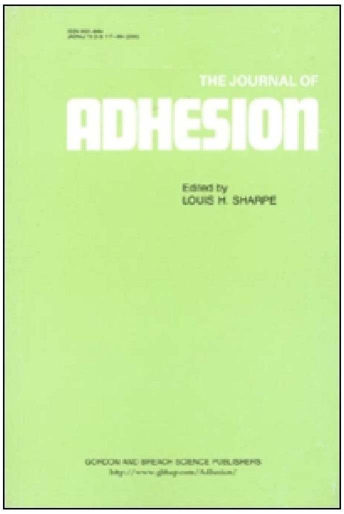
This article was downloaded by:
On: *22 January 2011*
Access details: *Access Details: Free Access*
Publisher *Taylor & Francis*
Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



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: An IGC Surface Energetics Study

Joyce M. Kaltenecker-Commerçon[a]; T. C. Ward[a]
[a] Department of Chemistry and NSF Science & Technology Center: High Performance Polymeric Adhesives and Composites, Virginia Polytechnic Institute and State University, Blacksburg, Virginia, USA

To cite this Article Kaltenecker-Commerçon, Joyce M. and Ward, T. C.(1993) 'Water Resistance of Poly(imide-siloxane) Adhesives: An IGC Surface Energetics Study', The Journal of Adhesion, 42: 1, 113 — 124

To link to this Article: DOI: 10.1080/00218469308026575
URL: http://dx.doi.org/10.1080/00218469308026575

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: http://www.informaworld.com/terms-and-conditions-of-access.pdf

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

J. Adhesion, 1993, Vol. 42, pp. 113–124
Reprints available directly from the publisher
Photocopying permitted by license only

Printed in the United States of America.

Water Resistance of Poly(imide-siloxane) Adhesives: An IGC Surface Energetics Study*

JOYCE M. KALTENECKER-COMMERÇON and T. C. WARD**

Department of Chemistry and NSF Science & Technology Center: High Performance Polymeric Adhesives and Composites, Virginia Polytechnic Institute and State University, Blacksburg, Virginia 24061, USA

(Received September 29, 1992; in final form January 7, 1993)

Inverse Gas Chromatography was utilized to examine the interaction of water vapor with the surfaces of a polyimide homopolymer and poly(imide-siloxane) random-block copolymers of increasing siloxane content. The studies employed 45–60 meter, thin-polymer-film mega-bore capillary columns to maximize surface area. The free energies of specific surface interaction with water and the dispersive components of the solid surface free energies were determined. An increase in the polymer siloxane content from 0-wt% to 10-wt% resulted in a decrease of approximately 4 kJ/mol in the free energy of water-specific surface interaction. A further increase in siloxane content to 30-wt% was not found to increase surface water resistance significantly. Dispersive components of the solid surface free energies of the copolymers were comparable to values reported for poly(dimethylsiloxane) homopolymer.

KEY WORDS poly(imide-siloxane) copolymers; adhesive water resistance; interaction of water vapor with polymer surfaces; free energy of specific interaction of water vapor; dispersive component of polymer surface free energy; capillary inverse gas chromatography.

INTRODUCTION

The durability of many adhesive-adherend systems is decreased by the ingression of water. Recent work[1] has shown that the incorporation of poly(dimethylsiloxane) segments into polyimides increases the adhesive polymer's resistance to water ingression. Both bulk and surface characteristics may contribute to this resistance. The high surface concentration of hydrophobic siloxane, revealed by ESCA studies, suggests a barrier to the initial entry of water into the bulk. The resistance to water may also be related to morphology. Sorption studies have shown not only that water mass uptake is decreased by increased siloxane content but also that it is dependent on siloxane segment length for a given weight-percent siloxane. Siloxane-containing

---

*Presented at the Symposium, "Adhesion Science and Technology," held in Washington, DC, USA, August 23–24, 1992 and sponsored by the Division of Polymeric Materials: Science and Engineering of the American Chemical Society.

**Corresponding author.

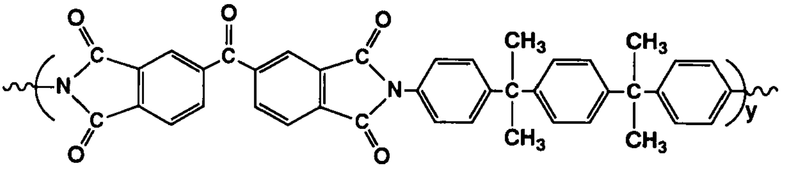
polyimides have also been found to have increased adhesive durability in hot/wet environments compared with homopolymer polyimides.[2] The influence of siloxane incorporation on water ingression can be examined by a study of the bulk and surface interactions of H_2O with a series of poly(imide-siloxane) copolymers of increasing siloxane content. In the present study, Inverse Gas Chromatography (IGC) was used to examine the interaction of water vapor with the polymer surfaces.

