Aspects of Surface Characterization of Polyurethane Adhesives

I. ULKEM and H. P. SCHREIBER*

Department of Chemical Engineering, Ecole Polytechnique, P.O. Box 6079,
Stn. A., Montreal, Quebec, H3C 3A7, Canada

SYNOPSIS

The performance of adhesives is strongly dependent on the contributions to overall surface energies from dispersion and nondispersion forces. In this work, surface energies have been studied for polyurethanes representing the categories of aliphatic and aromatic polyethers and aliphatic polyesters. The surface energies of the polymers were measured by static and dynamic contact angle methods. In addition to determining the energy values for polymers as received, evaluations were also made on the polymers following modification by an aminopropyl silane (APS), present at concentrations ranging from 0.1 to 20 wt %. The dispersion surface energies of the three polymers were roughly equal; however, the nondispersive surface energies strongly differentiated among them. Organic liquids were used for calculations of energy parameters from static contact angles. Data for water failed to follow theoretical expectations and were used instead to compute a work of adhesion parameter for the polymer/water interface. This correlated with nondispersion surface energies of the polyurethanes. Somewhat different values of the nondispersion surface energy were obtained from static and dynamic contact angles, an effect attributed to the tendency of polyurethanes to restructure when their surfaces were in prolonged contact with water during dynamic analysis. This behavior may be important to the type of adhesive bond formed by the polymers and to variations in bond characteristics with time. The use of APS was found to influence both static and dynamic contact angle values, with primary changes occurring in nondispersion contributions. The effects of APS addition were fully developed at concentrations of 1 wt % or less, raising doubts about the efficiency of using this additive at higher concentrations. © 1994 John Wiley & Sons, Inc.

INTRODUCTION

It is well known that the performance of adhesives, polymer blends, and composite materials is strongly dependent on the surface characteristics of their ingredients. This is simply because surface and interfacial properties are among the most important determining factors for adhesion, diffusion, transport, and adsorption.[1] These properties are critical for applications in biomaterials, membranes, adhesives, chromatographic supports, composite materials, and drug-delivery systems. One important parameter determining the applicability of a polymer in these

fields is the surface free energy. The determination of the surface free energy and its interpretation has always drawn much attention. An important contribution to the theory of interfacial interactions is that of Fowkes and Maruchi,[2,3] who showed that the surface free energy has two components: one apolar and another that involves acid–base interactions. The total free energy or surface tension of a solid "γ_s" can be written as

$$\gamma_s = \gamma_s^D + \gamma_s^{AB} \tag{1}$$

where D refers to the dispersion force, and AB, to acid–base interactions. Further, in terms of the work of adhesion, Wa, the following can be stated[2]:

$$Wa = \gamma_1(1 + \cos\theta) + \pi_e$$
$$= Wa^D + Wa^{AB} + Wa^P \tag{2}$$

where θ is the contact angle and Wa^D, Wa^{AB}, and Wa^P are the dispersive, acid–base, and polar contributions to the total work of adhesion, respectively, and π_e is any reduction of the surface energy of the polymer resulting from adsorption of the vapor of the test liquid. In general, π_e is expected to be negligibly small for high-energy liquids on low-energy solids. It follows from eq. (2) that a determination of the individual components of surface tension is essential for better understanding the type and eventually the strength of interactions. In 1805,[4] Young made the first qualitative observation of contact angles of liquids on solids. Since that time, this method has been widely applied.[5] The contact angle can then be used with the well-known Young–Dupre equation[4,6]:

$$Wa = \gamma_1 \cdot (1 + \text{Cos } \theta) \qquad (3)$$

from which the work of adhesion of the test liquids can be calculated. Since the work of adhesion is also given by[7-9]

$$Wa = 2 \cdot (\gamma_s^D)^{1/2} \cdot (\gamma_1^D)^{1/2}$$
$$ + 2 \cdot (\gamma_s^P)^{1/2} \cdot (\gamma_1^P)^{1/2} \qquad (4)$$

then, by defining the parameters a and b as

$$a = (\gamma_1^D)^{1/2} \quad \text{and} \quad b = (\gamma_1^P)^{1/2}$$

it follows that

$$Wa/2a = (\gamma_s^D)^{1/2} + (b/a) \cdot (\gamma_s^P)^{1/2} \qquad (5)$$

If $Wa/2a$ is drawn vs. b/a (known as the Kaelble plot[10]), then the slope and intercept gives $(\gamma_s^P)^{1/2}$ and $(\gamma_s^D)^{1/2}$, respectively.

