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A study of the effect of absorbed water on the T_g of a poly(amideimide) using DMA and DSC [1]

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Abstract

The absorption by and diffusion of water in a commercially available poly(amideimide), Torlon® 4203, and the dependence of the glass transition temperature (T_g) of this polymer on the weight % absorbed water have been investigated. Diffusion studies indicated that the activation energy for the diffusion process of water in this poly(amideimide) was 44.2 kJ mol^{-1} and that the permeability index was 1.17×10^{-5} $\text{m}^2\ \text{s}^{-1}$. The diffusion coefficient was found to increase from 1.79×10^{-13} $\text{m}^2\ \text{s}^{-1}$ at 303 K to 8.94×10^{-13} $\text{m}^2\ \text{s}^{-1}$ at 333 K. The T_g of the polymer, as determined from dynamic mechanical analysis (DMA), was found to decrease monotonically from 568 to 477 K as the weight % absorbed water in the polymer was increased from 0% to 4.25%. Linear least-squares analysis of the data indicated that the relationship between T_g and weight % absorbed water ($W_{\%\text{AW}}$) was given by $T_g = 576.4 - 22.0\ W_{\%\text{AW}}$ ($r^2 = 0.990$). T_g studies using differential scanning calorimetry (DSC) indicated that the diffusion of water from the sample had a major effect on correlations between T_g and % absorbed water. That is, at low heating rates absorbed water diffused from the sample before the sample was heated to the glass transition temperature and therefore the measured T_g was similar to that for a dry sample. The effect of absorbed water on the dimensional stability of this polymer when heated rapidly to temperatures in the vicinity of the glass transition temperature is also discussed.

INTRODUCTION

Poly(amideimide)s are characterized by high thermal stability, inherent flame resistance, good stress rupture resistance, and excellent dimensional stability and strength over an extended temperature range [1]. As a result of these properties, poly(amideimide)s have been used in high-temperature electrical connectors, electronic and aerospace applications, and as a replacement for metallic materials in certain parts of internal combustion engines. However, poly(amideimide)s absorb water when exposed to the

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environment and have been reported to absorb a maximum of 2.5% water by weight at 20°C and 50% relative humidity after approximately 10000 h [2]. The absorption of water by poly(amideimide)s is of concern because water acts as a plasticizer in certain thermoplastic materials and therefore affects the glass transition temperature (T_g) of the polymer.

The glass transition temperature (T_g) of a polymer, which is affected by a number of factors including the molecular weight (MW) of the polymer, the degree of cross-linking of the polymer, and the presence of diluents or plasticizers [3,4], defines the range in which the polymer will have certain mechanical properties. At temperatures below T_g, the polymer is hard and glass-like, while at temperatures above T_g, the polymer is soft and rubber-like. The free volume theory of the glass transition provides a semi-quantitative treatment of the effect of diluents such as water on T_g [5,6]. In general, it is observed that the T_g of a polymer decreases with increasing concentrations of plasticizer. For instance, the T_g of Nylon-6,6 decreased from 355 K to 273 K as the weight percent absorbed water increased from 0% to 8.9% [7].

The effect of a diluent (plasticizer) on the T_g of a polymer has been found to be dependent on a number of factors including the weight fraction of the diluent [8,9], specific interactions between the diluent and the polymer [7], and the structure of the polymer [10].

There are a number of thermal analytical methods for determining the T_g of polymers. These include dynamic mechanical analysis (DMA) [11] which records the change in the storage modulus (E'), loss modulus (E''), and tan δ with temperature, and differential scanning calorimetry (DSC) [12] which measures the change in the heat capacity of a sample as the temperature is varied.

In a DMA experiment, E', E'' and tan δ change rapidly in the vicinity of the glass transition and provide a particularly sensitive method for determining T_g. The storage modulus, which is the ratio of the in-phase stress to the maximum strain amplitude, is observed to decrease in the area of the glass transition, while the loss modulus, which is the ratio of the out-of-phase stress to the maximum strain amplitude, and tan δ, which is the ratio of E'' to E', are observed to reach a maximum in the area of the glass transition. The heat capacity of a polymeric material also changes rapidly in the area of the glass transition, and this is the basis of the measurement of T_g using DSC.