IGC's advantages of speed and the ability to characterize polymers in the highly concentrated state have caused its use to become more widespread. The theory and technique have been well discussed and reviewed by several authors.[3-5] Much of the more recent literature has been reviewed by Voelkel.[6] The early work of Smidsrød and Guillet[7] led the way for several studies involving the IGC detection of the glass transition, based on the change of the probe retention mechanism from surface adsorption well below the glass transition to predominantly bulk sorption well above the glass transition.[8,9] A large number of IGC studies have sought since then to exploit the bulk sorption retention mechanism in order to examine bulk polymer solution properties such as diffusion[10-13] and Flory-Huggins polymer-solvent and polymer-polymer interaction parameters.[14-17] Some work has involved poly(dimethylsiloxane) copolymers and blends.[18,19] Polymer surfaces have also been studied using IGC at temperatures well below the glass transition. Heats of adsorption, surface areas[20] and adsorption isotherms[21] can be determined for polymer or other solid surfaces. Studies have been done on the surface characteristics of solvent-cast polymers.[22,23] Acid/base interactions have been characterized at polymer surfaces[24-26] and at other surfaces such as carbon fibers[26-30] and glass beads/fibers.[31,32]

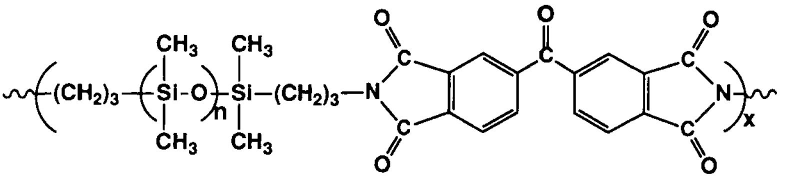
EXPERIMENTAL

The polymers used in this study were made by Dr. Attila Güngor associated with Dr. J. E. McGrath's Synthesis Group at VPI & SU. The randomly-segmented poly (imide-siloxane) copolymers were synthesized from benzophenone tetracarboxylic dianhydride (BTDA), bisaniline P (Bis P), and aminopropyl poly(dimethylsiloxane) (PDMS) pre-formed oligomers of an approximate molecular weight of 3600 g/mol (3.6 K). Phthalic anhydride was used as the end-capping agent. Two copolymers or roughly 10- and 30-weight-percent poly(dimethylsiloxane) were prepared. A polyimide control polymer was also prepared without the PDMS segments. The general structure of the copolymers is shown in Figure 1. The synthesis has been previously described.[33]

The IGC surface studies were performed using a Hewlett-Packard 5890 Series II gas chromatograph, which was equipped with a Series II thermal conductivity detector cell suitable for use with capillary columns. Prior to the collection of data, the columns were conditioned at 110°C under constant helium gas flow. The conditioning lasted for at least 24 hours or until a stable baseline with a threshold of zero or below was obtained. The experimental data from the chromatographic analyses were plotted and analyzed by an HP 3396A integrator linked to the gas chromatograph. Injections of probe vapor (mixed with nitrogen as a non-adsorbing marker)



1



2

FIGURE 1 Structures 1 and 2 represent the blocks of the random-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).

into the columns were accomplished with an HP 19395A headspace sampler. The carrier gas and approximate column flow rate used in all analyses were, respectively, dry helium and 5 ml/min. The probes used in this study were distilled water and the homologous series of n-alkanes from nonane to dodecane. All n-alkanes were from Aldrich Chemical Company, Inc. in the 99% or 99+% pure state.

The surface study employed capillary columns in order to maximize surface area and increase peak resolution. Polyimide control homopolymer and 10- and 30-weight-percent poly(imide-siloxane) copolymer capillary columns were successfully made using the static coating method.[34] Six Hewlett-Packard 30-meter mega-bore (0.53 mm I.D.) fused-silica capillary columns, two of each polymer, were prepared; final experimental columns ranged in length from 45 to 60 meters and consisted of the two columns connected in series. The capillary coating apparatus utilized to static-coat the columns was designed and built in the laboratory. It is shown schematically in Figure 2 and consisted primarily of a temperature-controlled double water bath and mobile pressurizable-depressurizable modified vials, which are depicted in Figure 3. The vials were placed at the head and the tail ends of the column.