Dynamic contact angle measurements also generate data on dispersive and polar contributions of surface tension. These values can be calculated by solving a set of simultaneous quadratic equations, using the harmonic mean method[8,9,11,12]:

$$(1 + \text{Cos } \theta_1) \cdot \gamma_1 = 4 \cdot ((\gamma_1^D \cdot \gamma_s^D/(\gamma_1^D + \gamma_s^D))$$
$$ + (\gamma_1^P \cdot \gamma_s^P/(\gamma_1^P + \gamma_s^P))) \qquad (6)$$

$$(1 + \text{Cos } \theta_2) \cdot \gamma_2 = 4 \cdot ((\gamma_2^D \cdot \gamma_s^D/(\gamma_2^D + \gamma_s^D))$$
$$ + (\gamma_2^P \cdot \gamma_s^P/(\gamma_2^P + \gamma_s^P))) \qquad (7)$$

Some conceptual and experimental difficulties complicate the apparent simplicity of the contact angle issue. On the conceptual side, there are reservations[13] on the use of Kaelble plots and of harmonic mean averaging in evaluating surface energies. These procedures, however, are convenient, internally consistent, and widely applied with polymer surfaces.[8,9,11,12] They have been retained for present purposes. Experimental difficulties also complicate the apparent simplicity of both static and dynamic contact angle measurements. For example, the preparation of samples from different initial concentrations and from different solvents has considerable effect on surface energy determinations.[14] This is critical, especially if the polymer under investigation has the capability of orienting in response to interaction with the environment to which it is subjected. Since surface tension is a thermodynamic quantity, it must be minimized at equilibrium. Similarly, the interfacial tension must be minimized under equilibrium conditions. Because of this, substrates usually affect the properties of adsorbed polymers. In the case of very thin coatings, the substrate may affect even the outer surface properties of the coating polymer. This phenomenon also applies to polymer alloys and blends.[15] Among the materials capable of this restructuring or reorientation are styrene–butyl–acrylate copolymers,[16] the A–B diblock copolymer of styrene and methacrylate of poly(ethylene glycol)monomethyl ether or methacrylate of poly(ethylene glycol),[17] two-part polyurethane adhesive formulations,[18] and soft-segment polyurethanes.[19]

The need to control wettability and specific interactions at interfaces has led to methods for the modifications of surfaces prior to their contact. Plasma and corona (atmospheric pressure plasma) techniques are among the promising techniques used for this purpose.[20] Utilization of coupling agents and compatibilizers is also a popular method for the surface modification of fillers, fibers, and polymers.[21] Among those, γ-aminopropyltriethoxysilane (γ-APS), because of its stability, is one of the most widely used coupling agent.

In this work, we studied surface properties of three water-based emulsions of polyurethanes. One was based on an aliphatic polyester (P1), one on an aromatic polyether (P2), and the third was an aliphatic polyether-based polyurethane (P3). One of our objectives was to evaluate the effect of γ-APS on the dispersive and nondispersive component of surface energies of these polymers. Another purpose was to see if they are capable of restructuring. Particular attention was given to polymer P3 to seek the effects of APS addition at concentrations of 1 wt % or less. Further, we attempted to correlate the characterization parameters with aspects of me-

chanical performance of the composites. For this purpose, the composites were prepared using sized glass fibers as the reinforcing agent. The sizing was polymer P3 with different concentrations of APS. Finally, an attempt was made to use dielectric analysis (DEA) to monitor the curing reactions at the surface of the polyurethanes.

EXPERIMENTAL

Materials

Sizing agents characterized in this research were aliphatic polyester (P1)-, aromatic polyether (P2)-, and aliphatic polyether (P3)-based polyurethanes, all obtained from Reichhold Chemicals Inc. In addition to being used as received, the effects of APS addition were fully developed in a broad range of concentration. Commercially available nylon 6,6 composites containing 30% of glass fibers sized with different versions of polymer P3 were used for mechanical performance tests as well as for electron microscopy studies.

Samples and Procedures

Static contact angle experiments were carried out on samples coated on precleaned E-glass microscope slides. The glasses were washed with isopropyl alcohol and then dried at 110°C. Clean glass specimens were then coated with polymers by dipping into polymer emulsions with or without added silane. Samples coated in this way were cured at 110°C for

1 h and tested immediately for their static contact angles with test liquids. The thickness of coatings exceeded 0.1 mm, ensuring that uncoated substrate would not affect the properties of the outer surface. The same technique was applied to prepare samples for dynamic contact angle (DCA) measurements. The substrates in this case were microscope slides 22 × 22 mm and 0.1 thick.

