Acid–Base Surface Properties of Modified Poly(ethylene Terephthalate) Films and Gelatin: Relationship to Adhesion

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SYNOPSIS

Characterization of poly(ethylene terephthalate) (PET) films surfaces through wettability measurements and inverse gas chromatography techniques leads to a better knowledge of the potential interactions with a coating. An important case is the one relative to gelatin coatings for photographic films. In order to favor adhesion on PET, it is of interest to examine the problem in terms of acid–base interactions. PET is found amphoteric and gelatin rather basic. Several surface treatments on PET like orientation on water and flame or plasma treatment in air lead to an increase in surface acidity. Adhesion with gelatin as determined by the peel test is increased through a flame treatment, because of the higher acidity of PET and subsequent chemical bonding at the interface. Determination of acid–base surface properties of PET and gelatin appears to be an excellent tool for adhesion prediction.

INTRODUCTION

Poly(ethylene terephthalate) (PET) films are used as substrates in many applications. One important case is that of photographic films, the polymer substrate being coated by a gelatin layer. The surface properties are very important to be known in order to obtain the best adhesion performances at the polymer–gelatin interface. Therefore, the characterization of the substrate surface and the improvement of wettability are key points for industrial applications. Some published work deals with the surface characterization of surface-treated poly(ethylene terephthalate) films. Modification of the surface properties of a film treated by corona discharge in air[1] has been examined by contact angle measurements and ESCA spectroscopy. There is a large increase in surface energy, essentially due to the higher oxygen or nitrogen content at the polymer surface. Similar measurements were performed with photooxidized films.[2,3] Oxidation produces carboxyl, carbonyl, and hydroxyl groups, and also low molecular weight products by chain scission.

The dispersive γ_S^D and polar γ_S^P components of surface free energy have been determined and it appears that the polar component undergoes the main variation. Through aging, a decrease of surface polarity is observed, due to diffusion of the oxidized products into the polymer bulk and reorientation. The ability of polymer surfaces to reconstruct themselves as a function of their environment is well known.[4-8]

Because of this ability and in order to produce a minimal interfacial free energy between the polymer surface and the environmental medium, there will be an enrichment in polar groups at the interface,[5] especially when in contact with water. The surface polarity evolution by migration and orientation of the polar groups at the polymer–water interface has been demonstrated through contact angle measurements on carboxylic acid grafted polyolefins.[5,7,8] It is thus possible to attribute a "potential surface energy" to the polymer, which represents its ability to be enriched in polar groups.[5,8] These observations have been correlated with adhesion ability. The increase of polarity can favor adhesion,[8] if short chains do not appear at the surface.[7]

The same methods of surface characterization are used for poly(ethylene terephthalate) films, in order to examine the surface properties evolution after different surface treatments, such as microwave plasma treatment and flaming. The dispersive γ_S^D and polar γ_S^P components of surface free energy are determined, by classical contact angle methods.

Another way to determine the dispersive component is the inverse gas chromatography method at infinite dilution.[9-11] This technique has been already applied to PET film by Anhang and Gray[10] and a value of 40 mJ m^{-2} has been found for γ_S^D. The acid–base properties can also be determined, using acidic or basic gaseous probes,[9] according to the method we have recently published.[11] A combination of these two techniques, contact angle measurements and inverse gas chromatography, leads to a better knowledge of surface modifications, which are very important for adhesion improvement.

EXPERIMENTAL

The poly(ethylene terephthalate) film of 100 μm thickness (Fuji Film Co. Ltd.) exhibits a 50–60% cristallinity. The molecular weight M_w ranges between 20,000 and 40,000, with a 1% oligomers content. The gelatin powder (Nitta Gelatine Co. Ltd.) is in particles of 250–500 μm diameter. The thin gelatin layer, 0.4 μm thick, is obtained by coating from a gelatin solution in hot water, with further cooling and drying.

The general formulas of these two compounds are given in Figure 1. The glass transition temperatures are, respectively, 74°C for PET and 145°C for gelatin.

The surface properties of the polymer film are determined by the now classical two liquid phase method[12]. The sample is immersed in water and alkane drops are deposited. The contact angle of the drop is determined within 30 s. The dispersive component, γ_S^D, and the polar component, γ_S^P, are therefore determined.