To summarize, the static coating method involved filling the column with the polymer solution. One end was then sealed (capped) and the solvent was slowly removed by vacuum-aided evaporation from the open end. As the evaporation meniscus travelled away from the open end and toward the capped end, the polymer was coated against the inside walls of the column in an annular film. The concentration of the polymer solution determined the final film thickness. The solvent chosen for the purpose was required to dissolve the polymer and not to have a high boiling point. In order for the coating procedure to be successful, the incorporation of

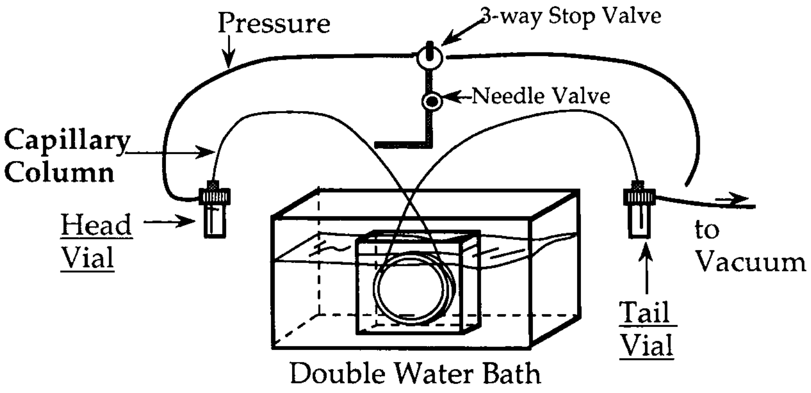


FIGURE 2 Schematic of the Capillary Column Coating Apparatus. Not shown in picture: mobile support system for the vials and vacuum line as well as the temperature controllers that were located in the outer portion of the double water bath.

dissolved air or air bubbles in the polymer solution in the column or at the sealed column end was avoided. If an air bubble was present in the solution-filled column when vacuum was applied to the open end, the bubble moved toward the vacuum and pushed the intervening polymer solution out of the column into the vacuum line.

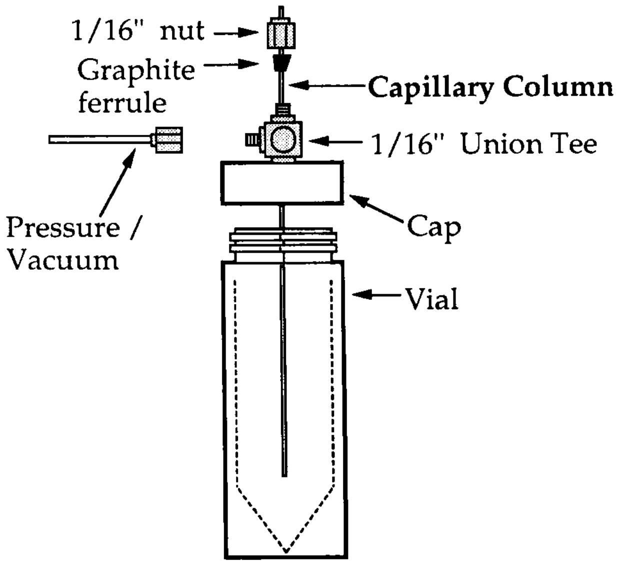


FIGURE 3 Detailed schematic of heavy-walled ≈ 10 milliliter pressurizable glass vial and modified vial cap. Stainless steel union tee fitting is put through a hole drilled in the cap and sealed in place with commercial epoxy.

The polymers were dissolved in methylene chloride to obtain solutions of approximately 0.75% (wt./wt.) concentration. One polyimide column was prepared using a 3.0% (wt./wt.) solution. (These resulted in film thicknesses of approximately one and four micrometers, respectively.) Immediately before beginning the coating procedure, the polymer solution was separately filtered using a coarse glass frit and then degassed *via* sonication under vacuum. The solution, located in the head vial, was pulled into the column under reduced pressure to avoid the re-incorporation of air. Once the column was filled in this manner, however, some extra solution was still pushed through the column in order to remove any possible axial concentration gradient formed by the solvent evaporation at the travelling meniscus, which was in contact with the vacuum.

Once filled, the column was sealed with a two-part, room-temperature curing, commercial epoxy at the tail end using a technique adapted from C. A. Pawlisch.[35] Degassed distilled water was used as a buffer liquid between the polymer solution and the epoxy. As soon as the column was appropriately filled, the buffer water was forced up one meter in length of the tail end of the column by means of pressurized helium. Care was taken not to introduce an air bubble between the polymer solution and water phases. The well-mixed epoxy was drawn into a short length of 1/50 inch (0.5 mm) I.D. silicone tubing *via* syringe. A small droplet of the distilled water was pushed out the column end by means of another syringe attached to the opposite end of the column. The epoxy-filled tubing was forced over the water droplet and the column end. The epoxy was then forced into the column end and was allowed to harden into a seal at least eight hours before vacuum was applied to the open end. This capping technique produced successful seals after only a few attempts.