Static Contact Angle Measurements

Static contact angle measurements were done with a Rame-Hart goniometer at 20°C and 22–26% relative humidity. Glycerol, formamide, glycol, tricresol phosphate, dodecane, and water were used as wetting liquids. Where necessary, contact angles were extrapolated to zero time to define an initial contact angle.[22]

Dynamic Contact Angle Measurements

A Cahn DCA-322 contact angle analyzer was used to obtain these data. Dodecane and water were the testing liquids; they represented nonpolar and highly polar characteristics, respectively.

Tensile Strength Measurements

The tensile strength of composite samples was measured using a table-type J.J. Instruments M30K traction machine. All tests were performed at 25°C and at an elongation speed of 5 mm/min.
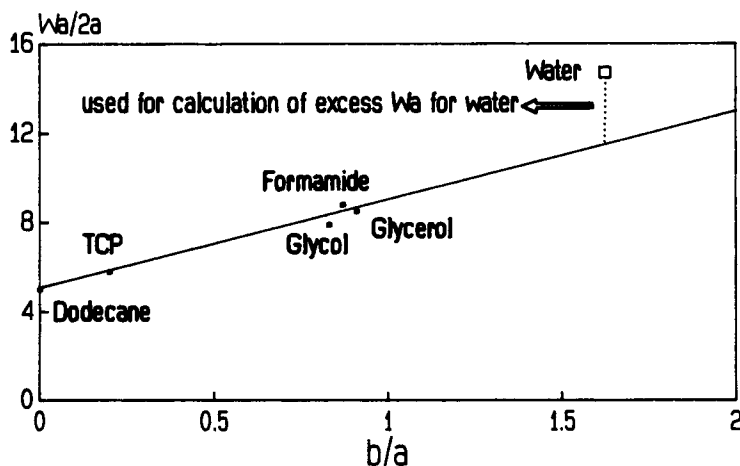

Figure 1   Kaelble plot and excess work of adhesion for water on P3.

Table I   Summary of Dispersive and Nondispersive Contributions of Surface Tension for Both Static and Dynamic Measurements, Relationship with Wa (H_2O) (All Units are in mJ/m^2)

Sample	Static		Wa (H_2O)	Dynamic	
	γ^D	γ^{ND}		γ^D	γ^{ND}
P1	23.4	26.4	2.6	25.1	29.4
P1 + 5% APS	24.4	8.2	5.7	24.8	23.1
P1 + 10% APS	24.5	11.4	5.1	25.0	21.9
P1 + 20% APS	23.4	18.8	4.1	25.0	21.9
P2	27.3	4.1	3.1	25.0	14.3
P2 + 5% APS	27.4	5.0	4.3	25.1	19.6
P2 + 10% APS	27.4	8.2	3.3	24.8	17.0
P2 + 20% APS	26.8	10.7	3.1	25.0	16.9
P3	26.4	7.2	2.2	24.7	13.9
P3 + 5% APS	26.6	10.6	4.6	24.9	21.9
P3 + 10% APS	26.6	10.4	5.0	24.7	21.4
P3 + 20% APS	26.4	10.4	5.0	25.0	22.4

Dielectric Analysis

A DuPont instruments DEA 2970 model dielectric analyzer was utilized to follow the curing of polyurethane samples. A single-surface ceramic electrode was used so as to restrict the origin of the signals to the surface of the specimens.

Scanning Electron Microscopy

A Jeol Model JSM-820 SCM was used to investigate the fracture surfaces of the nylon/glass fiber samples. These were identical to those used for tensile measurements, as described above.

RESULTS AND DISCUSSION

Contact Angles

The Kaelble plot was applied to calculate the γ^D and γ^{ND} of our materials, with results illustrated in Figure 1. Clearly, the datum for water does not follow theoretical expectations. Since in all cases it deviated from the line defined by the other contact liquids, it was excluded from γ^{ND} calculations and interpreted independently. This was done by defining the normal distance between the water datum and the reference line as an excess work of adhesion for water. The parameter is labeled $Wa(H_2O)$. Absolute values for $Wa(H_2O)$ can be calculated by multiplying this distance by $2a$. The procedure follows the precedent of Ref. 23, where the work of adhesion of water was considered during the preparation of polymeric films on glass surfaces for IR analysis.

