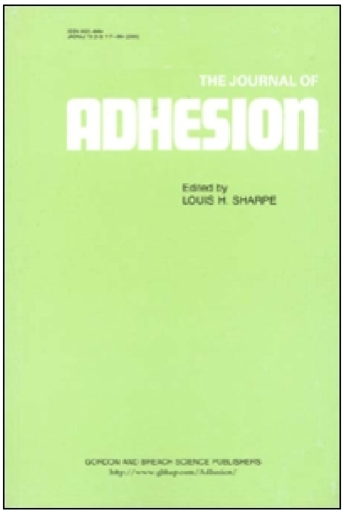

The Journal of Adhesion
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713453635

Evidence of Acid-Base Interfacial Adducts in Various Polymer/Metal Systems by IRAS: Improvement of Adhesion

M. Brogly[a]; M. Nardin[a]; J. Schultz[a]
[a] CNRS Institut de Chimie des Surfaces et des Interfaces, Mulhouse, Cedex, France

To cite this Article Brogly, M. , Nardin, M. and Schultz, J.(1996) 'Evidence of Acid-Base Interfacial Adducts in Various Polymer/Metal Systems by IRAS: Improvement of Adhesion', The Journal of Adhesion, 58: 3, 263 — 279
To link to this Article: DOI: 10.1080/00218469608015205
URL: http://dx.doi.org/10.1080/00218469608015205

J. Adhesion, 1996, Vol. 58, pp. 263–279
Reprints available directly from the publisher
Photocopying permitted by license only

Evidence of Acid-Base Interfacial Adducts in Various Polymer/Metal Systems by IRAS: Improvement of Adhesion*

M. BROGLY**, M. NARDIN and J. SCHULTZ

CNRS Institut de Chimie des Surfaces et des Interfaces, 15, rue Jean Starcky, B.P. 2488, F- 68057 Mulhouse Cedex, France

(Received June 5, 1995; in final form November 14, 1995)

The physical interactions of polymers with inorganic substrates are determined by two major contributions: Van der Waals forces and acid-base interactions, taken in the most general "Lewis" electron acceptor-donor sense. The present work shows that the work of adhesion can be very appreciably increased by the creation of interfacial acid-base interactions. Practically, polymers such as poly(ethylene-co-vinyl acetate) (EVA), terpene-phenol resins (TPR), and their blends, were solution cast on basic and acidic substrates. The nature of the interfacial bonds and the enthalpy of adduct formation through electron exchange are evidenced by Fourier transform infrared reflection-absorption spectroscopy (IRAS). Moreover, it is shown that, on the one hand, modification of the electron donor ability of the polymer functionalities reveals the amphoteric character of the substrate and, on the other hand, modification of the electron donor ability of the substrate changes the nature of the species involved in interfacial adduct formation. Then, practical adhesion tests were carried out in order to correlate the nature and strength of interfacial acid-base bonds with simultaneous increases in adhesive strengths. Thermodynamic considerations allowed us to propose estimated values of the acid-base work of adhesion, W^{ab}, and of the density of acid-base sites, n^{ab}.

KEY WORDS: Acid-base interactions; adhesion; infrared reflection-absorption spectroscopy (IRAS); polymer blends; polymer/metal oxide adhesion; ethylene-vinyl acetate copolymers (EVA); terpene-phenol resins; peel testing; aluminum; aluminum oxide (hydroxide); work of adhesion; surface free energy.

INTRODUCTION

The final performance of an adhesive joint depends strongly on the properties of the interface which is formed between the solids brought into contact. These properties are related to the nature, the magnitude and the number of interatomic and intermolecular bonds established, per unit area, at the interface. The most common interfacial forces result from Van der Waals and Lewis' acid-base interactions[1] and the magnitude of these forces can generally be related to fundamental thermodynamic quantities, such as the free energy of adduct formation and the surface free energy of the adhesive and adherend. Thus, the knowledge of these quantities is of fundamental importance for the prediction of the adhesive strength. The aims of the present study are first, the

---

[*] Presented at EURADH 94, Mulhouse, France, September 12–15, 1994, a conference organized by the Section Française de l'Adhesion, division de la Société Française du Vide.

[**] Corresponding author.

determination of the nature (entities involved) and the free energy of adduct formation in various polymer/metal systems by means of Fourier transform infrared reflection absorption spectroscopy (IRAS),[2-3] and secondly, to evidence the influence of interfacial acid-base interactions, through practical adhesion experiments, on the work of adhesion.