The acid–base character of the surface is also estimated by using solutions of variable pH, as proposed by Holmes-Farley et al.,[13] with the one liquid

method.[14] Aqueous sodium hydroxide and hydrochloric acid are used. In this case, Bronstedt acido-basicity is involved.

A more fruitful characterization is done by inverse gas chromatography at infinite dilution.[9-11] This method permits the calculation of the dispersive component, and also the characterization of surface acido-basicity in the sense of Lewis acceptor–donor interactions.

In gas chromatography measurements, the retention volume V_n corresponds to the volume of carrier gas (helium) necessary for the elution of the gaseous probe through the column containing the studied solid. There is a general thermodynamic relation between the retention volume V_n and the free enthalpy of adsorption $-\Delta G_A^0$, of 1 mol solute:

$$-\Delta G_A^0 = RT \ln V_n + K \qquad (1)$$

where K is a constant depending on the chosen reference states.

The adsorption enthalpy can be related to the energy of adhesion, W_A, between the probe and the solid by the relation

$$-\Delta G_A^0 = N a W_A \qquad (2)$$

N being Avogadro's number and a the area of one probe molecule in the adsorbed state.

By using Fowkes' theory,[15] it can be written

$$W_A = 2\sqrt{\gamma_S^D \gamma_L^D} \qquad (3)$$

and, by combining the three preceding equations,

$$RT \ln V_n = 2Na\sqrt{\gamma_S^D \gamma_L^D} \qquad (4)$$

The retention volume is determined for the reversible adsorption of alkanes, or polar gaseous probes with specific acid–base or amphoteric character, i.e. diethylether, tetrahydrofurane, acetone, ethylacetate, benzene, tetrachloro-, trichloro-, and dichloromethane. The representation used is: $RT \ln V_n = f(a\sqrt{\gamma_L^D})$ T being the temperature, R the ideal gas constant, a the area occupied by the adsorbed probe molecule, and γ_L^D the surface energy dispersive component of the liquid that corresponds to the gaseous probe injected in the column. With the alkanes, the slope of the obtained straight line permits to calculate the surface energy dispersive component of the solid, γ_S^D. It is possible to characterize acido-basic surface properties by examining the respective position of the representing point above the alkane reference line as shown in Figures 6 and 7.
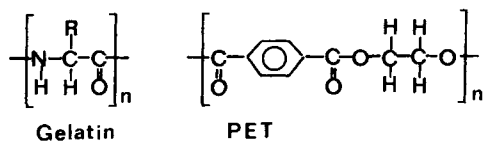

Figure 1 Chemical formulas of PET and gelatin.

The columns are prepared in the following manner. PET film is cut into small pieces of 750 μm dimension; gelatin was powdered with an electric mill and sieved to 250 μm diameter particicules. Stainless steel columns of 2 mm inside diameter and 1 m length were used. The optimum pressure drop of helium gas through the column was, respectively, 30 and 60 mm Hg.

Surface composition of PET and gelatin is examined by ESCA spectroscopy (C_{1s}, O_{1s}, and N_{1s} peaks) on the virgin and surface-treated samples. A Leyboldt spectrometer with Al K_α source is used, with a 90° X-rays incidence angle.

RESULTS AND DISCUSSION

Contact Angle Measurements

Samples before Treatment

Measurements made by the two liquid phase method for PET show that the dispersive component γ_S^D is 41 mJ m^{-2} and the polar component γ_S^P is 9.2 mJ m^{-2}. For the gelatin film, the values are respectively 21.8 and 5.3. The two surfaces appear to be polar, but the gelatin layer has a lower surface energy (γ_S = 27.1 mJ m^{-2}) than that of the PET film (50 mJ m^{-2}).

The surface acidity and basicity is also estimated as a function of the pH of the sessile drop with the one liquid method. As shown in Figure 2, there is a slight decrease of contact angle for the higher pH, which is an indication of the surface acidity of PET. The basic liquid can also react by esterification with acid surface groups and thus modify the contact angle. The gelatin film exhibits no clear behavior, the contact angle of the drops being constant whatever the pH (Fig. 2).