The individual components of surface tension from both static and dynamic measurements, and the excess work of adhesion of water, are given in Table I. One initial observation is that the polyester-based polyurethane P1 has a slightly lower γ^D than the polyether-based polyurethanes P2 and P3. The difference in γ^{ND} values for these two groups of polymers is much larger. This is probably due to the higher polarity of the aliphatic polyester arising from the presence of carbonyl groups. Further, there are considerable differences in the γ^{ND} for the polyether-based polyurethanes. This may be attributed to the lower chain mobility of the aromatic polyether P2 as compared with the aliphatic P3 and may be an indication of surface restructuring capability. Speculatively, in P3, polar moities can orient to the surface more easily than in P2, minimizing the inter-
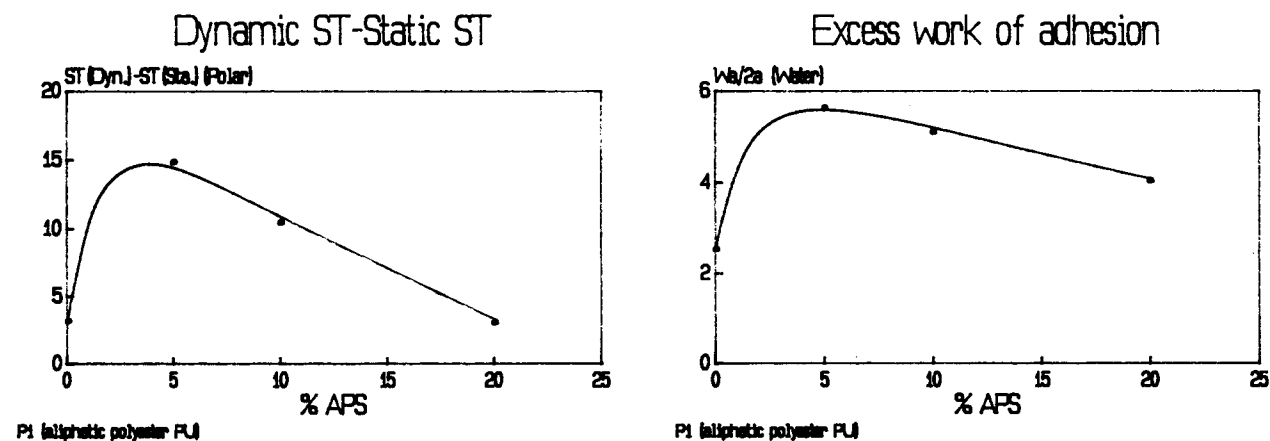

Figure 2a   Correlation between γ^{ND} (dynamic) and γ^{ND} (static) difference and $Wa(H_2O)$ with changing APS concentration for P1.
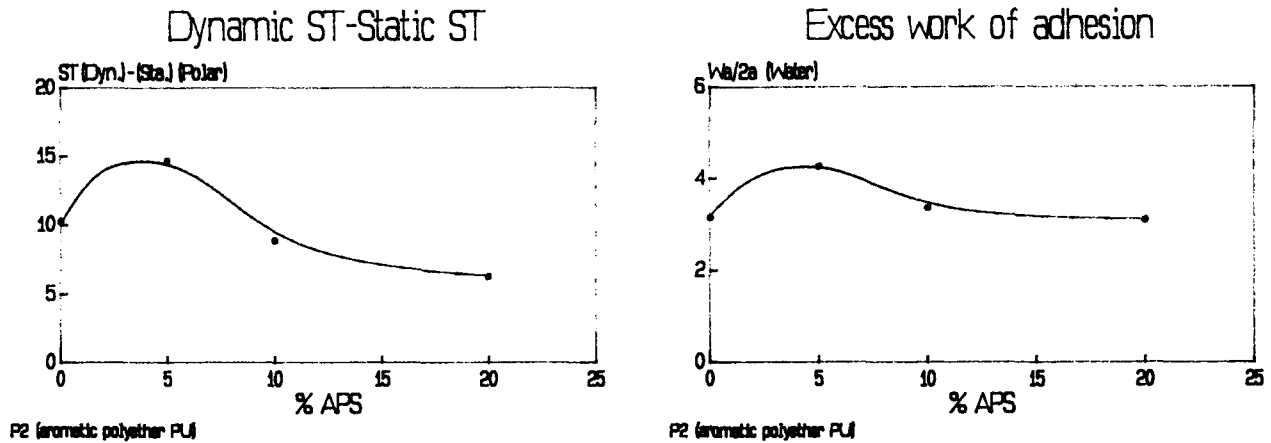
Dynamic ST-Static ST