The capillary column, filled with the polymer solution and successfully capped, was then placed in the equilibrated double water bath in order to shield it from temperature gradients during evaporation of the solvent. Vacuum was then applied to the open (head) end of the column and the meniscus moved slowly away from the vacuum and towards the capped tail end. The bath temperature for the polyimide columns was approximately 23°C. The bath temperatures for the two siloxane-containing polymers were required to be slightly lower in order to initiate the withdrawal of the travelling meniscus toward the capped end. The 10wt%(3.6 K)PDMS copolymer columns were coated at 20°C. The 30wt%(3.6 K)PDMS copolymer columns were coated at 17°C. Successful coating procedures produced complete, uniform annular films in the columns.

Errors were propagated in order to obtain an estimate of precision. The error in the infinite dilution values of the corrected retention times was determined as the error in the intercept of the regression line. Standard error propagation methods were used in cases of addition and multiplication of values with knowable errors. The final steps in the determination of the ΔG°_{sp} and γ_s^d values, however, involved a linear regression of the points obtained from the n-alkane injections to determine the dispersive reference line. The standard equations for errors in the slope and intercept of a regression line only take into account the error related to the fitting of the line to the data, not the errors associated with the data point coordinates themselves. "Weighted" regression methods which can include several values of the dependent "y" for each independent "x" do exist, but a standard method for propagating the calculated errors in the y-coordinates of the regression points into the errors of the regression slope and intercept was not readily available. In order to obtain propagated values, a method was developed which involved performing a linear regression on each possible combination of the n-alkane point (x,y) coordinate values, where y-coordinates vary as $y + \delta y$, y, and $y - \delta y$.[34] This gave 3^n possible combinations, where n is the number of n-alkane data points on the dispersive reference line. The linear equations thus obtained were used to determine 3^n coordinate values for the dispersive reference point for water and 3^n values for the dispersive slope. The average of the 3^n water reference points and 3^n slopes equaled the values obtained from the original regression line. The best estimate of the standard deviation (BESD) of each average was used as the propagated error for each value. Errors in the x-coordinate could not be propagated because regression analysis requires x to be the independent variable; in any case, the error in the ordinate values was approximately an order of magnitude greater than the error in the abscissa values.

THEORY

Inverse Gas Chromatography utilizes the same instrumentation and fundamental theory as conventional gas chromatography. The object of study is the stationary phase inside the column rather than the mobile injected material. The injected material consists of a single pure solvent (called a probe) whose properties are known. The partitioning of the probe molecules between the mobile carrier gas and the stationary phase causes the probe to be retained in the column for a period of time, which, relative to a non-interacting marker probe, is an indication if its affinity for the stationary phase. This raw retention time is the primary experimental datum.

IGC can be used to examine the dispersive and non-dispersive interactions of probes with the polymer stationary phase surface. The dispersive n-alkane reference line can be obtained through the following equations.[27] The free energy of adsorption or desorption, ΔG°, can be written:

$$\Delta G^\circ = RT \ln V_n + K \tag{1}$$

where "R" is the universal gas constant, "T" is the temperature, "K" is a sum of constants and the net retention volume, V_n, is a probe retention time corrected for experimentally variable factors. This union of surface thermodynamics and chromatography assumes the probe interacts with the surface at infinite dilution so that equilibrium is achieved. Equilibrium is ideally indicated by Gaussian elution peaks. The work of adhesion, w_A, per unit surface area, between a probe and a solid surface can be related to the free energy by:

$$\Delta G^\circ = N_A \, a \, w_A \tag{2}$$

where "N_A" is Avogadro's number and "a" is the probe molecule surface area. In the case of dispersive or Van der Waals type interactions, w_A can be written in this form:[36]

$$w_A = 2(\gamma_s^d \gamma_l^d)^{1/2} \tag{3}$$

where γ_s^d and γ_l^d are, respectively, the dispersive components of the solid and liquid surface free energies. By substitution one obtains:

$$RT \ln V_n = 2\, N_A\, (\gamma_s^d)^{1/2}\, a\, (\gamma_l^d)^{1/2} + K \tag{4}$$

A plot of "a $(\gamma_l^d)^{1/2}$" *versus* the left-hand-side of the equation gives a straight line for a homologous series of normal alkanes. The dispersive component of the solid surface free energy, γ_s^d, of the polymer stationary phase can be determined from the slope of this reference line.

$$\gamma_s^d = (\text{slope}/2N_A)^2 \tag{5}$$

A polar probe is capable of having both dispersive and non-dispersive interactions with the stationary phase surface. Data corresponding to the injection of a polar probe will, therefore, fall above the dispersive reference line. The free energy of specific surface interaction is obtained by subtracting the corresponding dispersive interaction, obtained from the reference line, from the total interaction of the polar probe. The mathematical expression is:

$$\Delta G_{sp}^{\circ} = RT \ln\, (V_n/V_{nR}) \tag{6}$$

where V_n is the net retention volume of the polar probe and V_{nR} is the corresponding value from the dispersive reference line. The temperature, T, must be well below the glass transition temperature of the polymer.