The well-known surface modification of polymers bearing polar groups through orientation also appears in the case of PET. In Figure 3, the results obtained for dispersive and polar components with the two-liquid phase method as a function of contact
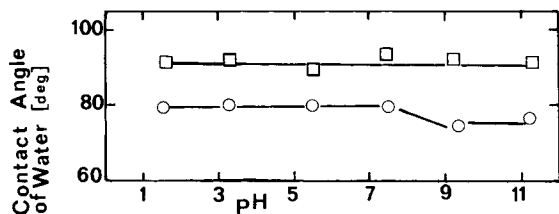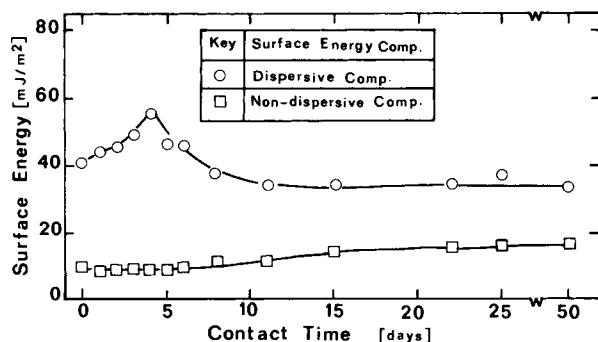
Figure 3 Evolution of dispersive component γ_S^D and polar component γ_S^P of the surface energy of a PET film as a function of contact time on water at ambient temperature.

time on water at 23°C show a nonmonotonic evolution of γ_S^D and an increase of γ_S^P. This behavior is the same as that observed with other polymers[5,7] like acrylic acid grafted polyethylene or maleic anhydride grafted polypropylene. In Figure 4 are shown the results for the gelatin surface. A small increase of polarity is seen.

It appears that the PET film has a surface acidity, and the mobility of the macromolecular chains is sufficient to increase the surface polarity (from 9 to 19 mJ m^{-2}) when in contact with a polar orienting medium such as water.

For the gelatin film, after 2 days of contact with water, at room temperature, a constant value of the surface properties is observed, slightly higher than the value before contact with water. This could be due to the movement of the chains when in contact with water and a kinetic of evolution much faster than the observation time. Indeed the first measurement is made after 1 day of contact and the main evolution is probably achieved after a few minutes or hours.[16]
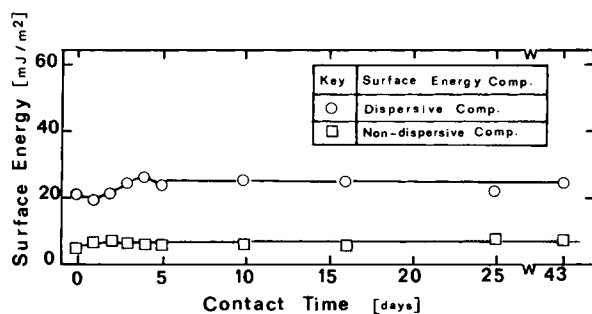
Figure 2 Contact angle of PET (O) and gelatin (□) as a function of pH.

Figure 4 Evolution of dispersive component γ_S^D and polar component γ_S^P of surface energy of a gelatin film as a function of contact time on water at ambient temperature.

Flame-Treated Samples

The surfaces have been modified by a classical flame treatment with a methane–air flame. The distance between burner and sample is 8 mm; the volumetric fraction of methane is 1/1. The treatment time for one passage is 0.075 s. The results obtained by wettability measurements with the two liquid method for PET and gelatin are shown in Table I. An important surface energy increase is observed for the two samples.

As an example, the dependency as a function of pH of the contact angle measured by the one liquid method is shown in Figure 5. For PET samples, wettability is improved and a higher acidity appears, as shown by the contact angles decrease at higher pHs.

For gelatin samples, wettability is also improved. The contact angle decrease for pH higher than 7 means that acidity is slightly increased but the balance between acidic and basic properties is not significantly modified.

Microwave-Plasma-Treated Samples

The microwave plasma treatment was performed in an air pressure of 0.2 Torr, with an output power of 50 W and a microwave frequency of 2.45 GHz. The time of treatment was 3 s. The results are also given in Table I. There is a high increase of both polar and dispersive component for PET and gelatin.

From Figures 4 and 5, it can be concluded that a plasma treatment leads to a higher acidity of PET whereas, in the case of the gelatin film, the basicity is increased.

