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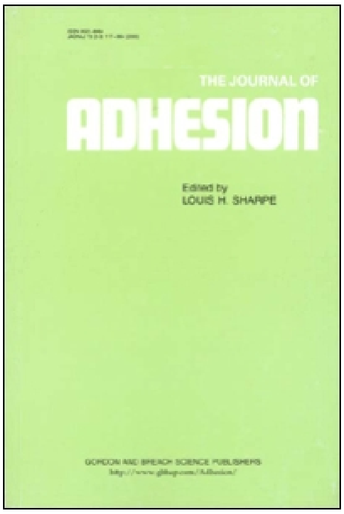

The Journal of Adhesion
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713453635

Water Resistance of Poly(Imide-Siloxane) Adhesives: Diffusion Coefficients by Gravimetric Sorption

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To cite this Article Kaltenecker-Commerçon, Joyce M. , Ward, Thomas C. , Gungor, Attila and McGrath, James E.(1994) 'Water Resistance of Poly(Imide-Siloxane) Adhesives: Diffusion Coefficients by Gravimetric Sorption', The Journal of Adhesion, 44: 1, 85 — 102

To link to this Article: DOI: 10.1080/00218469408026618

URL: http://dx.doi.org/10.1080/00218469408026618

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J. Adhesion, 1994, Vol. 44, pp. 85–102
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Water Resistance of Poly(Imide-Siloxane) Adhesives: Diffusion Coefficients by Gravimetric Sorption

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(Received July 6, 1993; in final form October 29, 1993)

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Diffusion coefficients of water vapor in a polyimide homopolymer and poly(imide-siloxane) multi-block copolymers of different siloxane concentration were determined from gravimetric sorption experiments. Diffusion coefficients were of the order of magnitude of 10^{-8} cm^2/sec. Higher levels of siloxane incorporation caused a definite increase in the diffusion coefficient, indicating a decreased resistance to water ingression. The increase in diffusion was found to be influenced by siloxane block length and was interpreted in terms of free volume and morphology. The diffusion coefficient of the 10-weight-percent PDMS copolymer, however, was found to be the same within error as that of the polyimide. This and a previous surface study suggested that an increased surface water resistance may be achieved at low siloxane concentrations without greatly increasing the bulk diffusive properties to undesirable levels.

KEY WORDS Poly(imide-siloxane) copolymers; adhesive water resistance and durability; water vapor diffusion in polymers; diffusion coefficient; water vapor gravimetric sorption; polyimides.

INTRODUCTION

The durability of many adhesive-adherend systems is decreased by the ingression of water. High humidity environments are considered aggressive environments for adhesive joints because the presence of water in the adhesive can influence overall bulk polymer properties and can cause interfacial failure due to the displacement of the adhesive from the adherend by the polar water molecules. The decrease in adhesive strength in hot/wet environments also tends to be accelerated by the application of stress.[1] Increasing the water resistance and durability of an adhesive joint is, therefore, of great interest. During the past several years, it has been shown that the incorporation of poly(dimethylsiloxane) segments into polyimides increases the possible-adhesive polymer's resistance to water ingression.[2,3] Multi-block poly(imide-siloxane) segmented copolymers were found

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also to have increased durability in hot/wet environments compared with homopolymer polyimides. The incorporation of 10-weight-percent siloxane was found to increase the time to failure for single lap shear specimens by a factor of three.[4] To predict and characterize the copolymer adhesive durability effectively, it is important to understand the mechanism of water ingression (or indeed the tendency of water resistance). Both the bulk and the surface characteristics of the microphase-separated copolymer may contribute to this water resistance. XPS surface characterization studies have revealed that the concentration of hydrophobic siloxane at the surface is greater than the proportional amount incorporated into the copolymer.[2,4] This high concentration of the hydrophobic poly(dimethylsiloxane) segment at the surface suggests a possible barrier to the initial entry of water into the bulk. The resistance to water may also be influenced by morphological bulk properties. Sorption studies involving the water immersion of poly(imide-siloxane) copolymers have shown that water mass uptake is decreased by an increasing concentration of siloxane.[2] The equilibrium mass uptake was dependent not only on weight percent incorporated siloxane but also on the molecular weight of the siloxane segment for a given weight-percent siloxane incorporated into the copolymer.

The purpose of the present research was to examine the possible surface and morphological bulk factors involved in the increased water resistance of such copolymers. If the relative importance of a factor's contribution to water resistance could be ascertained, the siloxane-containing copolymers might then be synthetically tailored to maximize the water resistant qualities. The influence of siloxane incorporation on water ingression was investigated by studying the bulk and surface interactions of water vapor with a series of poly(imide-siloxane) copolymers of different siloxane concentration. The surface study, which has been reported in a separate paper,[5] utilized Inverse Gas Chromatography (IGC) to examine the interaction of water vapor with the various polymer surfaces. This paper represents the second part of the overall study and concerns the determination of diffusion coefficients by gravimetric sorption experiments of free-standing thin films as a measure of the interaction of water vapor with the bulk polymer. The speed with which water was able to move through the bulk of the polymer and perhaps toward a bonded interface was of interest, since interfacial water is often considered to be the most detrimental to adhesive properties.

There are numerous studies of the sorption and diffusion of water and water vapor into various types of polymer systems. Bending beam techniques have been utilized to determine diffusion coefficients of water into various polyimides, their copolymers[6] and their blends.[6,7] Recent work also includes a study of the diffusion and distribution of water and deuterated water in Kapton polyimide films[8] as well as studies of water sorption and mechanical properties of carbon fiber composites with epoxy,[9] poly(ether ether ketone) (PEEK) and poly(phenylene sulfide) (PPS)[10] matrices. Although Fickian diffusion is theoretically valid only for the case of rubbery polymers, the above glassy systems were reported to have Fickian water sorption characteristics. Fickian kinetics have been reported in other humidity durability studies as well.[1,11] Diffusion studies of solvents[12,13] and permanent gases[14,15] into polyimides have revealed both Fickian and non-Fickian sorption characteristics, with the non-Fickian sorption being attributed to relaxational processes occurring on the same time scale as the diffusion process. Water sorption into poly(ethylene terephthalate) (PET) and poly(butylene terephthalate) (PBT)