DISCUSSION AND RESULTS

Maximum injected amounts were estimated to be in a range of approximately 1 to 3 micrograms (μg) using the ideal gas equation and various injection conditions involving capillary split ratio and headspace sampler factors such as gas sampling valve volume, sample-vial volume and temperature. Rough estimates employing the approximated maximum amounts place the minimum injected amounts in the tenths of micrograms. These injection amounts are just inside and above the range of injection amounts recommended by Conder and Young[37] for infinite dilution surface analysis. The water vapor peaks showed little asymmetry and were considered Gaussian. The n-alkane peaks, however, did show some tailing, which decreased as the study temperature increased. (Higher column temperatures may allow the partitioning process to come closer to achieving equilibrium.) Retention times corrected for dead volume were extrapolated to infinite dilution values using from six to ten injections for each probe at each study temperature; retention times were generally independent of the amount injected, although a slight dependence was seen for the higher n-alkanes at the lower temperatures. The most reliable data for the infinite-dilution-based theory is considered to be that from the study at 50°C.

The physical properties of the probes required by the theory were either estimated or obtained from the literature. The dispersive components of the liquid surface free energies (γ_l^d) of the probes were obtained from Kaelble[38] and Jasper.[39] The surface area of a probe molecule, a, was estimated for the n-alkanes by an extrapola-

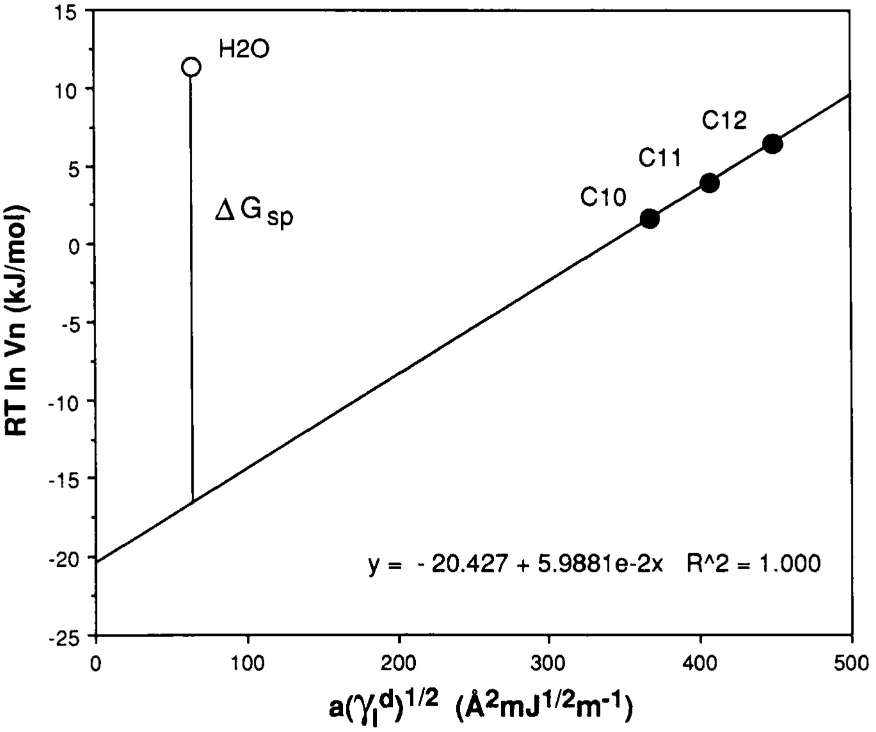


FIGURE 4 Surface energetics plot of equation (4) for injections of n-alkanes and water onto polyimide homopolymer control column at 50°C.

tion of the n-alkane surface area data given by Schultz and Lavielle.[28] The surface area of the molecular probe water was estimated using Van der Waals radii and bond lengths to be approximately 14 Å^2. This estimated value compares relatively well with the value of 12.5 Å^2 reported by McClellan and Harnsberger[40] as the area per adsorbed water molecule averaged from several values obtained from experiments reported in the literature. Values in the literature range from approximately 11 to 21 square Angstroms.[40,41] The estimated values for the experimental probes should be sufficient for a valid relative comparison between the polymer systems.

The surface energetics plot obtained for the polyimide homopolymer at 50°C is shown in Figure 4. The open circle represents the water datum. The dispersive reference line was obtained by injecting the n-alkanes decane, undecane, and dodecane. The difference between the ordinates of the water datum point and the point directly below it on the dispersive reference line represents the free energy of specific surface interaction. Similar surface energetics studies were conducted on the 10- and 30-weight-percent siloxane copolymers. The 30-weight-percent study at 40°C, which involved the injection of nonane as a fourth n-alkane, is shown in Figure 5.