In this paper, the absorption and diffusion of water in a poly(amide-imide), Torlon® 4203, are investigated and the effect of absorbed water on the glass transition temperature of this polymer, as measured using DMA and DSC, is reported. Knowledge of the effect of absorbed water on T_g is especially important at higher temperatures where a reduction in the glass transition temperature of the material can reduce the temperature range in which the material has useful mechanical properties.

MATERIALS AND EQUIPMENT

The poly(amideimide) used in this study, Torlon® 4203, was obtained from Amoco Performance Products, Napierville, Illinois. Poly(amideimide) coupons (35 mm long × 11 mm wide × 2 mm thick) were dried in an oven (Blue M Electric Company, Blue Island, Illinois) at 433 K for 100 hours prior to the start of water absorption studies. Water absorption studies were carried out in a thermostated water bath (Haake K Model F3 Digital, Berlin, West Germany) at 333.4 ± 0.2 K, 318.2 ± 0.2 K and 303.15 ± 0.2 K. To monitor water absorption, samples were removed from the water bath, wiped dry, and weighed.

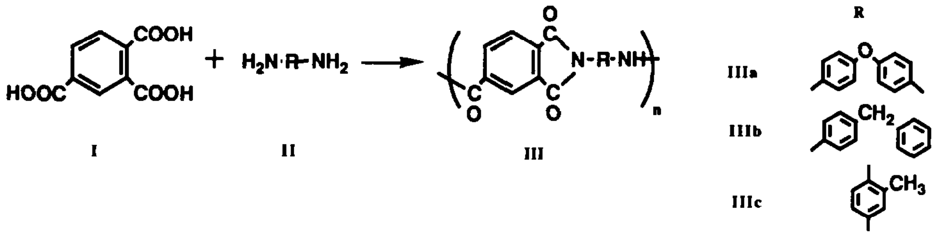
The infrared (IR) spectra of Torlon® 4203 was recorded on a Perkin-Elmer System 2000 Fourier transform IR spectrometer using 16 scans and 8 cm^{-1} resolution. Dynamic mechanical analysis (DMA) was carried out using a Du Pont Model 983 dynamic mechanical analyzer in the fixed frequency mode at 1 Hz. A displacement amplitude of 0.3 mm and a heating rate of 5 K min^{-1} were used for all DMA analysis unless otherwise noted. The T_g measured using DMA was taken as the maximum in a plot of E'' versus temperature.

Differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA) were carried out using a Du Pont 2910 DSC and a Du Pont Model 951 TGA respectively. Typically, 10 mg samples were used for both DSC analysis and TGA analysis. The DMA, DSC and TGA instruments were interfaced to a Du Pont thermal analyst 2100 data analysis system. The DSC was calibrated using an indium standard (melting point 429.76 K). The melting temperature of the indium standard, measured as the onset temperature, was determined to be 429.91 K. The calibration was confirmed using the melting points of tin (m.p. 505.1 K) and potassium perchlorate (m.p. 572.1 K) standards, which were determined to be 504.8 K and 572.7 K.

Poly(amideimide)s

Poly(amideimide)s (**III**) are prepared by the condensation polymerization of trimellitic anhydride (1,2,4-benzenetricarboxylic anhydride) (**I**) and aromatic diamines (**II**). The reaction between trimellitic anhydride and an aromatic amine is shown in Scheme 1, where R is a structure containing aromatic rings.

Infrared (IR) spectroscopy and pyrolysis gas chromatography/mass spectrometry (Py GC/MS) were used to determine the nature of the aromatic diamine in Torlon® 4203. The IR spectrum of a film of Torlon® 4203 from dimethyl formamide (DMF) solution is shown in Fig. 1 and is consistent with a poly(amideimide) prepared using diaminodiphenyl ether as the aromatic diamine (**IIIa**) [13]. Py GC/MS analysis indicated that



Scheme 1. The reaction between trimellitic anhydride and an aromatic amine.

phenol, aniline and phenoxyaniline were all released during the pyrolytic degradation of this poly(amideimide). These molecular fragments are also consistent with the degradation of a poly(amideimide) prepared using diaminodiphenyl ether.