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and their glass fiber composites has also shown non-Fickian sorption kinetics.[16] Other studies include water sorption into segmented polyurethanes,[17-19] polyamides,[20-22] graft copolymers,[23] epoxy coatings,[24] and various blends.[25, 26] A diffusion study of permanent gases into a glassy-polystyrene/rubbery-polybutadiene block copolymer with well-defined lamellar morphology has been recently reported as well.[27]

Diffusion can be described as the movement of matter within a system due to molecular motions within that system. Fick's first and second laws describe entropic diffusion driven by random responses to a concentration gradient. There have been many approaches and developments in theories of diffusion, which have been reviewed.[28-34] Many of these theories share a similar phenomenological assumption that the diffusion of a penetrant is the rate of movement of that penetrant into and out of a series of vacancies or "holes" in its random walk in the direction of the concentration gradient. This visualization has led many theories of diffusion to include various free-volume relations. Several[35-39] have incorporated the Williams-Landel-Ferry equation or its modified forms to describe the temperature dependence of the fractional free volume. Although this restricts valid application to diffusion in rubbery polymers, a modifying parameter has been added in an attempt to apply such theory to the diffusion of very small concentrations of penetrant in glassy polymers.[38, 40] A theory has also been derived for diffusion of a finite concentration of penetrant in a glassy polymer.[41-43] Constitutive equations for small penetrant diffusion with respect to temperature, stress and concentration conditions above and below the glass transition temperature have been developed.[44] An Arrhenius-type expression described the temperature dependence in the glassy state.

DIFFUSION THEORY

For uni-directional diffusion, Fick's first law of diffusion states that the amount of matter transferred through a plane of unit area during a unit time is proportional to the concentration gradient of the diffusing species in that direction. Experimental approaches to obtaining diffusion coefficients are based on various solutions to Fick's second law,

$$\frac{\delta c}{\delta t} = D\left(\frac{\delta^2 c}{\delta x^2}\right) \tag{1}$$

which gives the change of concentration with time at any plane in the material. It is applicable to systems in which the diffusant is dilute and significantly more mobile than the material, which should act as a "fixed" reference frame. This is the assumed case for the diffusion of low-molecular-weight gases and non-solvating vapor penetrants into polymers. Solutions to this basic differential equation depend on the sample geometry and also on the chosen boundary conditions. Various experimental techniques for determining diffusion coefficients are discussed by Vieth[28] and Felder and Huvard.[30]

The sorption method is based on the solution for diffusion into a semi-infinite film exposed to an infinite bath of the penetrant. The concentration at the faces of the film reach equilibrium immediately and diffusion into the edges of the film is negligible. For sorption at short times, the solution can be approximated by:

$$\frac{M_t}{M_\infty} = \frac{4}{\pi^{1/2}}\left(\frac{Dt}{L^2}\right)^{1/2} \tag{2}$$

where M_t is the mass uptake of penetrant into the film at time, t, and M_∞ is the equilibrium uptake at infinite (long) times. The fractional uptake is given by M_t/M_∞ and L is the film thickness. A plot of the fractional uptake against the square root of time divided by film thickness is termed a reduced sorption plot. The diffusion coefficient is obtained from the initial slope of this plot.

Some important characteristics of Fickian diffusion are the following: Plots of fractional uptake *versus* the square root of time are initially linear for both sorption and desorption studies. For sorption, the plot must be linear up to at least 0.6 of the fractional uptake. The sorption curves must be concave to the abscissa after the initial linear region. Reduced sorption plots are the same for films of different thicknesses. Sorption and desorption plots coincide when the diffusion coefficient is not a function of concentration but is a constant.

EXPERIMENTAL

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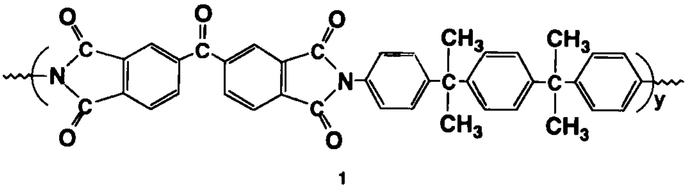
A polyimide homopolymer and three poly(imide-siloxane) copolymers were utilized in this study. The randomly segmented multi-block poly(imide-siloxane) copolymers were synthesized using a solution-imidization technique from benzophenone tetracarboxylic dianhydride (BTDA), bisaniline P (Bis P) and aminopropyl-terminated polydimethylsiloxane (PDMS) oligomers of two different number average molecular weights. The siloxane oligomers had approximate number average molecular weights of 3600 g/mol and 1500 g/mol. Target molecular weight for the polymers was 25,000 g/mol. Phthalic anhydride (PA) was used as an end-capping agent. A BTDA-Bis P-PA polyimide homopolymer was synthesized as a control. The BTDA-Bis P-PDMS copolymers consisted of two copolymers containing approximately 10 and 30 weight percent of the "3.6 K" PDMS segment and one copolymer containing 30 weight percent of the "1.5 K" PDMS segment. Figure 1 gives the general polymer structure. The specific details of the synthesis have been well described elsewhere.[4,5]

Polymer films were cast from solution. The general procedure involved filtering an approximately 5 percent wt/wt polymer solution through a coarse glass frit directly into a flat glass dish, at the bottom of which rested a ferrotype plate with the chromium face upward. The filled dish was covered with perforated aluminum foil to slow solvent evaporation. After 24 hours, the formed film was removed from the ferrotype plate. Further solvent removal was accomplished by heating incrementally to approximately 215°C in a vacuum oven. All films were cast from chloroform, except the (1.5 K) segment siloxane-containing copolymer which was cast from methylene chloride. Polyimide homopolymer films were cast directly against the flat glass dish. Films were stored in a desiccator.