The free energies of H_2O-specific surface interaction obtained from the surface energetics studies on the three polymers at the various temperatures are given in

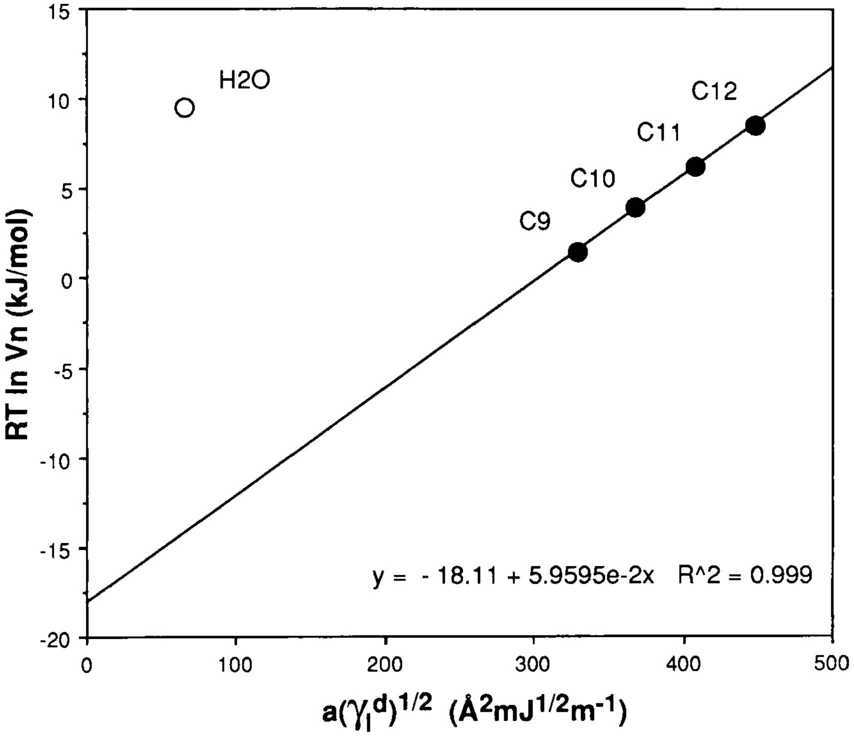


FIGURE 5 Surface energetics plot of equation (4) for injections of n-alkanes and water onto 30-weight-percent siloxane copolymer column at 40°C.

Table I. All the values are slightly above the range of bond energies expected for permanent dipole-dipole interactions such as hydrogen bonds (excluding fluorine) and other dipole-dipole interactions (excluding hydrogen bonds).[42] It is interesting to note that although the calculated surface area for the water probe allows for a valid comparison between systems, it is still a somewhat arbitrary choice. Its value directly influences the values obtained for the free energies of specific interaction. The use of a smaller reported value would have increased the values, whereas the use of a slightly larger reported area would have placed the results more comfortably into the expected range for hydrogen bonds.

TABLE I
Free energy of specific surface interaction (ΔG°_{sp} in kJ/mol)

	50°C	40°C	30°C
Control	27.9±0.9	26.6±1.3	26.7±1.2
10 wt% PDMS	23.7±0.8	25.2±1.0	23.9±1.4*
30 wt% PDMS	22.9±1.2	23.7±0.8	22.9±1.2

*Actual Study Temperature: 35°C

TABLE II
Solid surface free energy dispersive component at 50°C (γ_s^d in mJ/m^2)

Control	24.7 ± 2.1
10 wt% PDMS	20.6 ± 1.7
30 wt% PDMS	21.1 ± 2.6

The 10-percent increase in siloxane from the polyimide control to the 10-weight-percent copolymer resulted in an approximately 4 kJ/mol decrease in the free energy of H_2O-specific surface interaction at 50°C. The hydrophobic and flexible poly(dimethylsiloxane) has a lower surface free energy that drives it to migrate to the surface of the copolymer, which causes the reduction in water interaction.[43] The surface study at 50°C conducted using the 30-weight-percent siloxane copolymer shows a further 0.8 kJ/mol decrease in the water specific interaction. This decrease is not significant given the precision of these experiments. Decreases in the interaction free energy with increasing siloxane content are also seen at the lower study temperatures. The accuracy of these values, however, is considered to be less than that of the 50°C study for reasons stated above.

