium is reached with the bath. The theoretical lines in the figures were calculated using equation 8. The value $D=3 \cdot 10^{-13} \text{ m}^2 \cdot \text{s}^{-1}$ results in a correlation coefficient of 0.895 with the experimental data up to 500 minutes for 1,1,1-trichloroethane and $D=10^{-11} \text{ m}^2 \cdot \text{s}^{-1}$ results in a correlation coefficient of 0.995 with the experimental data up to 10 minutes. The correlation coefficient is defined as the covariance of the experimental and the theoretical values divided by the product of the standard deviations of the experimental and theoretical values.

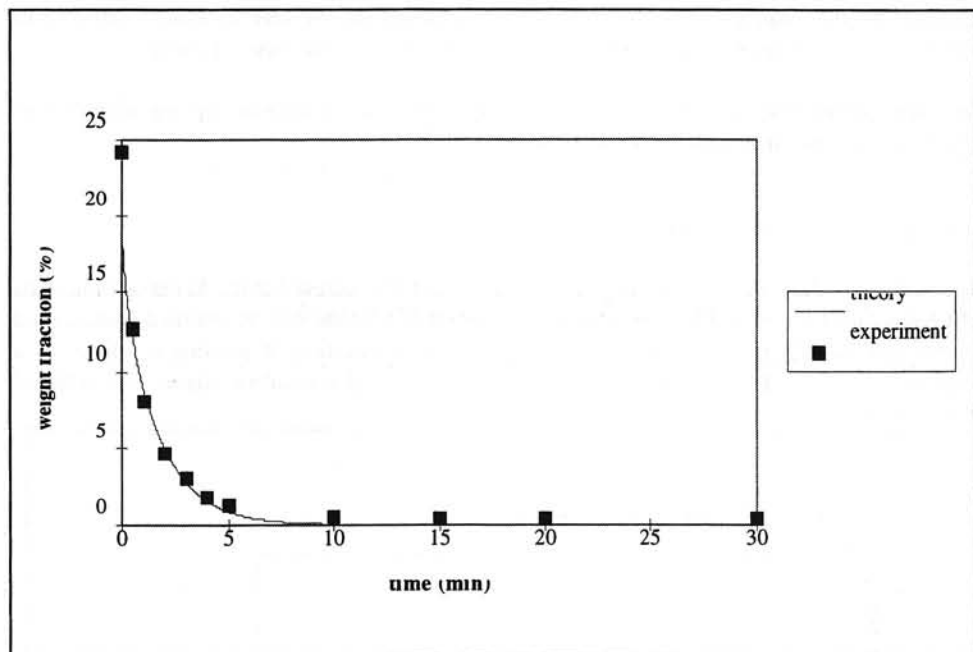


Figure 8 Acetone weight fraction in PEI in a bath of ethanol. The theoretical line was calculated with $D=10^{-11} \text{ m}^2/\text{s}$.

An attempt was also made to replace the acetone in the swollen PEI with water. As can be seen in Figure 9, the acetone concentration did decrease slowly after the swollen sample was immersed in water, but weighings revealed that at room temperature hardly any water penetrated the sample. However, if the swollen PEI was immersed in a bath of water at 80°C , the acetone concentration decreased as can be seen in Figure 9 for $50 \mu\text{m}$ samples. The acetone was replaced by water, as the weight of the dry PEI was about 85% of the weight of the samples.