Immediately prior to sorption, the cast films were given final heat treatments in order to remove remaining traces of solvent and also to relax fully any stresses in the films resulting from the solvent casting. A Fisher Scientific Isotemp Programmable Model 838F forced air convection oven was utilized to accomplish two thermal treatments: a quenching from well above the glass transition temperature and an aging just below T_g. Sample films were ramped at approximately 10°C/min to either 275°C for the copolymers or 280°C for the polyimide homopolymer. A given film was held at its maximum temperature for 2 to



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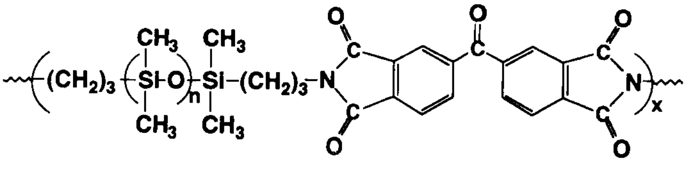

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FIGURE 1 Structures 1 and 2 represent the blocks of the multi-block poly(imide-siloxane) copolymers. Benzophenone tetracarboxylic dianhydride (BTDA) and Bisaniline P (Bis P) form the polyimide block (1). Poly(dimethylsiloxane) preformed oligomers of known molecular weight constitute the other block (2).

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2.5 hours. Quenching involved quickly removing the film from the oven at this time and placing it on a bench top at room temperature-causing it to cool very rapidly. The aging treatment involved ramping the oven temperature down from above T_g at approximately 10°C/min to a temperature 5°C below the T_g which was then held constant for 24 hours. The aged film was then quenched from $T_g - 5°C$ to room temperature.

The sorption experiments were performed on five films. There were two polyimide control films, one quenched film and one aged film. There was one film each of the three siloxane-containing copolymers. Two sorption/desorption cycles were done in the sample chamber on all films except the 30-weight-percent (1.5 K) PDMS copolymer; secondary sorption cycles were done without an intermediate thermal treatment. The 10- and 30-weight-percent (3.6 K) PDMS copolymer films were utilized for both quenched and aged sorption experiments. The films were initially quenched and two sorption/desorption cycles conducted on each. The films were again taken above T_g, in order to attempt to erase any structural memory of sorption, and then the films were aged at $T_g - 5°C$. The films were then sorbed and desorbed twice. The 30-weight-percent (1.5 K) PDMS copolymer film was quenched from well above T_g and sorbed only once. First and second sorption cycles were completed, respectively, within 24 and 48 hours after quenching or aging thermal treatments. Thicknesses of the sorption films are listed in Table I. The film width was limited to approximately 2 centimeters by the size of the mouth of the sorption apparatus sample chamber. Lengths varied between 5 and 6 cm.

Gel permeation chromatography was performed in N-methylpyrrolidinone (NMP) utilizing a Waters 150-C ALC/GPC fitted with a Chromatrix KMX-6 low angle laser light scatterer and a Viscotek differential viscometer. Universal calibration and polystyrene standards were used. Thermal analysis was performed using a Perkin-Elmer TGA 7 Thermogravimetric Analyzer and a Perkin-Elmer DSC 7 Differential Scanning Calorimeter. A Digital DECstation 325c computer with Perkin-Elmer Thermal Analysis Version 2.00 software was used to control the instruments as well as to collect and analyze the data. All TGA experiments were performed in a flowing air

TABLE I
Sorption Film Thickness
(mm)

Film	Thickness
Polyimide Quenched	0.191 ± 0.018
Polyimide Aged	0.163 ± 0.035
10wt% (3.6K) PDMS	0.128 ± 0.004
30wt% (3.6K) PDMS	0.130 ± 0.009
30wt% (1.5K) PDMS	0.139 ± 0.007

environment at a heating rate of 10°C per minute from 30°C to 850–900°C. DSC experiments were performed at a heating rate of 10°C per minute from 30°C to 300°C. Dynamic mechanical thermal analysis was accomplished using a Polymer Laboratories Dynamic Mechanical Thermal Analyzer (DMTA). Subambient to above-ambient temperature scans were run at 2.5°C per minute at frequencies of 1, 5 and 10 Hz.

The sorption of water into the sample films upon exposure to water vapor was determined gravimetrically. The instrumentation utilized for this experiment is shown schematically in Figure 2. A Perkin-Elmer TGS-2 Thermogravimetric System analyzer was fitted with a lengthened sample hook and a sample chamber through which either dry or humid air could be passed. A cylinder of compressed breathing air was used as an "infinite" source of dry air flow through the tubing system and sample chamber, with the outlet at atmospheric pressure. The flowrate was adjusted to be approximately 100 ml/min at the open system's outlet. The dry air could be routed directly to the

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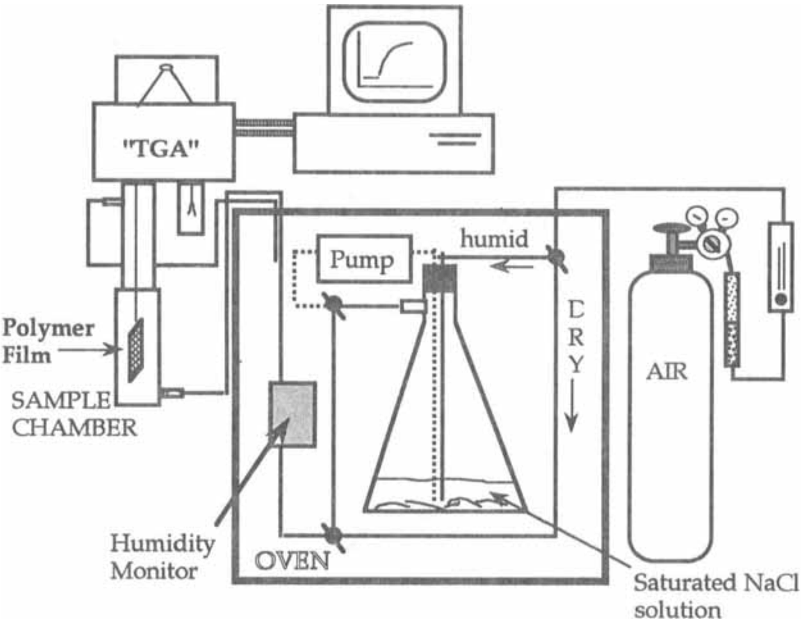

FIGURE 2 Schematic of the gravimetric sorption apparatus. The closed flow path used to pre-equilibrate humidity in the salt solution chamber is indicated by the dotted line.