The dispersive components of the solid surface free energy determined for the three polymers in the 50°C study are listed in Table II. The values for the two siloxane-containing copolymers are indistinguishable given the error associated with the measurement. As previously noted, the copolymers are expected to have a surface dominated by the PDMS component and so should have surface characteristics very similar to a PDMS homopolymer. The dispersive component of the solid surface free energy of PDMS has been reported to be 21.7 mJ/m^2 by Owens and Wendt.[44] The measured dispersive components of 20.6 and 21.1 mJ/m^2 are equal, within error, to this value. One might also reasonably expect the value of the dispersive component of the solid surface free energy of the polyimide control to be higher than that for a methyl-dominated PDMS-type surface.

These studies suggest that the siloxane surface coverage has reached a maximum effective level at 10-weight-percent PDMS incorporation, at least with regard to interactions with water and n-alkane vapor. However, a maximized siloxane surface coverage might be attained at lower siloxane contents. Although 3600 g/mol PDMS-containing copolymers of this system with lower weight percents siloxane were unavailable for study, general surface characterization has been conducted on a number of other PDMS-containing block copolymers.[1,33,45–50] As little as five percent incorporated siloxane can result in an appreciable amount of siloxane at the surface of block copolymers.[1,50] Surface coverage, however, has also shown a dependence on the molecular weight of the siloxane block, with higher molecular weights leading to an increased ease of microphase-separation and more complete siloxane surface coverage.[46,50]

CONCLUSIONS

It has been shown that the incorporation of siloxane segments into the polyimide decreases the specific interaction of water vapor with the polymer surface. This indicates that the surface does have some role to play in the water resistance. The further increase in the amount of siloxane to 30-weight-percent has not been shown to reduce significantly the specific interaction or increase the water resistance compared with the 10-weight-percent copolymer. This suggests that only 10-weight-percent siloxane (or less) is needed to maximize the surface contribution to the water resistance. The incorporation of such low percentages of siloxane is favorable for structural adhesives in that the higher strength properties of the continuous polyimide phase are maintained.

References

1. C. A. Arnold, J. D. Summers, Y. P. Chen, R. H. Bott, D. Chen and J. E. McGrath, *Polymer* **30**(6), 986 (1989).
2. R. H. Bott, J. D. Summers, C. A. Arnold, L. T. Taylor, T. C. Ward and J. E. McGrath, *J. Adhesion* **23**, 67 (1987).
3. J. M. Braun and J. E. Guillet, *Adv. Polym. Sci.* **21**, 108 (1976).
4. J. S. Aspler in *Pyrolysis and GC in Polymer Analysis*, Vol 29, Chromagraphic Science Series, S. A. Liebman and E. J. Levy, Eds. (Marcel Dekker, Inc., New York, 1985), p. 399.
5. J. E. G. Lipson and J. E. Guillet, *Development in Polymer Characterization-3*, J. V. Dawkins, Ed., (Applied Science Pub., London, 1982).
6. A. Voelkel, *Crit. Rev. Anal. Chem.* **22**(5), 411 (1991).
7. O. Smidsrød and J. E. Guillet, *Macromolecules* **2**(3), 272 (1969).
8. J. M. Braun and J. E. Guillet, *Macromolecules* **9**(2), 340 (1976).
9. J. Y. Wang and G. Charlet, *Macromolecules* **22**(9), 3781 (1989).
10. D. G. Gray and J. E. Guillet, *Macromolecules* **6**(2), 223 (1973).
11. D. S. Hu, C. D. Han and L. I. Stiel, *J. Appl. Polym. Sci.* **33**, 551 (1987).
12. P. Munk, T. W. Card, P. Hattam, M. J. El-Hibri and Z. Y. Al-Saigh, *Macromolecules* **20**(6), 1278 (1987).
13. C. A. Pawlisch, A. Macris and R. L. Laurence, *Macromolecules* **20**(7), 1564 (1987).
14. D. Patterson, Y. B. Tewari, H. P. Schreiber and J. E. Guillet, *Macromolecules* **4**(3), 356 (1971).
15. O. Olabisi, *Macromolecules* **8**(3), 316 (1975).
16. Z. H. Shi and H. P. Schreiber, *Macromolecules* **24**(12), 3522 (1991).
17. Z. Y. Al-Saigh and P. Munk, *Macromolecules* **17**(4), 803 (1984).
18. M. Galin and M. C. Rupprecht, *Macromolecules* **12**(3), 506 (1979).
19. T. C. Ward, D. P. Sheehy, J. S. Riffle and J. E. McGrath, *Macromolecules* **14**(6), 1791 (1981).
20. J. Jagiello and E. Papirer, *J. Coll. Interface Sci.* **142**(1), 232 (1991).
21. D. G. Gray and J. E. Guillet, *Macromolecules* **5**(3), 316 (1972).
22. M. D. Croucher and H. P. Schreiber, *J. Polym. Sci.: Polym. Phys. Ed.* **17**, 1269 (1979).
23. H. P. Schreiber and M. D. Croucher, *J. Appl. Polym. Sci.* **25**, 1961 (1980).
24. H. P. Schreiber, M. R. Wertheimer and M. Lambla, *J. Appl. Polym. Sci.* **27**, 2269 (1982).
25. F. Chen, *Macromolecules* **21**(6), 1640 (1988).
26. A. E. Bolvari and T. C. Ward in *Inverse Gas Chromatography*, D. R. Lloyd, H. P. Schreiber and T. C. Ward, Eds., *ACS Symposium Series No. 391*, (American Chemical Society, Washington, D.C., 1989), p. 217.
27. J. Schultz, L. Lavielle and C. Martin, *J. Adhesion* **23**, 45 (1987).
28. J. Schultz and L. Lavielle in *Inverse Gas Chromatography*, D. R. Lloyd, H. P. Schreiber and T. C. Ward, Eds., *ACS Symposium Series No. 391* (American Chemical Society, Washington, D.C., 1989), p. 185.
29. S. P. Wesson and R. E. Allred in *Inverse Gas Chromatography*, D. R. Lloyd, H. P. Schreiber and T. C. Ward, Eds., *ACS Symposium Series No. 391* (American Chemical Society, Washington, D.C., 1989), p. 203.
30. S. P. Wilkinson and T. C. Ward, *Int. SAMPE Symp. Exhib.* **35**(2, Adv. Mater.: Challenge Next Decade), 1180 (1990).
31. E. Osmont and H. P. Schreiber in *Inverse Gas Chromatography*, D. R. Lloyd, H. P. Schreiber and T. C. Ward, Eds., *ACS Symposium Series No. 391* (American Chemical Society, Washington, D.C., 1989), p. 230.
32. A. C. Tiburcio and J. A. Manson, *J. Appl. Polym. Sci.* **42**, 427 (1991).
33. C. A. Arnold, J. D. Summers and J. E. McGrath, *Polym. Eng. Sci.* **29**(20), 1413 (1989).