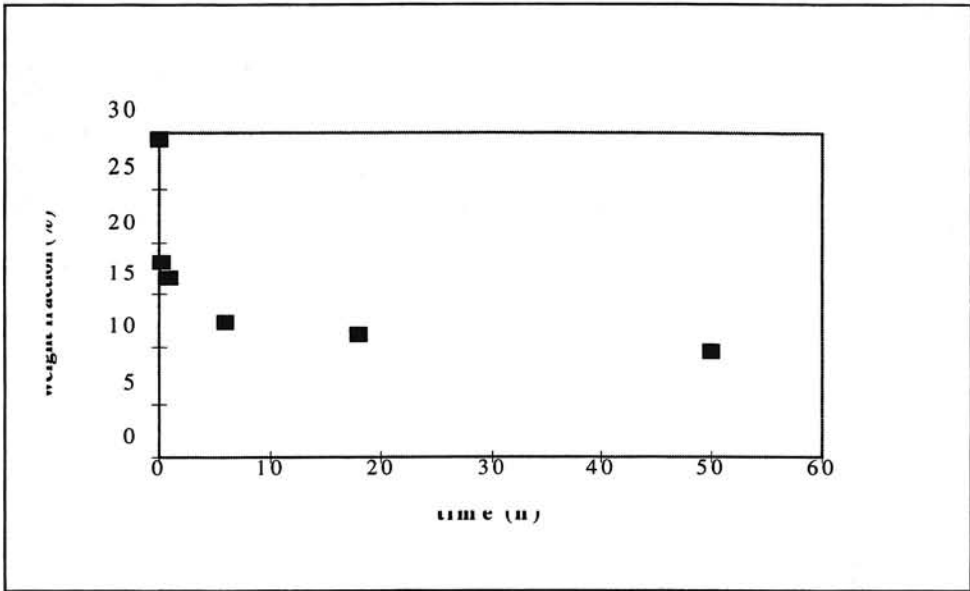


Figure 9 Acetone weight fraction in PEI in a bath of water at 20°C.

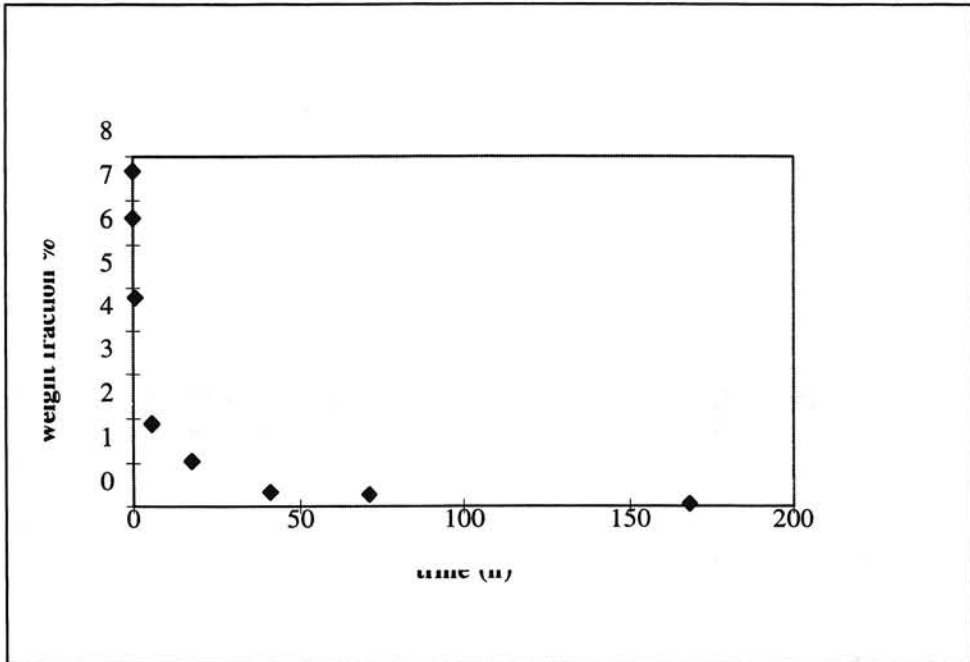


Figure 10 Acetone weight fraction in PEI in a bath of water at 80°C.

Foaming

Several attempts were made to foam PEI impregnated with 1,1,1-trichloroethane. Using PEI films of 50 μm that had been immersed in 1,1,1-trichloroethane for 96 hours at 20°C, it was found that a temperature of at least 185°C was required. If the temperature during foaming was lower, the foam would not rise quickly enough to keep up with the press. If the foam does not follow the press, thus rises without counter-pressure, the adhesion between the foam and the facing is very poor.

Also, sandwiches were made using PEI films of 135 μm containing $8.2 \pm 0.2\%$ 1,1,1-trichloroethane by weight. and sandwiches using the same PEI films containing $17.2 \pm 0.4\%$ ethanol by weight. The process parameters used are shown in the following table:

Table 3 Process parameters used for foaming

temperature (°C)	200
initial pressure (bar)	40
heating time (s)	25
opening speed (mm/s)	0.5
final height (mm)	11

A cross section of one of these sandwiches can be seen in the Figure 10.