ESCA Results

Surface analysis is performed by ESCA. C_{1s} peaks are examined. The carbon peak contains the main peak due to $C-C$ bonds and lateral peaks attributed to carboxylic$-O-C=O$, carbonyl $C=O$, and hydroxyl $C-OH$ groups.[2,3]
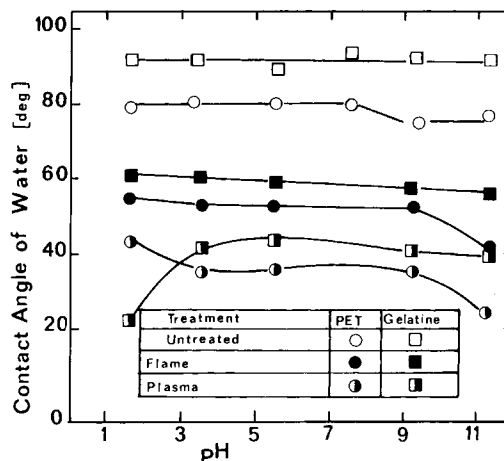
The results are given for PET in Table II as the

Figure 5 Contact angle of water for treated surfaces of PET (○) and gelatin (□) as a function of pH.

ratio of C_{1s} peak height relative to $C-OH$ or $-O-C=O$ groups to peak height of $C-C$ bonds. For gelatin, the ratios for $C=O$ peak and N_{1s} peak to $C-C$ peak are also shown in Table II.

The two treatments (flame or plasma) lead to an increase of surface-oxidized groups concentration. In the case of gelatin, there seems to be no difference in nitrogen surface composition before and after treatment.

It appears that through flame treatment, the PET surface becomes more acidic, owing to the increase of acid $-O-C=O$ groups and to the decrease of $-C-OH$ groups, which are comparatively more basic. Through plasma treatment, a simultaneous increase of acid groups and slight decrease of $C-OH$ groups, as compared with the untreated film, also lead to enhanced surface acidity. These groups are usually found after an electrical discharge or photooxidation treatment.[2,3]

For the gelatin samples, the basicity increase is essentially due to the $C=O$ groups and to a slightly higher nitrogen content. No carboxylic groups were detected.

Inverse Gas Chromatography

The dispersive component γ_S^D of surface free energy is determined with the alkane probes. The results obtained at a column temperature of 45°C are given in Table III. The surface acid–base character is determined by estimating the interaction with different acid and base probes according to the method recently published for carbon fiber surfaces.[11] The representation $RT \ln V_n = f(a\sqrt{\gamma_L^D})$ at a temperature of 45°C for PET and gelatin is given in Figures

Table I Surface Properties of PET and Gelatin (Wettability)

		Untreated (mJ m^{-2})	Flame Treated (4 × 0.075 s)	Microwave-Plasma Treated (3 s)
PET	γ_S^D	40.9	48.5	61.3 ± 3
	γ_S^P	9.2	17.9	19.6
Gelatin	γ_S^D	21.8	31.6	61.1
	γ_S^P	5.3	16.7	16.3

Table II   ESCA Peak Height Ratios

	PET		Gelatin	
	C—OH/C—C	—O—C=O/C—C	C=O/C—C	N/C—C
Untreated	0.17	0.170	0.33	0.76
Flame-treated	0.10	0.195	0.41	0.83
Plasma-treated	0.14	0.24	0.41	0.81

6 and 7. It is necessary to choose column temperatures lower than the polymers glass transition temperatures. By comparing for a given probe the ordinate difference between the representative point of the probe and the alkane reference line, one obtains an estimation of the level of the specific interactions with the chromatographic support, and hence the acid–base character can be evaluated. The higher the difference between a basic polar probe representative point and the corresponding point on the alkane line, the higher the acidic character on the solid surface and vice-versa.

It can therefore be concluded from Figure 6 for PET and Figure 7 for gelatin that PET surface is acidic and also basic and that gelatin surface is more basic than acidic, in the sense of Lewis. Parameters characterizing the acido-basicity of the surface could be calculated according to our method,[11] but in this case a semiquantitative estimation of these properties directly from Figures 6 and 7 is sufficient to get a clear picture of the two surfaces.

In accordance with Fowkes,[15] it would be interesting to increase the acidity of PET in order to reach a maximal adhesion at the interface.

Peel Test Measurements

The classical peel test at 90° angle has been used to evaluate the separation energy between PET and gelatin. Comparison established between measurements in air and in a liquid permits to determine the chemical contribution to the adhesion energy, according to a classical method developed in our laboratory.[17]

**Table III   Dispersive Component of Gelatin and PET Surface Energy (Inverse Gas Chromatography)**

	Temperature (°C)	Dispersive Component γ_S^D (mJ m^{-2})
Gelatin	45.0	26 ± 3
PET	45.5	31 ± 3

The principle is that adhesion energy W is the sum of a physical contribution W_g and a chemical contribution W_{chem}.