34. J. M. Kaltenecker-Commerçon, Ph.D. Dissertation, Virginia Polytechnic Institute and State University (1992).
35. Adapted from C. A. Pawlisch, Ph.D. Dissertation, University of Massachusetts (1985).
36. F. M. Fowkes, *Ind. Eng. Chem.* **56,** 40 (1964).
37. J. R. Condor and C. L. Young, *Physicochemical Measurement by Gas Chromatography* (John Wiley & Sons, New York, 1979).
38. D. H. Kaeble, P. J. Dynes and E. H. Cirlin, *J. Adhesion* **6,** 23 (1974).
39. J. J. Jasper, *J. Phys. Chem. Ref. Data* **1**(4), 914 (1972).
40. A. L. McClellan and H. F. Harnsberger, *J. Coll. Interface Sci.* **23,** 577 (1967).
41. S. J. Gregg and K. S. W. Sing, *Adsorption, Surface Area and Porosity* (Academic Press, New York, 1982), 2nd ed., pp. 262–282.
42. A. J. Kinloch, Ed., *Durability of Structural Adhesives* (Applied Science Publishers, New York, 1983), p. 15.
43. M. J. Owen in *Silicon-Based Polymer Science,* J. M. Zeigler and F. W. Gordon Fearon, Eds., *Adv. Chem. Ser. No. 224* (American Chemical Society, Washington, D.C., 1990), p. 705.
44. D. K. Owens and R. C. Wendt, *J. Appl. Polym. Sci.* **13,** 1741 (1969).
45. C. A. Arnold, Y. P. Chen, D. H. Chen, M. E. Rogers and J. E. McGrath, *Mat. Res. Soc. Symp. Proc.* **154,** 149 (1989).
46. D. Dwight, J. E. McGrath, G. Lawson, N. Patel and G. York, in *Multiphase Macromolecular Systems,* B. M. Culbertson, Ed. (Plenum Publishing Corporation, New York, 1989).
47. N. M. Patel, D. W. Dwight, J. L. Hedrick, D. C. Webster and J. E. McGrath, *Macromolecules* **21**(9), 2689 (1988).
48. R. L. Schmitt, J. A. Gardella, Jr., J. H. Magill, L. S. Salvati, Jr., and R. L. Chin, *Macromolecules* **18**(12), 2675 (1985).
49. R. L. Schmitt, J. A. Gardella, Jr. and L. S. Salvati, Jr., *Macromolecules* **19**(3), 648 (1986).
50. S. D. Smith, J. M. DeSimone, H. Huang, G. York, D. W. Dwight, G. L. Wilkes and J. E. McGrath, *Macromolecules* **25**(10), 2575 (1992).