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sample chamber or it could be diverted first into a 6 liter chamber containing at bottom a saturated sodium chloride/distilled water solution. The salt solution chamber was connected in a separate closed loop to an aquarium air pump, so that controlled humidity could be built up and equilibrated prior to the introduction of the dry air into the solution chamber. Precautions were taken in order to have a properly controlled humidity. The dry air entering the salt solution chamber was passed through the liquid of the saturated solution in order to maximize the humidifying contact. Humidity was monitored by means of a Dickson Temperature/Humidity Meter located in a small chamber immediately before the tubing exited the oven for the sample chamber. The probe tip was placed in the chamber such that it was shielded from direct flow path of the air. The jump in humidity took approximately two minutes to approach maximum.

The average oven temperature was 25 ± 3°C and the average relative humidity provided by the NaCl salt solution at this temperature was 82 ± 2 percent. As a failsafe measure against possible condensation in the insulated bridging tubing, the sample chamber temperature was heated to a slightly higher temperature by means of an exterior thermal tape wrap. The temperatures in the wrap and inside the bottom of the sample chamber were monitored using an Omega 871 Digital Thermometer and Type K thermocouples. The average inner sample chamber temperature over all runs was 32 ± 4°C. The relative humidity inside the sample chamber was estimated using the known average humidity at 25°C and the definition of relative humidity to be approximately 55 percent. Humidity and mass uptake data were collected using a Gateway 2000 386/25 computer and a data collection program. Figure 3 shows the raw mass uptake and humidity curves for the first sorption cycle of the quenched polyimide film. Prior to sorption, each sample film was dried to constant weight in the sample chamber in a flow of dry (approximately 0% R.H.) air. Data points collected at this

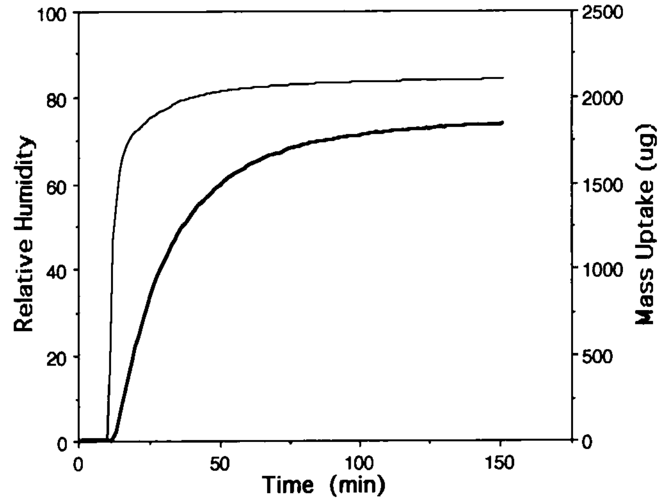

FIGURE 3 Plot of raw data of mass uptake of water vapor in micrograms and relative humidity for polyimide sorption experiment. Thin line is humidity increase; thick line is water weight gain.

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constant weight referenced zero mass uptake. The last data point collected before humid air entered the sample chamber was considered to be the point of time zero.

A blank run of an empty sample chamber was done using the same overall conditions as the sample runs and was subtracted from all sample sorption runs in order to correct for mass uptake not directly related to sorption in the film. The gain in weight was less than 60 micrograms at maximum. Figure 4 is an example of the results of the correction for the first sorption of the aged polyimide sample film.

RESULTS AND DISCUSSION

Gel permeation chromatography was performed on the polymers using NMP as the chromatographic solvent. Both the polyimide control and the BTDA-Bis P-30-wt% (1.5 K) PDMS copolymer were completely soluble in the solvent. The 10- and 30-weight-percent (3.6 K) PDMS copolymer solutions were, however, slightly cloudy and had to be filtered. The GPC viscosity chromatograms of all the polymers are shown in Figure 5. These reveal no evidence of homopolymer contamination in the copolymers; the small peaks to the right are solvent peaks. The intrinsic viscosity of the polyimide homopolymer was found to be 0.54 dL/g, indicating a high molecular weight was attained during polymerization. The number average molecular weight was determined to be 2.46 × 10^4 g/mol and the polydispersity was 2.5. The molecular weight determination of randomly-segmented copolymers by GPC is perhaps less exact due to a lack of predictable correlation between a multicomponent chain's molecular weight and its hydrodynamic volume in a given solvent. The intrinsic viscosities of the 10- and 30-weight-percent (3.6 K) PDMS and 30-weight-percent (1.5 K) PDMS copolymers

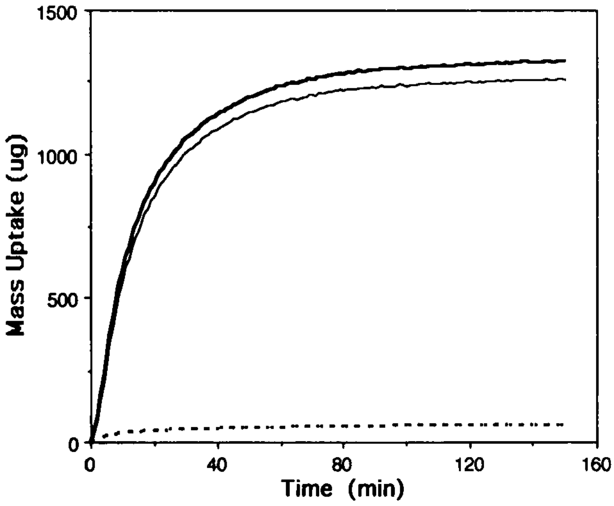

FIGURE 4 Example of the subtraction of the blank run sorption curve from the raw uptake data of the first sorption cycle of the aged polyimide film. The broken line is the blank sorption curve; the thick line is the raw uptake data; the thin line is the corrected uptake data.