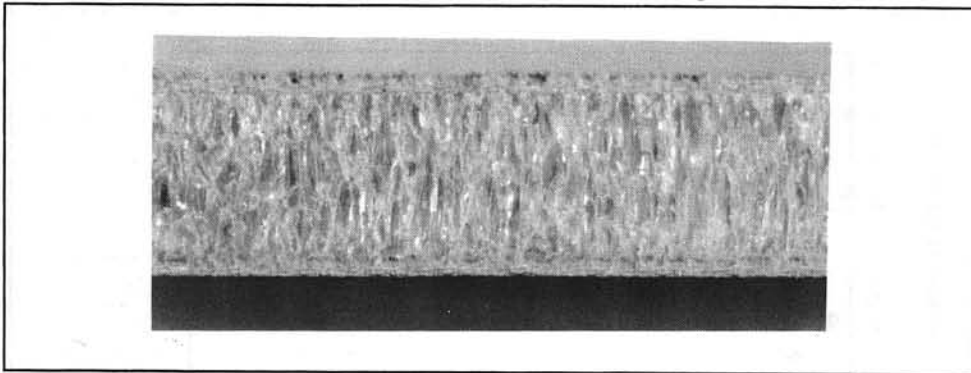


Figure 10 Cross section of a sandwich.

Using a higher pressure and a higher temperature, sandwiches were made with PEI containing $15.0 \pm 0.5\%$ water by weight. The expansion factor that was obtained was 4, thus the density was about 0.3 g/cm^3 , which is rather high.

After foaming the sandwich plates, the plates were dried in an oven. Although no exact drying times were determined, it was obvious that this took much longer for sandwiches foamed with 1,1,1-trichloroethane and ethanol than with methylene chloride or acetone. As PEI hardly absorbs the former two, it is easily understandable that the diffusion process takes much longer.

Mechanical Properties

At first flat tensile tests were performed. In this way the quality of the foam and of the bond between foam and facing could be tested at the same time. The results are given in the following tables. As an in-plane cross-section of the needle-like cells of the foam shows polygonal shapes, it is expected that the compressive strength, like that of honeycombs, will be dependent on the density²³. For the calculation of the densities, it was assumed that the each of the facings had a weight of 0.0903 g/cm² and that the total thickness of two facings was 0.85 mm.

Table 4 Tensile strength of sandwiches foamed with 1,1,1-trichloroethane

sample number	height (mm)	density (kg/m ³)	strength (MPa)
1	9.7	92.5	1.1
2	9.8	88.9	0.3
3	9.8	84.2	0.9
4	10.0	87.6	0.8
5	9.9	90.1	0.7
6	9.8	87.1	1.5

Table 5 Tensile strength of sandwiches foamed with ethanol

sample number	height (mm)	density (kg/m ³)	strength (MPa)
7	10.0	86.8	5.0
8	10.0	88.4	3.5
9	10.0	84.8	> 3.3
10	10.0	87.1	3.4
11	10.0	83.1	2.6
12	9.2	89.8	2.8
13	9.6	86.5	2.3

All the tensile tests performed, except for sample 7, resulted in adhesion failure between foam and facing.

The results of the compression tests are given in the following tables:

Table 6 Compression strength of sandwiches foamed with 1,1,1-trichloroethane

sample number	height (mm)	density (kg/m ²)	strength (MPa)
14	9.9	89.8	1.2
15	9.7	85.9	1.4
16	9.8	88.2	1.0
17	9.9	92.6	1.4
18	9.8	90.1	1.6

Table 7 Compression strength of sandwiches foamed with ethanol

sample number	height (mm)	density (kg/m ²)	strength (MPa)
19	10.0	89.2	1.0
20	10.1	80.0	1.0
21	10.0	87.9	2.0
22	10.0	91.7	2.5

V. Conclusions

A new method for impregnating polymer films has been introduced. Advantages of this new method are the low cost and the fact that it can be accomplished with liquids that are non-solvents. This is particularly interesting in cases where a blowing agent must be introduced in a polymer film. Often the boiling point of solvents are too high to be able to produce a foam. With this method a non-solvent liquid with a low boiling temperature can be used to obtain a foamable film.

At first swelling agents for PEI were selected with solubility parameters close to that of PEI. According to the theory discussed in chapter II, χ_s can be calculated using equations 2, 4 and 5 with the results of the swelling measurements (see table 2). The following values are then obtained:

Table 8 Calculated values of χ_s

swelling agent	χ_s with PEI
acetone	0.19
methyl ethyl ketone	-1.68
methyl acetate	-0.58
methyl propionate	-3.76
nitroethane	0.24

As unrealistic values are obtained for χ_s , we can only conclude that the theory is not exact for polydisperse systems. The theory can only be used as a mere guideline for finding swelling agents.