RESULTS AND DISCUSSION

Diffusion coefficients for water in poly(amideimide)

For a material that exhibits Fickian absorption behavior in the initial stage of absorption, the relationship between the weight of absorbed liquid and the diffusion coefficient of a sample with planar geometry [14,15] is given by

$$M_t/M_\infty = 4(Dt/\pi l^2)^{1/2} \qquad (1)$$

where M_t and M_∞ represent the weight gain of the sample immersed for time t and the total weight gained by the sample at infinite immersion time, respectively, D is the diffusion coefficient, t is the time of immersion and l is the sample thickness.

The plots of M_t/M_∞ versus $t^{1/2}/l$ for a sample of Torlon® 4203 immersed in water at 303, 318 and 333 K are shown in Fig. 2. M_∞ was estimated from the total weight gain of the sample after immersion for

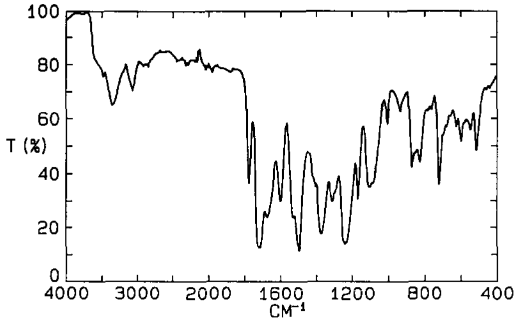


Fig. 1. Infrared spectra of a sample of Torlon® 4203.

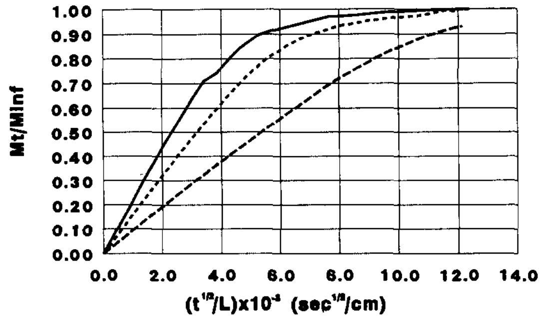


Fig. 2. Fractional weight gain of samples of Torlon® 4203 immersed in water at 303 K (-----), 318 K (------) and 333 K (———).

greater than 1700 h at 333 K. At this point the weight gain of the sample over the previous 200 h immersion was negligible. The shape of the absorption curve is typical of materials that exhibit Fickian sorption behavior [16], that is, the curve is linear for $M_t/M_\infty < 0.5$ and then becomes concave towards the x-axis as the fractional weight gain approaches 1.0.

The diffusion coefficients for samples of poly(amideimide) at 303, 318 and 333 K were calculated from the slopes ($G = 4(D/\pi)^{1/2}$) of the linear portion of the curves shown in Fig. 2 using

$$D = (\pi/16)G^2 \tag{2}$$

The diffusion coefficients are listed in Table 1 and were observed to increase with an increase in temperature. For Fickian diffusion, the temperature dependence of the diffusion coefficient D can be expressed by the Arrhenius equation

$$D = D_0 \, e^{(-E_a/RT)} \tag{3}$$

where D_0 is the permeability index, E_a is the activation energy for the diffusion process, R is the gas constant and T is temperature in degrees Kelvin. The activation energy for the diffusion process, determined from the slope of the plot of ln D versus $1/T$, was 44.2 kJ mol^{-1}, and the permeability index, determined from the y-intercept of the best fit straight line was 1.17×10^{-5} m^2 s^{-1}.