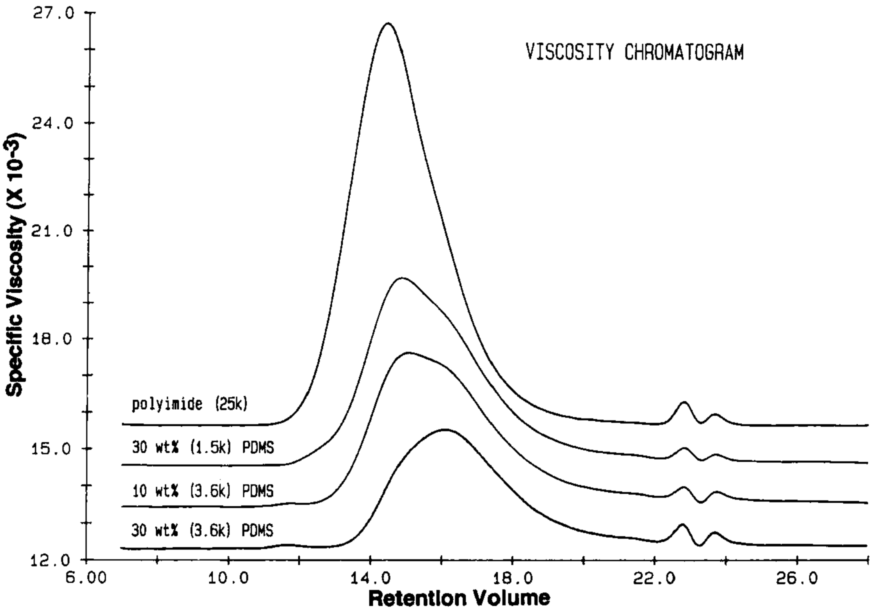

FIGURE 5 GPC elution traces for the polyimide and the poly(imide-siloxane) copolymers.

were 0.28, 0.20, and 0.31 dL/g, respectively. The reduction in intrinsic viscosity and the increase in the retention volume of the copolymers compared with the homopolymer may, in part, be due to the flexibility of the siloxane segments allowing for a more compact hydrodynamic volume.

Thermal gravimetric analysis was performed on the quenched films prepared for the sorption experiments. The TGA traces for the polymers are shown in Figure 6. No appreciable weight loss occurred near the polymer glass transition temperatures, thus indicating the prior removal of the casting solvent. Initial weight loss, which was less than one percent, occurred below 100°C and was confirmed to be the loss of adsorbed surface water by repeated testing of the same sample below degradation temperatures.

Dynamic mechanical thermal analysis (Figure 7) of the films prepared for the sorption experiment revealed more than one transition temperature evident in the drop of the storage modulus. This confirmed the existence of microphase separation in the copolymers. The multi-block copolymers used in this study were expected to exhibit microphase separation. The chemical structures and the solubility of the imide-block and the siloxane-block are very different. The solubility parameter, δ, for the polyimide homopolymer was calculated to be approximately 13.1 $(\mathrm{cal/cm^3})^{1/2}$ using Fedor's table of additive properties of cohesive energy and molar volume listed in Van Krevelen's *Properties of Polymers: Their Estimation and Correlation with Chemical Structure.*[46] Polydimethylsiloxane's solubility parameter has been reported[47] in the range 7.3–7.5 $(\mathrm{cal/cm^3})^{1/2}$. Such chemical dissimilarity promotes microphase separation even when lengths of PDMS are relatively short. (Domain formation of size 30 Å has been reported

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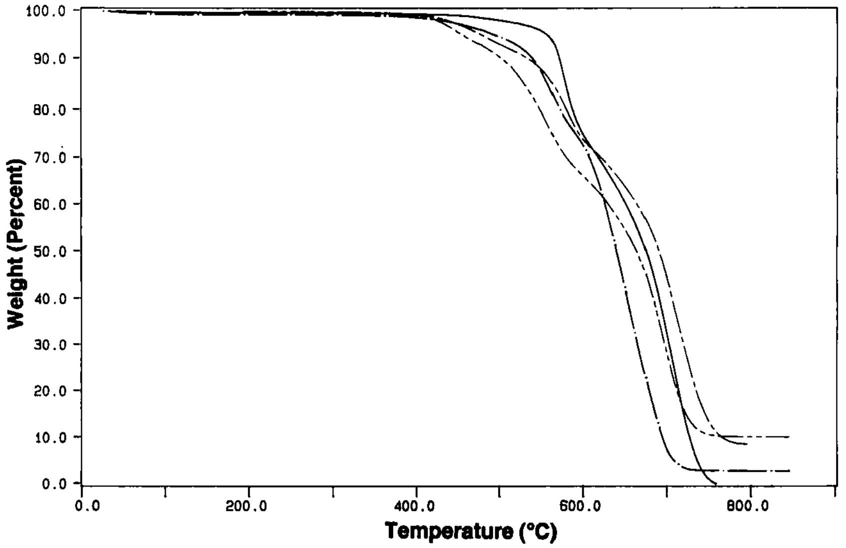

FIGURE 6 TGA weight percent loss in air of polyimide and poly(imide-siloxane) copolymers. Solid line is polyimide. Broken lines with dot, dash and double dash are, respectively, 10 wt%(3.6 K) PDMS, 30 wt%(3.6 K) PDMS and 30 wt%(1.5 K) PDMS copolymers.

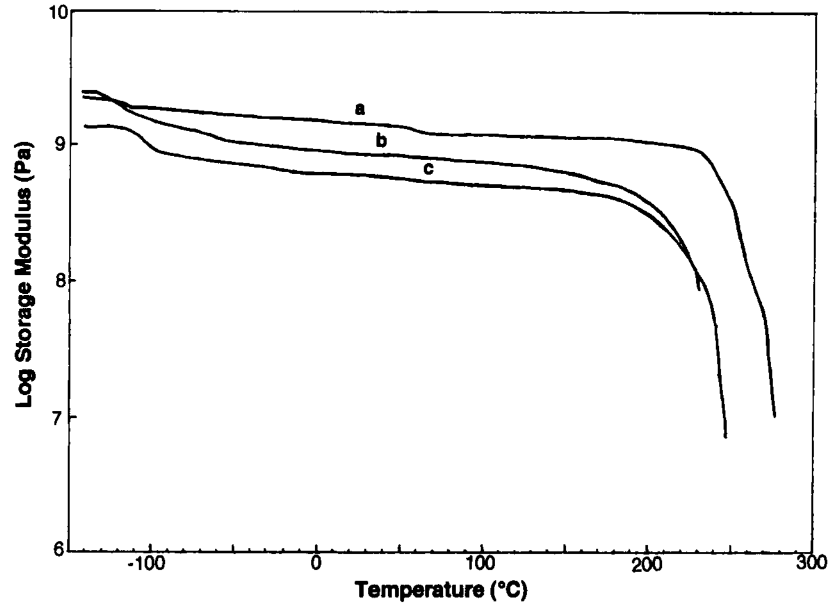

FIGURE 7 DMTA log storage modulus *vs.* temperature at 5 Hz for a) 10 wt%(3.6 K) PDMS, b) 30 wt% (1.5 K) PDMS, and c) 30 wt%(3.6 K) PDMS copolymers.