The diffusion process for acetone in dry PEI is obviously Case II Sorption.

After swelling PEI with acetone and placing it in a bath with another liquid, it was found that the acetone is replaced. Ethanol ($\delta_{\text{ethanol}} = 26.0 \text{ MPa}^{1/2}$) replaces acetone much more quickly than 1,1,1-trichloroethane ($\delta_{1,1,1\text{-trichloroethane}} = 19.0 \text{ MPa}^{1/2}$). It seems that not only the difference in solubility parameter between that of the liquid and that of PEI ($\delta_{\text{PEI}} = 21.5 \text{ MPa}^{1/2}$), but also the size of the molecules determines the rate of replacement. The rate of diffusion of acetone out of the PEI films is well described by Fick's law, as can be seen in Figures 6 and 7.

It was not possible to replace the acetone in PEI with water at room temperature. As it was possible to replace the acetone with other liquids, the hydrogen bonding capacity could be an important factor. This is supported by the theory²⁴ that solvents for a certain resin can be found within an area in a map with the solubility parameter and the hydrogen bonding index on the axes. Systems of polymers with two liquids have been described in literature²⁵, but these are mainly systems in equilibrium. Therefore the experiments performed here cannot be described by these theories. Replacing acetone with water at 80°C is possible. The PEI becomes white as soon as it is immersed in the water, indicating crazing. This is caused by the large stresses that are a result of the expansion of the acetone.

It proved to be possible to use liquids that are non-solvents and non-swelling agents as a blowing agent for the in-situ foaming of PEI. Foaming PEI with acetone as a blowing agent is possible at temperatures down to about 160°C. Attempts to foam with 1,1,1-trichloroethane and ethanol at temperatures far below the glass transition temperature (T_g) of dry PEI (between 215 and 219°C) were unsuccessful. Although the percentage of free volume seems to be the same compared to PEI films swollen with acetone, the glass transition temperature is obviously much lower in the latter case. In accordance with the free volume theory²⁶, it appears as if not only the free volume but also the nature of the material filling the free volume determines T_g . This is supported by the fact that foaming with water was not possible below 210°C. At higher temperatures foaming is possible but until now expansion factors greater than 4 have not been obtained.

The mechanical tests showed that there is a difference in strength between the sandwiches foamed with 1,1,1-trichloroethane and those foamed with ethanol. Especially the adhesion was better in the latter case. The fact that dry PEI absorbs slightly more ethanol than 1,1,1-trichloroethane might indicate that the facing is affected more by ethanol during foaming, resulting in a better adhesion. In the following table the average results are compared to those of sandwiches foamed with other blowing agents with densities in the same range.

Table 9 Average strengths of sandwiches with the standard deviation in parentheses

blowing agent	tensile strength (MPa)	compression strength (MPa)
ethanol	3.3 (0.9)	1.6 (0.8)
1,1,1-trichloroethane	0.9 (0.4)	1.3 (0.2)
acetone ⁶	3.9 (1.0)	2.0 (0.2)
methylene chloride	4.7 (0.2)	1.9 (0.1)

Although the process parameters for foaming with ethanol must be further optimized, the results of the mechanical tests performed on the sandwiches approach those of tests performed on sandwiches foamed with methylene chloride or acetone. Sample 7 shows that it is possible to obtain an adhesion that is stronger than the foam.

It is expected that other mechanical properties will give similar results compared to PEI foamed with methylene chloride or acetone.

Preliminary results indicate that this process of impregnating a film and foaming it in a similar way is possible with other polymers.

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A new method is described to make foamable films for the production of in-situ foamed sandwiches. The method consists of placing a polymer film in a bath with a swelling agent and, when equilibrium swelling has been reached, placing the film in a bath with a second liquid. If the liquids are miscible the swelling agent in the film will be replaced by the second liquid. The polymer used for the research described in this report was polyetherimide and the swelling agent was acetone. Sandwiches were produced with the foamable films made in this manner using ethanol, 1,1,1-trichloroethane and water as blowing agents. Some mechanical properties of these sandwiches were tested.

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