TABLE 1

Diffusion coefficients for the diffusion of water in Torlon® 4203 at 303, 318 and 333 K

Diffusion coefficient (D) (m^2 s^{-1})	Temperature (K)
1.79×10^{-13}	303
5.07×10^{-13}	318
8.94×10^{-13}	333

T_g *of poly(amideimide) samples by DMA*

Plots of the storage (E') and loss moduli (E'') of samples of poly(amideimide), stored under ambient conditions of temperature and humidity for one year and dried at 433 K for 100 h, against temperature are shown in Figs. 3(a) and 3(b), respectively. The glass transition temperatures of the two samples, determined from the maxima in the E'' versus temperature plots, were found to differ by greater than 40 K. The sample stored under ambient conditions had a T_g of 525 K and the sample that had been dried at 433 K for 100 h had a T_g of 568 K.

To demonstrate that the observed difference in the glass transition temperatures of these two samples was due to the presence of absorbed water, samples of poly(amideimide) were dried at 433 K for 100 h, weighed to determine their dry weight, and immersed in a water bath at 333 K. The weight gain of the samples was monitored gravimetrically and the T_g of samples containing known weights of water were determined from maxima in the plots of E'' versus temperature.

A plot of T_g versus weight % absorbed water ($W_{\%AW}$) is shown in Fig. 4. Linear least-squares analysis of the data gave the relationship between T_g and ($W_{\%AW}$) as $T_g = 576.4 - 22.0\ W_{\%AW}$, $r^2 = 0.990$, where $W_{\%AW}$ refers to the weight of water absorbed by the sample prior to the DMA experiment. However, during DMA analysis water could diffuse from the sample and

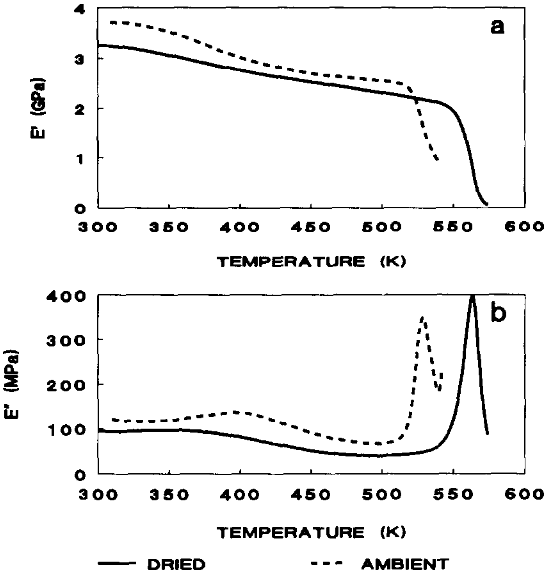


Fig. 3. Plots against temperature of (a) storage and (b) loss moduli of samples of Torlon® 4203 stored under ambient conditions of temperature and humidity and dried at 433 K for 100 h.

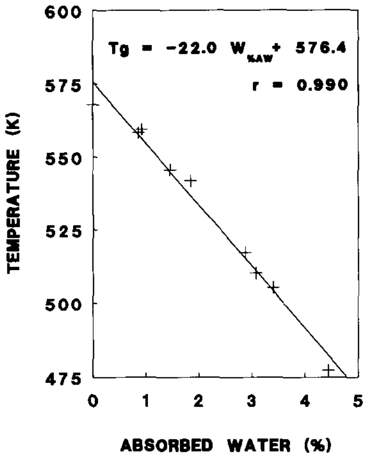


Fig. 4. T_g versus percent absorbed water for Torlon® 4203 samples.

the actual weight of water in the sample at the glass transition temperature would be diminished.

T_g *of poly(amideimide) samples by DSC*

The DSC traces of a sample of poly(amideimide) containing 2.7% absorbed water and a sample of poly(amideimide) dried at 433 K for 100 h are shown in Fig. 5. A heating rate of 5 K min^{-1} was used for both samples. In contrast to the results obtained from DMA analysis, the T_g values of the two samples determined using DSC were both approximately 553 K. This suggested that the absorbed water in the sample containing 2.7% water had sufficient time to diffuse to the surface of the sample and evaporate before the sample was heated to the glass transition temperature.