When peeling in a liquid medium, only the physical contribution is modified by the presence of the liquid and the chemical contribution remains constant. So from the peel results in air and in liquid, the chemical contribution can be easily evaluated, the physical contribution being calculated from the measured dispersive and polar components of the surface energy of the solids.

For example, the adhesion properties between the nontreated and a flame-treated PET have been compared, bearing in mind that the PET surface is rather acidic after flame treatment and the gelatin surface is known to be slightly basic. Peel test measurements performed on the assemblies at a peeling rate of 5 mm/min show a neat increase of separation energy after the surface treatment of PET (Table IV).

By comparing results obtained in air and in a liquid like methanol, it can be concluded that the chemical contribution to adhesion was maximal in the case of the treated PET, for which practically no decrease in separation energy was observed in a methanol environment. This means that the chemical contribution was nearly 100%.[17]
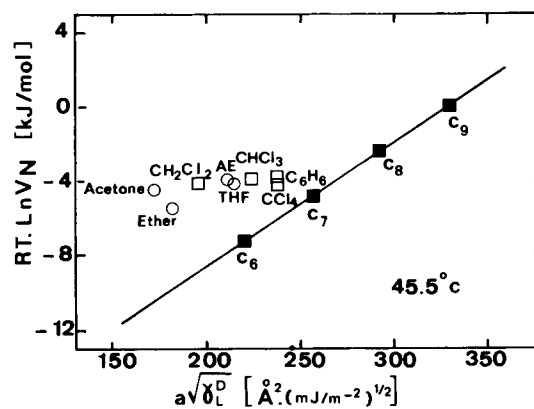
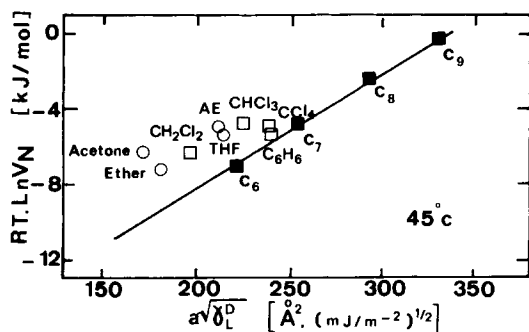**Figure 6**   Gas chromatography results for PET at 45.5°C.

Figure 7 Gas chromatography results for gelatin at 45°C.

DISCUSSION

The surface properties of the PET film examined by contact angle measurements and inverse gas chromatography show the amphoteric character of PET. Through characterization by these two techniques, it appears that the nontreated PET surface is acidic and weakly basic. As shown by the results observed after contact on water, the surface polarity undergoes an evolution. There is an increase in polarity from 9 to 19 mJ m^{-2}, after 20 days on water at room temperature. This is to be compared with the results observed on grafted polyolefins,[5] but the value obtained with PET takes also into account the influence of absorbed water.

Measurements performed with solutions of varying pHs indicate that after plasma or flame treatment, the PET surface is more acidic, in the sense of Bronstedt.

It seems therefore possible to modify the PET surface properties either by reorientation of the macromolecular chains, during contact with water, or by an appropriate surface treatment (flame or plasma). Given the importance of acido-basic interaction in adhesion,[15] these properties can be particularly useful.

With the same techniques, it is possible to characterize the gelatin surface, which also exhibits an amphoteric but rather basic behavior. By plasma treatment for instance, the surface becomes more basic, but by flame treatment the results show a more acidic behavior. Nevertheless, in contact with water, it was not possible to observe an important surface evolution. This may be due to a very rapid reorientation in 1 or 2 days, leading to an equilibrium situation, and can be attributed to a greater mobility of the chains, in comparison with the more rigid PET film. By plasma treatment, for instance, the surface becomes more basic, but by flame treatment a more acidic behavior appears.

If one compares the three treatments—orientation during contact with water, flame, and microwave treatments (Table I)—it is shown that, for PET, the polarity increase is nearly the same whatever the treatments. For gelatin, it is only with flame or microwave plasma treatments that a higher polarity is obtained. It is interesting to observe also that the surface properties are very close for the two substrates after the most energetic treatments. This may correspond to a strong modification, as shown by Amouroux et al.,[1] who observe a γ_S^P value of 30 mJ m^{-2} on a corona discharge treated film.