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for BTDA-DDS-20 wt% (2.0 K) PDMS copolymers, where DDS stands for 3,3'-diaminodiphenylsulfone.[48])

It was difficult to detect the low temperature siloxane glass transition of these copolymers by differential scanning calorimetry. Upper glass transition temperatures corresponding to the imide-block were determined by DSC and are listed in Table II. The T_gs show a dependence on composition. The T_g is considered to be dependent on the imide-block molecular weight in much the same way as homopolymer T_gs vary with molecular weight below the higher entanglement molecular weight. The flexible siloxane segments do not provide much constraint to the polyimide blocks, which can then imitate low molecular weight homopolymer properties. The T_g decreases with decreasing block length. This dependency has been previously observed for poly(bisphenol A carbonate-dimethylsiloxane) microphase-separated multi-block copolymers.[49] For the (3.6 K) PDMS-containing copolymers, the increase from 10- to 30-weight-percent must entail the incorporation of more PDMS blocks on average into a given multi-block copolymer chain, which is assumed here to be in the range of the target molecular weight. The average length of the imide-block must, therefore, decrease and the T_g decreases as well. The T_g of the 30-weight-percent (1.5 K) PDMS copolymer is decreased relative to the T_g of the 30-weight-percent (3.6 K) PDMS copolymer. A greater number of (1.5 K) PDMS segments must be in a given chain (compared with the number of (3.6 K) PDMS segments) to reach a 30-weight-percent incorporation. This further decreases the probable average imide-block length.

Diffusion coefficients were determined for the polyimide and three copolymers from reduced sorption plots of the gravimetric sorption of water vapor. The sorption into free-standing polymer films was determined by following the mass increase of each film as it was rapidly exposed to an environment of approximately 55 percent relative humidity. The mass uptake at infinite times was determined as the average of the corrected mass uptake data points after equilibrium was reached. The fractional uptake was plotted against the square root of the time in seconds divided by the film thickness to give the reduced sorption plots. All of the sorption plots had the similar Fickian characteristics of being linear up to 0.6 fractional uptake as well as being concave to the abscissa above 0.6 fractional uptake and reaching an uneventful equilibrium. Figures 8 and 9 give reduced sorption plots for the first sorption cycles of quenched films and aged films, respectively.

In the reduced sorption data plots, there is a slight deviation from the initial linearity expected for Fickian sorption. This involves a shift along the abscissa away from the origin, which is limited to the first two data points of the sorption curves and is considered to be related to the initial two-minute lag time in the humidity increase. Jou *et al.*[6,13] have recently published reduced sorption plots which have characteristics

TABLE II
Upper T_g of Quenched Films
(°C)

Polyimide Control	260
10 wt% (3.6 K) PDMS	244
30 wt% (3.6 K) PDMS	228
30 wt% (1.5 K) PDMS	220

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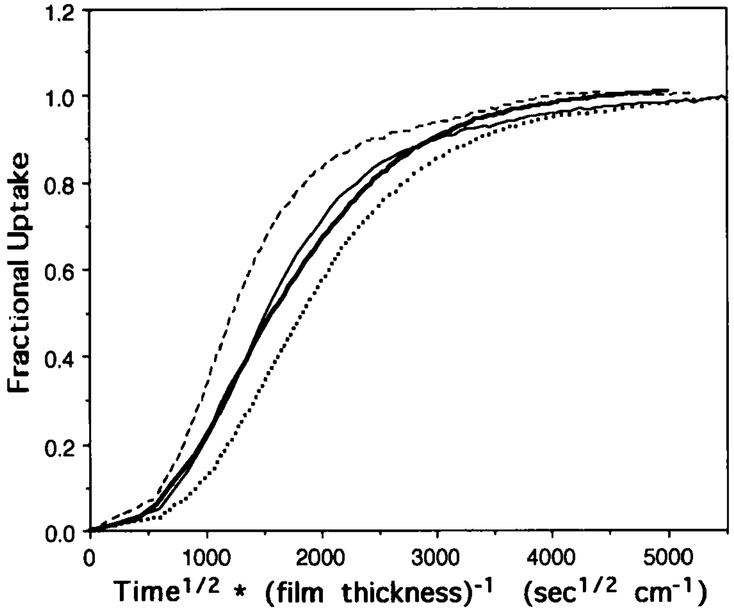

FIGURE 8 Reduced sorption plots for first sorption cycle of quenched films. Curves: polyimide = thick solid line; 10 wt%(3.6 K) PDMS = thick dotted line; 30 wt%(3.6 K) PDMS = thin solid line; 30 wt%(1.5 K) PDMS = thin dashed line.

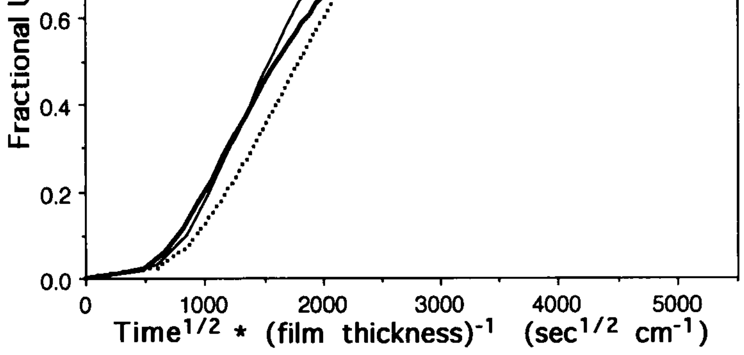

FIGURE 9 Reduced sorption plots for first sorption cycle of $T_g - 5°C$ aged films. Curves: polyimide = thick solid line; 10 wt%(3.6 K) PDMS = thick dotted line; 30 wt%(3.6 K) PDMS = thin solid line.

rather similar to those presented here. Bending beam techniques were utilized to follow the sorption of water[6] and NMP vapor[13] into pyromellitic dianhydride-4,4'-oxydianiline (PMDA-ODA), pyromellitic dianhydride-*p*-phenylenediamine (PMDA-PDA) and 3,3',4,4'-benzophenone tetracarboxylic-*p*-phenylenediamine (BPDA-PDA) polyimides. Uptake was termed Fickian in all cases except for NMP vapor into PMDA-PDA, which was Case II. An initial deviation to the otherwise Fickian sorption curves was noted as an "induction period" and not explained in detail. The NMP/PMDA-ODA sorption induction periods tended to increase as film thickness decreased, indicating perhaps a dependence on film thickness exaggerated by the reduced sorption plot. The water/polyimide studies, however, revealed no clear correlation between induction times and film thickness; the longest induction period occurred in the BPDA-PDA polyimide which the authors considered the most hydrophobic of the three polyimides. In the data presented here, one might argue that the longest "induction period" belongs to the 10-wt%-PDMS (3.6 K) siloxane-containing copolymer. However, it is premature to conclude that this is a manifestation of an extra resistance to water since there are experimental artifacts at work.