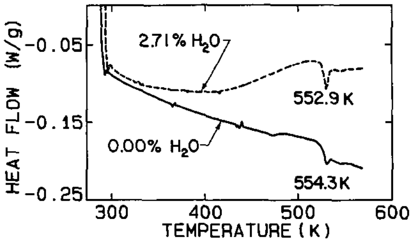


Fig. 5. DSC traces and T_g for samples of Torlon® 4203 containing 2.71% absorbed water and no absorbed water.

TABLE 2

DSC determination of the variation in the glass transition temperature (T_g) of samples of Torlon® 4203 using heating rates between 5 and 40 K min^{-1}

Rate (K min^{-1})	% H_2O	T_g	T_g (0% H_2O)
5	4.50	281	281
10	4.55	271	286
20	4.34	273	289
30	4.37	272	291
40	4.30	265	293

Diffusion of water during DSC analysis

To determine if the diffusion of water from the 'wet' sample was responsible for the similarity in the T_g values measured for the wet and dried samples using DSC, the T_g of samples of poly(amideimide) containing between 4.3% and 4.5% absorbed water were measured using heating rates of 5, 10, 20, 30 and 40 K min^{-1}. The results of the analysis are listed in Table 2. The T_g of dry poly(amideimide) samples measured using identical heating rates are included for comparison.

The T_g values of the samples containing absorbed water decreased as the heating rate was increased from 5 to 40 K min^{-1}. This suggests that the apparent independence of the glass transition temperature of this polymer on % absorbed water, when measured using DSC at slower heating rates, can be attributed to diffusion of water to the surface of the sample and evaporation. At higher heating rates, absorbed water does not have sufficient time to completely diffuse from the sample and thus some water remains in the sample and is responsible for the observed depression in T_g.

For dry poly(amideimide) samples, the measured T_g increased monotonically from 554 to 566 K as the heating rate was increased from 5 to 40 K min^{-1}. The increase in T_g for the dry samples as the heating rate is increased results from the dependence of the position of the glass transition on the heating rate [5]. As the heating rate is increased, the T_g of a sample is higher relative to that measured at a slower heating rate.

Figure 6 shows the TGA results of weight loss versus temperature for poly(amideimide) samples containing 4.6% absorbed water. All samples weighed approximately 10 mg and the heating rate was varied from 1 to 40 K min^{-1}. For the sample heated at a rate of 1 K min^{-1}, most of the absorbed water in the sample had diffused to the sample surface and evaporated by the time the sample temperature was 453 K. Because the sample contained no absorbed water when it was heated to the glass transition region, i.e. 553 K, the T_g measured in the DSC experiment did not reflect that the sample had originally contained absorbed water. At heating rates of 5 and 10 K min^{-1}, most of the absorbed water had diffused

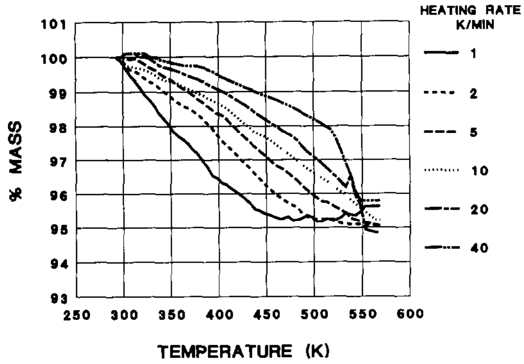


Fig. 6. TGA traces for samples of Torlon® 4203 containing 4.6% absorbed water at several heating rates.

to the sample surface and evaporated at approximately 563 K. The T_g for samples heated at these rates showed a slight dependence on the absorbed water as a small amount remained in the sample in the vicinity of the glass transition temperature. The samples heated at 20 and 40 K min^{-1} still contained considerable amounts of water at temperatures in the vicinity of the glass transition temperature and this water caused a decrease in the T_g for these samples as measured by DSC.