Excess work of adhesion

Figure 2b   Correlation between γ^{ND} (dynamic) and γ^{ND} (static) difference and $Wa(H_2O)$ with changing APS concentration for P2.

facial tension at the polymer/water interface. Further to be noted in Table I are the greater γ^{ND} values obtained from dynamic measurements than from static contact angle data. This also may be caused by restructuring phenomena. Samples used for dynamic experiments were in contact with water for almost 5 min, sufficient to respond to so-polar a liquid. In contrast, the contact time in static measurements was only about 0.5 min. The longer contact time would favor the reorientation of specific polar groups toward the surface to minimize the interfacial tension at the polymer/liquid contact. If indeed the difference in γ^{ND} values were due to the longer contact times with water, then the parameter γ^{ND} (dynamic) $- \gamma^{ND}$ (static) may give specific information about the effect of water on the polar contribution to surface tension and should correlate with the

$Wa(H_2O)$ parameter. The addition of silane coupling agents is a known, effective way to alter the nondispersive component of surface tension.[24] Accordingly, both $Wa(H_2O)$ and γ^{ND} (dynamic) $- \gamma^{ND}$ (static) might be expected to vary with the APS concentration. These expectations are tested in Figures 2(a)-(c). Clearly, the parameters appear to correlate well, since both follow very similar trends with APS concentration. A reasonable expectation would have been for both parameters to tend toward zero as the concentration of APS is increased. Indeed, in the case of P1 and P2, the expected trend is observed, although even at the highest APS concentration a zero value is not attained. The behavior of P3 deviates strongly from expectation, with values of $Wa(H_2O)$ increasing to a plateau. The presence of APS thus appears to increase the adhesion be-
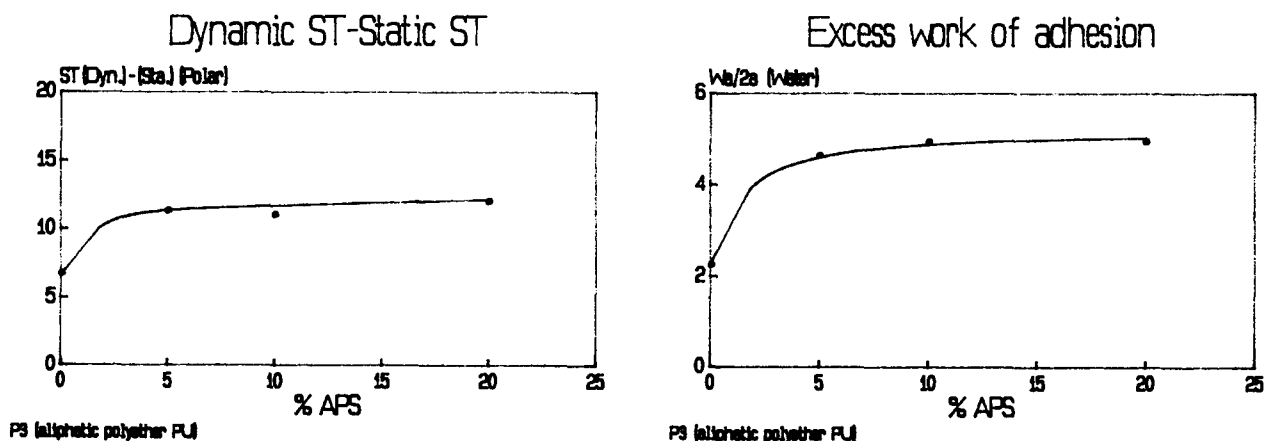
Dynamic ST-Static ST

Excess work of adhesion

Figure 2c   Correlation between γ^{ND} (dynamic) and γ^{ND} (static) difference and $Wa(H_2O)$ with changing APS concentration for P3.
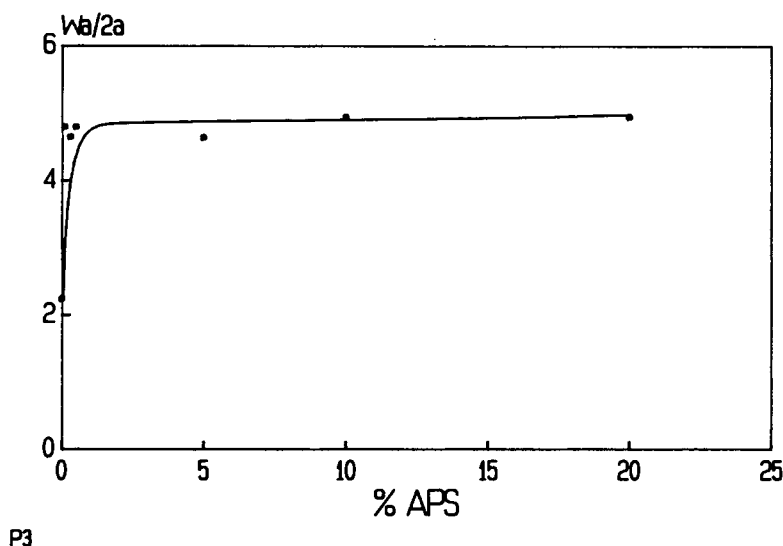
Figure 3 Maximizing of excess work of adhesion of water with APS addition for P3.