EXPERIMENTAL

Materials

The ethylene-vinylacetate copolymer (EVA) was supplied by Elf-Atochem (France) and has a vinylacetate content (VA) of 28% by weight, a glass transition temperature of −36°C and a crystallinity content of 12%. Weight-average and number-average molecular weights are, respectively, 27,000 g/mol. and 9,200 g/mol. The EVA copolymer is supposed to have a strong electron donor ability through its carbonyl group. The terpene-phenol resin (TPR) oligomer (DRT Lab., France) has an average number of phenol groups per molecule of 0.7 for TPR1, 1.1 for TPR2 and 1.4 for TPR3. Weight-average and number-average molecular weights values are, respectively, 570 g/mol. and 470 g/mol. The terpene-phenol resin is supposed to exhibit electron acceptor ability. In order to reveal interaction selectivity at the metal oxide/polymer interface, binary EVA/TPR blends were formulated.

These polymers were solution cast on three types of substrates. First, aluminum foils 100 μm thick and of 99.4% purity, supplied by l'Alsacienne d'Aluminium were used. The aluminum oxide covering the metal is considered as an electron donor. XPS measurements show that the surface is carbon contaminated. Therefore, the amount of hydroxyl surface sites may be relatively low. A second type of aluminum foil, 125 μm thick and of 99.9% purity, supplied by Goodfellow (Cambridge, UK) was used. These foils were first cleaned in methylene chloride (18 min in an ultrasonic bath) and hydroxyl regeneration was performed by immersion in cold water. XPS measurements confirm the extremely low carbon contamination. The surface is considered as highly hydroxylated (*i.e.* strong electron donor ability). The third kind of surface consists of optical quality glass sheets.

FTIR Analysis

Infrared spectra for polymers and polymer blends/metal interfaces were recorded on a Bruker IFS66 Fourier transform infrared spectrometer at a resolution of 2 cm^{-1} by averaging 200 scans. Infrared Reflection-Absorption Spectroscopy (IRAS) appears to be a powerful tool for the study of adsorbed species on metal surfaces. Theoretical work[4-5] shows that a metal surface generates strict dipolar selection rules and that the infrared absorption of an adsorbed molecule is governed by the dielectric behaviour of the metal. As a consequence, the infrared electric field is sharply magnified for an incident beam polarized in the incident wave plane and under high incidence angles (86°). In these conditions, vibration modes having a dynamic dipolar component normally-oriented at the surface could be excited (surface selection rules). IRAS could then reveal the surface orientation of adsorbed species. For insulating materials, surface selection rules are less selective, and the incident angle has to be shifted to lower values (60° for silica glass). As a consequence, the response of the bulk polymer increases relative to the response of the interface.

Practical Adhesion Experiments

The consequence of the establishment of interfacial polymer/metal bonds, namely, the failure strength of polymer blends/aluminum assemblies, has been measured in different media (air, ethanol) by using a 180° peel test. Peel experiments were performed at 20°C for a large range of separation rates, R_s, from 8.4×10^{-6} to 8.4×10^{-3} m.s^{-1}. The rheological model of adhesion[6] states that the peel energy, G, can be expressed as:

$$G^{A,L} = G_0^{A,L} \Phi^{A,L}(R_S, T) \tag{1}$$

where G_0 is the intrinsic fracture energy of the interface and Φ is a dissipative function corresponding to the energy irreversibly expended in viscoelastic and plastic deformations in the bulk adhesive. The function Φ depends on both the separation rate, R_s, and the temperature T, and follows a time-temperature equivalence law such as that of Williams, Landel and Ferry[7] for elastomers. The superscripts A and L refer to the medium in which the experiment is conducted, respectively air or liquid medium. Under particular conditions,[8] here verified, the dissipative function, Φ, is equal in air and in liquid media. Thus, assuming to a first approximation that the intrinsic fracture energy of the interface, G_0, is proportional to the reversible energy of adhesion, W_0, Equation (2) is obtained:

$$\frac{G^L}{G^A} = \frac{G_0^L}{G_0^A} = \frac{W_0^L}{W_0^A} \Leftrightarrow \frac{G^A - G^L}{G^A} = \frac{W_0^A - W_0^L}{W_0^A} \tag{2}$$