The different results from the DMA and DSC experiments can be related to the size of the samples used in the DMA and DSC experiments. The samples used in the DMA experiment weighed between 1.3 and 2.5 g, whereas the samples used in the DSC experiment weighed between 10 and 15 mg. At low heating rates, the absorbed water in the smaller samples used in the DSC had time to diffuse to the surface of the sample and evaporate before the sample reached its T_g. As the heating rate was increased, the loss of water was diminished and this was reflected in the lower T_g for the sample. For the larger samples used in the DMA experiment at a heating rate of 5 K min^{-1}, very little of the absorbed water had time to diffuse to the surface of the sample and evaporate, and therefore the water remaining in the sample caused a decrease in the T_g of the sample.

The T_g of samples of poly(amideimide) containing approximately 3.5% water determined using DMA analysis and heating rates of between 5 and 40 K min^{-1} are shown in Table 3. In contrast to the DSC results, the measured T_g values for these samples are found to increase by 10°C as the heating rate is increased from 5 to 40 K min^{-1}. This shows that loss of water from the sample is much less important for the larger samples used in the DMA than was found for the smaller samples used in the DSC. That is, although the loss of water due to diffusion and evaporation would be largest for the sample heated using the lowest heating rate, the difference in weight loss for the various heating rates is small. Therefore the change

TABLE 3

The variation in the glass transition temperature (T_g) of samples of Torlon® 4203 with heating rate as determined using DMA

Ramp (K min^{-1})	% H_2O	T_g	T_g (0% H_2O)
5	3.45	227	299
10	3.66	227	307
20	3.31	236	309
30	3.55	236	312
40	3.54	237	315

in heating rate has more effect on the position of the T_g than the change in absorbed water concentration for the samples studied using DMA.

Effect of absorbed water on the dimensional stability

Absorbed water was also observed to cause poly(amideimide) samples to swell when they were heated through the glass transition to 573 K. Sample coupons that had contained 0%, 0.8%, 2.8% and 4.2% absorbed water are shown in Fig. 7 following heating to 573 K. It can be seen that the amount

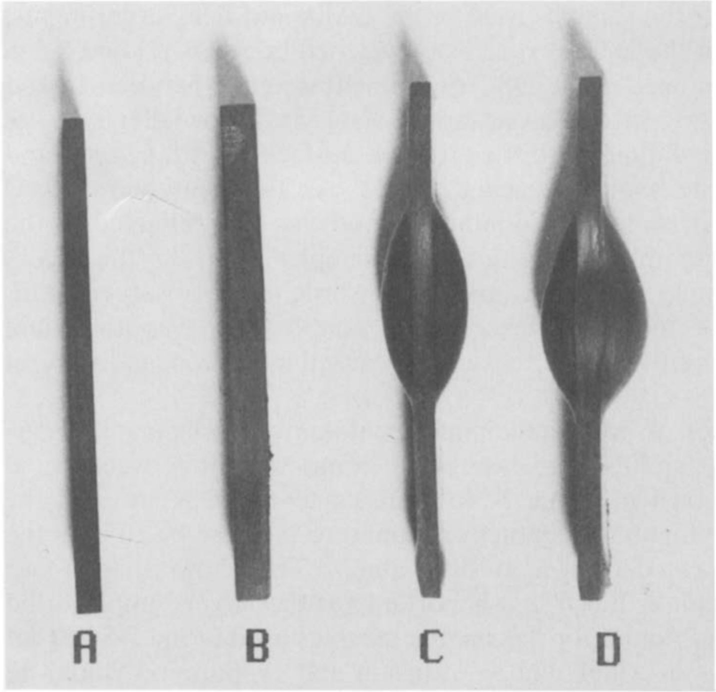


Fig. 7. Photograph of samples of Torlon® 4203 containing (A) 0%, (B) 0.85% (C) 2.80% and (D) 4.25% absorbed water following heating to 573 K.