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Attempts were made to remove the humidity-increase lag-time but they were unsuccessful due to the design of the sorption apparatus itself. The measurement of approximately 1–2% uptake in small, thin sample films required the incorporation of a sensitive balance such as that in the TGS-2 instrument. The turbulence of rushing water vapor into a pumped-down chamber would have easily dislodged the balance components. Immersion in water would have effectively removed the lag-time, but the interaction with the vapor was of more interest. If the induction period were due to an interfacial resistance one might expect all of the siloxane copolymers to exhibit induction periods greater than that of the polyimide, which would not be expected to have much, if any, delay in uptake. Yet all the induction periods are rather similar. Therefore, it is not felt that this induction period detracts from the primary goal of the paper, which is to determine the bulk diffusion kinetics of the siloxane-containing polymers in comparison with the polyimide homopolymer to observe effects possibly contributing to long-term bond durability.

The initial linear slope of the reduced sorption curves is directly proportional to the square root of the diffusion coefficient. The slope utilized was that of the line of the reduced plot data up to 0.6 fractional uptake. For all experiments, the squared correlation coefficient of the linear regression was between 0.998 and 1.000, indicating very good correlation. The diffusion coefficients obtained from all sorption cycles are listed in Table III. Errors were calculated by standard error propagation rules using only the error in the determination of the film thickness since it is by far the largest contributing error.

The diffusion coefficients were of the order of magnitude of 10^{-8} cm^2/sec. This is larger than most of the diffusion coefficients commonly reported for polyimides in the literature ($\approx 10^{-9}$ cm^2/sec). This increase in diffusion coefficient may be due to several possibilities. Polyimides in the literature are often bulk-imidized and probably have some cross-linking which would reduce the "openness" of the resulting polymer compared with the solution-imidized polymers studied here. The Bis P component of the imide structure may allow for greater flexibility than some of the more commonly-studied polyimides. Small amounts of low molecular weight impurities such as solvent or a larger number of chain ends compared with literature polyimides would have also

TABLE III
Diffusion coefficients
$D \times 10^8$ (cm^2 sec^{-1})

	Quenched	Aged
First Sorption Cycle:		
Polyimide Control	4.2 ± 0.8	4.5 ± 1.9
10 wt% (3.6 K) PDMS	4.2 ± 0.2	4.8 ± 0.3
30 wt% (3.6 K) PDMS	6.1 ± 0.9	6.9 ± 1.0
30 wt% (1.5 K) PDMS	10.0 ± 1.0	nd*
Second Sorption Cycle:		
Polyimide Control	3.9 ± 0.7	4.2 ± 1.8
10 wt% (3.6 K) PDMS	3.7 ± 0.2	4.5 ± 0.2
30 wt% (3.6 K) PDMS	6.3 ± 0.9	6.7 ± 0.9
30 wt% (1.5 K) PDMS	nd	nd

* not determined

increased free volume and influenced diffusion. TGA experiments, however, indicated polymers without solvent impurity.

Although there appears to be slight decrease in diffusion coefficient in many cases for the second sorption cycle, all but one of the sorption cycle pairs are the same within error. A comparison of the results of the quenched and aged films for both the first and second sorption cycles reveals, if errors are ignored, a slight apparent increase in diffusion coefficients. For the 3.6 K PDMS copolymers, whose films were used for both the quenched and aged sorption studies, it might be suggested that this is the result of the previous sorption cycles opening the structure; however, the aged polyimide film, which shows the same trend, had not been previously sorbed. The quenched and aged values for these conditions are generally not significantly different given the error involved.

The most significant results from these sorption experiments are contained in the comparison of the diffusion coefficients of the different polymers studied. The discussion will focus on the values determined for the primary sorption study of the quenched samples only. The diffusion coefficients of the polyimide control and the 10-weight-percent (3.6 K) PDMS copolymer are the same within error. The diffusion coefficient of the 30-weight-percent (3.6 K) PDMS copolymer increases to 1.5 times that of the 10-weight-percent (3.6 K) PDMS copolymer and is significantly different. Although perhaps not strictly comparable, since the film was cast from methylene chloride, the diffusion rate in the 30-weight-percent (1.5 K) PDMS copolymer was much faster than the other polymers: 1.6 times faster than the 30-weight-percent (3.6 K) PDMS copolymer and 2.4 times faster than the polyimide and 10-weight-percent (3.6 K) PDMS copolymer. It is apparent from this trend that the incorporation of PDMS into the polyimide tends to increase the ease of diffusion of a penetrant, in this case water vapor. This is not very surprising if viewed in terms of a free volume phenomenology of diffusion.