tween the modified polymer surface and water. Two possibilities may account for this: One is that the modifier is unevenly distributed on the polymer surface, leaving open polyurethane sites that are able to bond particularly strongly with water. Another is that the orientation of the APS is such as to promote the adhesion of water, thus accounting for the rise in the $Wa(H_2O)$ parameter. It is clear from Figure 2(a) and (b) that in all of these polyurethanes the use of silane beyond a low, definable concentration has little justification. This is consistent with the literature[25,26] that cautions against excessive silane concentrations. For this reason, APS addition was restricted to concentrations of 1% and less. The response of the excess work of adhesion of water to APS concentration for P3, shown in Figure 3, is even more pronounced. The parameter rises to a constant plateau value, which is attained at APS concentrations well below 1%, again suggesting that concentrations above this may be of limited value.

Mechanical Properties

A question of obvious importance is the existence of possible relationships between the various surface properties documented above for the polyurethane sizings and mechanical properties of composites making use of them. The subject was considered through the availability of glass fiber-reinforced nylon 6,6 composites, where the fibers were sized with polymer P3 alone and with P3 modified by various quantities of added APS. Initial attention focused on the tensile strength of composite samples and

the parameter $Wa(H_2O)$. As shown in Table II, in spite of high APS concentration, the tensile strength value shows essentially no response, which is also seen in Figure 4, the variation of about 5% being within the experimental error of measuring this quantity. Thus, no correlation can be drawn with the work of adhesion parameter, which increases sharply in going from P3 sizings to P3 modified by the silane additive. Additional properties of the composites were therefore examined, the hydrolytic stability of mechanical properties meriting particular attention. Indeed, as shown in Table II, TS*, the tensile strength measured at 265°F following the immersion of samples in water for 24 h, responds to APS addition in analogy with the variation of $Wa(H_2O)$. Thus, a qualitative correlation can be drawn between these variables, and the inference can be drawn that the surface characterization parameter may be useful to predict industrially important properties of polymer composites.

Table II   Correlation Between Excess Work of Adhesion of Water and Tensile Strength of Nylon 6,6 and Glass Fiber Composite for Polymer P3

Sample Code	Wa (H_2O)	TS (psi)	TS* (psi)	% Retention
P3 (without APS)	2.2	20,000	8,500	42.5
P3 + 5% APS	4.6	21,000	10,750	51
P3 + 10% APS	5.0	21,000	10,750	51
P3 + 20% APS	5.0	21,000	10,750	51