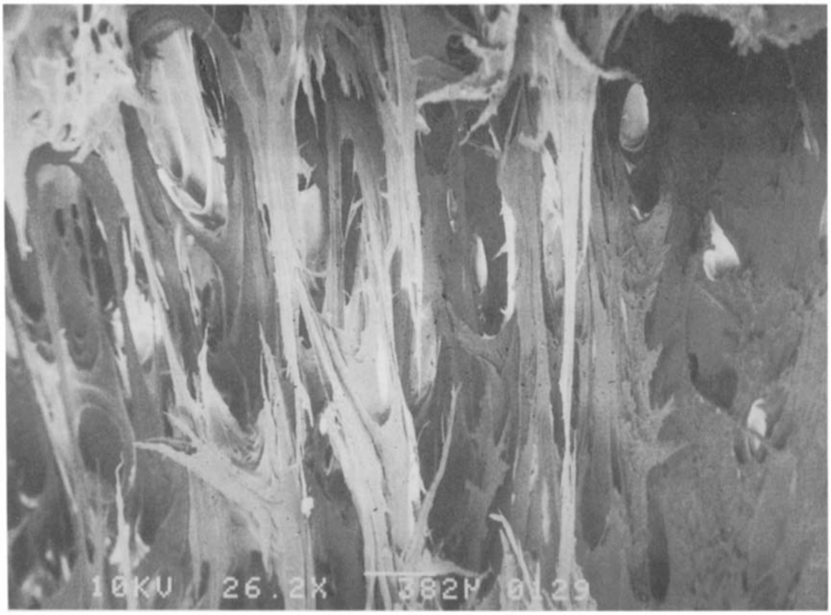


Fig. 8. Scanning electron micrograph of a cross section of a sample of Torlon® 4203 containing 4.25% absorbed water following heating to 573 K.

of swelling of the coupons is dependent on the amount of absorbed water originally in the sample. The distortion is caused by the vapor pressure of the absorbed water that is trapped in the sample as it is heated to the temperature of the glass transition. In the vicinity of T_g, the modulus of the polymer drops rapidly and the vapor pressure of the absorbed water is high enough to cause the polymer to flow. Figure 8 shows a scanning electron micrograph of a cross section of a sample of Torlon that had distorted upon heating to 573 K. The flow of the polymer caused by the trapped water vapor can be seen in this micrograph.

Distortion of this type is important in uses where the dimensional stability of the polymer is important. If the polymer contains absorbed water and is heated rapidly to temperatures in the area of the glass transition, then distortion will take place. However, with smaller samples or slower heating rates, absorbed water can diffuse to the surface of the sample and evaporate, and sample swelling will not take place.

CONCLUSIONS

The absorption of water and the effect of absorbed water on the dynamic mechanical properties of a poly(amideimide), Torlon® 4203, have been investigated. The activation energy and the permeability index (D_0) for the absorption of water by this polymer were found to be 44.2 kJ mol^{-1} and 1.17×10^{-5} m^2 s^{-1} respectively, and the diffusion coefficient for water in poly(amideimide) was found to decrease from 8.94×10^{-13} to 1.79×10^{-13} m^2 s^{-1} as the temperature decreased from 333 to 303 K. The T_g, determined as the maximum in a plot of E'' versus temperature, was found to decrease monotonically with % absorbed water. The relationship between T_g and % absorbed water ($W_{\%AW}$) was given by $T_g = 303.6 - 22.1W_{\%AW}$, and had a correlation coefficient (r^2) of 0.990.

The effect of absorbed water on the T_g was more difficult to follow using DSC. This was attributed to the small sample size used in DSC analysis and to the fact that at slower heating rates, absorbed water diffused to the surface of the sample during heating and evaporated before the sample was heated to the glass transition temperature. Results consistent with the plasticization of poly(amideimide) by water were observed when higher heating rates were used and complete diffusion of absorbed water to the surface of the sample and subsequent evaporation were not possible. Distortion of poly(amideimide) samples containing absorbed water, when heated rapidly to the vicinity of the glass transition temperature, must be considered if this polymer is to be used where dimensional stability is important.

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