In agreement with Fowkes,[15] when Lewis acid–base interactions are possible at the interface between two different substrates, adhesion is increased when one is acidic and the other basic for example. The formation of chemical bonds can nevertheless not be excluded.

As shown by the different techniques developed in this study, adhesion can be increased between PET and gelatin, owing to the amphoteric character of these materials. It is observed in the case of a flame-treated PET that adhesion against gelatin is higher and that a chemical contribution exists, as given by the peel test measurement results in air and in methanol (Table IV). With the flame-treated PET, there is no decrease in separation energy and this means that chemical bonds are present at the interface with gelatin, according to the principle of the method.[17]

These observations open the way of adhesion improvement between PET and gelatin.

CONCLUSION

Surface properties of PET and gelatin films as determined by contact angle measurements show the polar nature of the two surfaces and their acid–base character. The "potential surface free energy" of PET has been determined during contact with water, demonstrating the possibility of surface properties evolution.

Table IV   Peel Test Results

	Separation Energy of PET–Gelatin Assemblies (J m^{-2}) in Air	Separation Energy Decrease in Methanol
PET (untreated)	0.3 ± 0.1	83%
PET-flame-treated	2.0 ± 0.1	0%

The acid–base properties have been determined by contact angle measurements with solutions of different pHs and also by inverse gas chromatography. Though amphoteric, the PET surface is found to be rather acidic and that of gelatin slightly basic.

Surface modifications by flame or microwave plasma treatments lead to a polarity increase for both surfaces. The PET surface becomes more acidic; the gelatin surface becomes slightly acidic after a flame treatment and more basic after a plasma treatment. All these modifications are favorable for bonding through acid–base interactions. As an example, this is confirmed by measuring the adhesive strength in the case of a flame-treated PET surface.

REFERENCES

1. J. Amouroux, M. Goldman, and M. F. Revoil, *J. Polym. Sci. Polym. Chem. Ed.*, **19**, 1373 (1982).
2. J. Peeling, G. Courval, and M. S. Jazzar, *J. Polym. Sci. Polym. Chem. Ed.*, **22**, 419 (1984).
3. D. Briggs, D. G. Grange, C. R. Kendall, and A. R. Blythe, *Polymer*, **21**, 895 (1980).
4. A. Baszkin, M. Nishino, and L. Ter.-Minassian.-Sarraga, *J. Colloid Interface Sci.*, **54**, 317 (1976).
5. L. Lavielle and J. Schultz, *J. Colloid Interface Sci.*, **106**(2), 438 (1985).
6. J. D. Andrade, S. M. Ma, R. N. King, and D. E. Gregonis, *J. Colloid Interface Sci.*, **72**(3), 488 (1979).
7. J. Schultz and L. Lavielle, *Macromol. Chem., Macromol. Symp.*, **23**, 343 (1989).
8. J. Schultz, A. Carre, and C. Mazeau, *Int. J. Adhesion Adhesives*, **4**, 163 (1984).
9. C. Saint-Flour and E. Papirer, *Ind. Eng. Chem. Prod. Res. Dev.*, **21**, 666 (1982).
10. J. Anhang and D. G. Gray, *J. Appl. Polym. Sci.*, **27**, 71 (1982).
11. J. Schultz, L. Lavielle, and C. Martin, *J. Adhesion*, **23**, 45 (1987).
12. J. Schultz, K. Tsutsumi, and J. B. Donnet, *J. Colloid Interface Sci.*, **59**, 272 (1977).
13. S. R. Holmes-Farley, R. H. Reamey, T. J. McCarthy, J. Deutch, and G. M. Whitesides, *Langmuir*, **1**, 725 (1985).
14. D. K. Owens and R. C. Wendt, *J. Appl. Polym. Sci.*, **13**, 1741 (1969).
15. F. M. Fowkes, *Rubber Chem. Technol.*, **57**, 328 (1978).
16. D. R. Absolom, W. Zingg, and A. W. Neumann, *J. Colloid Interface Sci.*, **112**(2), 599 (1986).
17. A. Carré and J. Schultz, *J. Adhesion*, **18**, 171 (1984).