$Wa/2a$ in mJ/m^2 and tensile strength in psi units. TS* is the tensile strength at 265°F after 24 h water immersion.
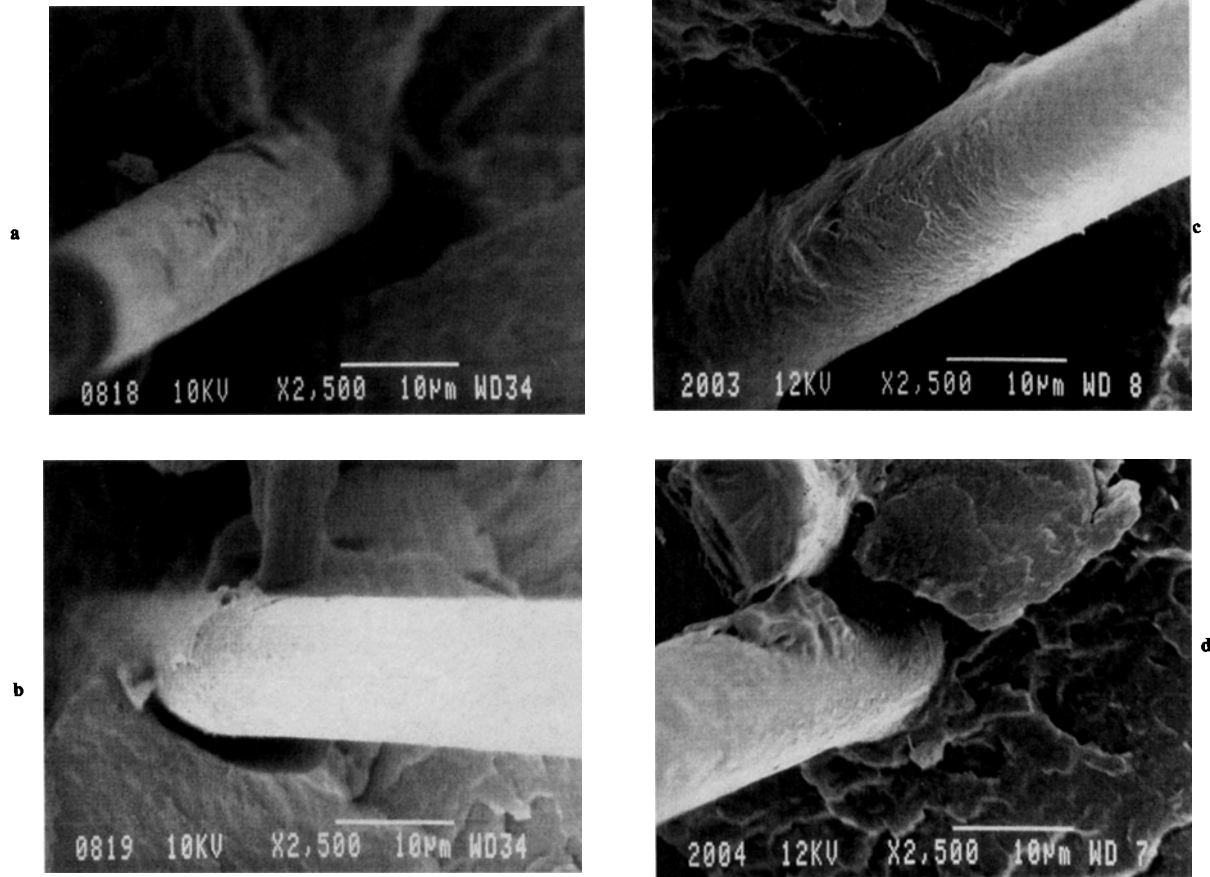
Figure 4 Morphology at the fracture surfaces of P3-treated samples: (a) without APS; (b) with 5% APS; (c) with 10% APS; (d) with 20% APS.

Dielectric Analysis

As noted earlier, an initial attempt was made to use the DEA method for monitoring cure rates in polyurethane sizings, a process variable of potential importance in controlling properties of the final product. For this purpose, two polyurethane latex specimens were used. These are labeled V404 and V407. They differ primarily in latex particle size, the difference between the two being of the order of 10, as shown in Table III. It is reasonable to expect some difference in surface properties in films solidified

Table III   Effect of Particle Size of Polymer on γ^{ND} and Wa

Sample Code	$\gamma_{Dyn.}^{D}$	γ_{Dyn}^{ND}	$Wa/2a$ (H$_2$O)	$\gamma_{Sta.}^{D}$	$\gamma_{Sta.}^{ND}$	PS (μm)	$\Delta\theta$
V404	24.0	23.7	5.0	27.4	10.2	3.3	4.6
V407	24.2	12.7	1.4	27.0	4.3	0.3	27.6

All units are in mJ/m^2. $\Delta\theta$ is the difference between advencing and receding contact angles during dynamic measurements.

from these materials, reflecting the different surface/volume ratios of parent particles. The difference in advancing and receding contact angles, measured by DCA, confirms the expectation, the small particle latex leading to a solid with much greater surface heterogeneity. Cure kinetics may also be expected to differentiate between the two versions of polymer, a documentation of this being found in Figure 5. Detailed analysis of the DEA traces is not within the scope of the present article. It is evident, however, that substantial differences exist, the cure rate for latex V404 being considerably faster than that for V407. The DEA method is attractive for the simple approach it affords to monitoring the curing process and merits additional development as a practical investigative tool for control uses.