References which discuss free-volume-related diffusion theories in more detail have been given in the introduction. Generally the assumption is that the penetrant diffuses by jumping in and out of holes equal to or larger than the penetrant size. For the case of small penetrant molecules in a polymer matrix, the jump rate of the small molecules is

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much greater than the rate of formation of adjacent vacancies. Therefore, the diffusion coefficient becomes proportional to a limiting rate of adjacent critical size hole formation which is influenced largely by the available free volume related to the mobility of segments of the polymer chains. The greater is the probability of hole formation, the greater should be the rate of diffusion. Only a simple version of the free volume approach will be used here for the purpose of discussion. The WLF equation, which has often been used in free volume based diffusion theories, assumes a linear increase with temperature in fractional free volume above the glass transition temperature. The fractional free volume, f_g, at the glass transition temperature is similar for all polymers and has been estimated to be 0.025.[50] A simplistic explanation for the increase in diffusion coefficient with incorporation of siloxane is contained in this equation. The glass transition temperature of the polyimide homopolymer film was 260°C. The T_g of poly(dimethylsiloxane) is approximately -127°C.[51] The temperature of the sorption experiments was just above room temperature so the polyimide is well below its T_g while the PDMS is well above its T_g. Assuming no physical aging, polyimide fractional free volume is fixed at the T_g value of f_g. The fractional free volume of the PDMS is much greater than that of the polyimide. The incorporation of siloxane into the polyimide, therefore, increases the available free volume for diffusion. A similar conclusion is possible if one considers the extreme flexibility of PDMS compared with the polyimide. (Flexibility is, of course, intimately related to chain chemical structure and the glass transition. The diffusion coefficient of water in a silicone has been reported to be 3.5×10^{-5} cm^2/sec near room temperature.[1])

The increase in free volume due to the incorporation of the flexible, low T_g siloxane can be used as a general explanation for the increase in the rate of diffusion as determined by experiment. The actual trends observed are perhaps better explained in terms of a consideration of the expected bulk morphology of the microphase-separated copolymers. The siloxane domains are localized areas of increased free volume. If the areas of increased free volume become more probable, or in other words are more greatly and uniformly distributed throughout the polymer, then the probability of adjacent hole formation is increased and the movement of the diffusing species is made easier. The diffusion coefficient will thus increase. In the case of the 10-weight-percent (3.6 K) PDMS copolymer, it is expected that the siloxane domains are dispersed in a continuous phase of polyimide. The polyimide phase is perhaps of high enough molecular weight to have small-scale motion properties similar to that of the polyimide homopolymer. The number of localities of free volume increase is small since the copolymer is only ten weight percent PDMS and ninety weight percent polyimide. The probability of a diffusant encountering increased local free volume is increased slightly compared with the control polyimide, but perhaps this cannot be capitalized upon due to a limiting rate of diffusion in the surrounding polyimide phase. The diffusion coefficient was not found to increase significantly given the error.

In the other siloxane-containing polymers, the diffusion coefficient does increase. The greater incorporation of siloxane allows for a greater amount of siloxane to be distributed throughout the polymer--thus increasing the hole formation probability and the diffusion coefficient. A comparison of the diffusion coefficients of the two 30-weight-percent PDMS copolymers indicates that the decrease in siloxane segment length causes an increase in diffusion as well. This is again due to an increase in the probability of increased local free volume for hole formation. The 1.5 K PDMS segments are of lower molecular weight and a greater number of segments must be incorporated into a given multiblock chain to attain 30 weight percent. The number of covalent bonds between the two dissimilar blocks must increase making complete phase-separation more difficult. The structural linkages are a built-in contribution to entropy which forces the imide segments to be more closely associated with the flexible siloxane. This distributes free volume more evenly and increases local hole-formation probability. Another way to view this involves the imide-block molecular weight. The lightly restrained imide-blocks were described above to imitate homopolymer properties with regard to upper glass transition temperatures, which involve large scale macromolecular motions. In homopolymers, the lowering of the T_g with decreasing molecular weight (below an entanglement weight) can be visualized in terms of an increase in free volume associated with chain ends. In the copolymers, it might be considered that the available free volume for small scale motions in the polyimide phase itself becomes influenced by the decrease in molecular weight of the imide-blocks.

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CONCLUSION

Diffusion coefficients determined by gravimetric sorption were slightly larger than expected when compared with common literature values for polyimides, but they were not unreasonable. The incorporation of higher levels of polydimethylsiloxane into the copolymers was found to cause a definite increase in the rate water diffusion. The increase in diffusion rate for the 30-wt% siloxane-containing copolymers was found to be influenced by siloxane segment length and was explained in terms of a free volume interpretation. The flexible, low-T_g siloxane segments were considered to contribute extra free volume in localized regions of the microphase-separated copolymers. The increased diffusion coefficients suggest a decreased resistance to water ingression. The diffusion coefficient of the 10-wt% PDMS copolymer, however, was found not to be significantly increased relative to the polyimide, indicating that perhaps the regions of increased free volume were too localized. Slower diffusion in the polyimide phase was believed to be a limiting factor.

In this paper, and in a previous paper,[5] bulk and surface properties of poly(imide-siloxane) copolymers have been characterized in an attempt to determine the important factors in resistance to water ingression. Inverse gas chromatography was previously used to conduct a surface energetics study on the two (3.6 K) PDMS-containing copolymers and the polyimide homopolymer control. The incorporation of siloxane into the polyimide was shown to increase resistance to water vapor due to the hydrophobicity of the siloxane-rich surface and it appeared that there was a minimum weight-percent of siloxane incorporation required to maximize the water resistance of the copolymer's surface. Although siloxane incorporation increases hydrophobic surface resistance to water, higher siloxane concentrations also increase the rate of diffusion of water inside the bulk of the polymer. This would presumably allow water to speed toward an adhesive bondline and possibly decrease durability. It appeared from this work, however, that an increased water resistance of the surface can be achieved at lower siloxane concentrations without greatly decreasing bulk mechanical or increasing the bulk diffusive properties to undesirable levels.

The original question of the reason for the increased hot/wet durability of the lap shear joints bonded with siloxane-containing polyimides might be more completely answered by a study of the stress distribution in the joint adhesive layer during the swelling of the polymer upon water sorption. Water has a decreased solubility (which is related to total equilibrium mass uptake) in copolymers that have an increased hydrophobic character not only at the surface but also throughout the bulk. The smaller the amount of water that can sorb into a given adhesive bonding layer, the lower will be the associated swelling stresses. The increased adhesive bond durability of these copolymers may be in part related to a reduction of such swelling stresses.

Acknowledgements

The authors would like to thank Mr. Tim Flynn for providing the 30-weight-percent (1.5 K) PDMS copolymer, Dr. Laura Kiefer for providing 1.5 K aminopropyl-terminated PDMS precursors, Dr. Saikat Joardar for the dynamic mechanical analysis, Dr. Martin Konas for the GPC analysis, and Dr. H. Francis Webster for the data collection program of the sorption experiment.

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