CONCLUSIONS

The results of this work have led to the following conclusions:
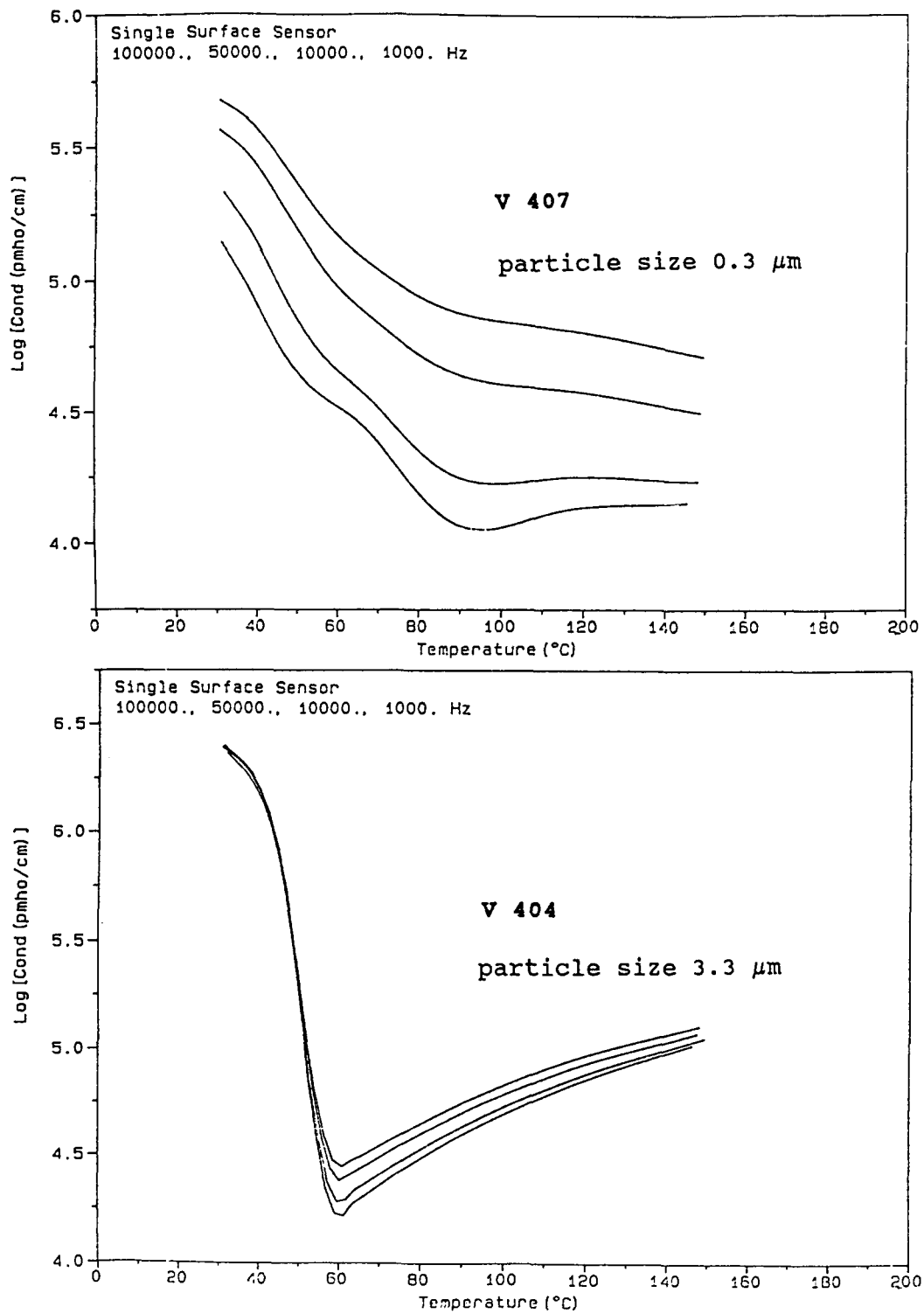
Figure 5   Observation of the different curing kinetics by the DEA technique.

1. Static and dynamic contact angle experiments identify polar and apolar contributions to the surface energy of polyurethane sizing formulations.

2. Differences observed between static and dynamic evaluations of the nondispersive surface energy can be used as an indication of surface restructuring by the polymer.

3. A new interaction parameter, $Wa(H_2O)$, an excess work of adhesion of water to the polymer surface, has been defined and used to show the effects on surface energetics of adding silane surface modifiers and of differences in the particle size of latexes from which polymer films are formed.

4. The new parameter was found to correlate well with the hydrolytic stability of mechanical properties in composites using polyurethane-sized glass fibers. It appears useful as a laboratory tool for predicting specific aspects of composite performance.

5. Cure rates in polyurethanes have been followed by dielectric analysis, a technique that shows promise as an investigative tool for controlling cure kinetics in these sizing formulations.

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