Given that the dissipation factors cancel, changes in the interfacial properties can be directly predicted from peel measurements. The ratios of Equation (2) can be determined directly, either experimentally ($G^A - G^L/G^A$) or by calculation ($W_0^A - W_0^L/W_0^A$) according to thermodynamic considerations. In a general case, the work of adhesion, W_{12}, between two components 1 and 2 may be expressed by only two terms: a dispersive one, W_{12}^D, due to London interactions and a non-dispersive one, W_{12}^{ND}, including Debye and Keesom interactions as well as acid-base interactions (in the Lewis sense). Fowkes[9] has also considered that the dispersive part of these interactions can be well quantified as twice the geometric mean of the dispersive components of the surface energy, γ^D, of both entities:

$$W_{12} = W_{12}^D + W_{12}^{ND} = 2(\gamma_1^D \gamma_2^D)^{1/2} + W_{12}^{ND} \tag{3}$$

Then, we can express the reduction of adhesion strength due to the presence of a liquid medium (relative to air medium) as:

$$\frac{W_0^A - W_0^L}{W_0^A} = \frac{2\,[(\gamma_P^D \cdot \gamma_L^D)^{1/2} + (\gamma_S^D \cdot \gamma_L^D)^{1/2} - \gamma_L] + W_{\mathrm{PL}}^{\mathrm{ND}} + W_{\mathrm{SL}}^{\mathrm{ND}}}{2(\gamma_P^D \cdot \gamma_L^D)^{1/2} + W_{\mathrm{PS}}^{\mathrm{ND}}} \tag{4}$$

where superscripts P, S and L refer to the polymer, the substrate and the liquid, respectively. One must be aware of the fact that all these calculations suppose that only physical interactions take place during the solid/solid and solid/liquid contact. Values of the dispersive component of the surface free energy of polymers and substrates as well as W_{PL}^{ND} and W_{SL}^{N} are determined by wettability measurements. A comparison between experimental values and calculated values allows us to, first, evidence the nature of interfacial polymer/substrate bonds and, second, to estimate the magnitude of the interfacial work of adhesion.

RESULTS AND DISCUSSION

FTIR-IRAS Analysis

Two kinds of laminates were prepared for the study of polymer/metal interfaces: solution casting of pure polymer films on the metal and hot-pressed polymer blends/metal laminates. The interface can be studied only if thin layers of polymer are formed. Therefore, the concentration of the polymer solution is adjusted in order to control the interface thickness in the case of solution case laminates. A linear relationship was found between the solution concentration and the case film thickness. Therefore, the absorbance of a characteristic vibration band, not involved in interfacial adsorption (CH_2 bending mode) is related to the thickness of the adsorbed film and is used as a standard (Fig. 1). Hot-pressed interfaces were analysed after dissolution of a part of the polymeric film in chloroform, in order to render the interfacial zone accessible. To begin, the IRAS analysis focused on the description of molecular mechanisms of adduct formation at the interface between pure polymers and various metal oxides.

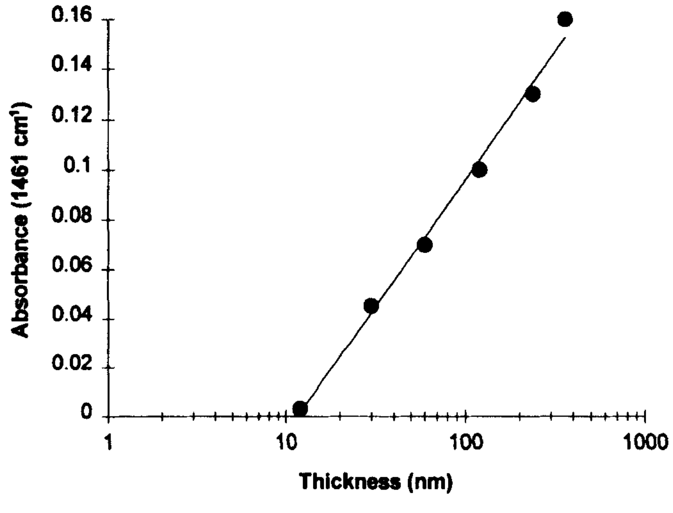

FIGURE 1 Evolution of the absorbance of the 1461 cm^{-1} band with the polymer thickness.

EVA Copolymer/Aluminum Interface

The EVA copolymer shows, on a classical transmission spectrum, a fundamental stretching vibration band of the carbonyl (C=O) group located at 1738 cm^{-1}. An IRAS spectrum performed on 12 nm thick EVA film cast on a weakly hydroxylated aluminum sheet (Fig. 2), shows that the carbonyl group stretching frequency is split into two absorption frequencies; the first one at 1740 cm^{-1} is due to free carbonyls whereas the second one, located at 1724 cm^{-1}, is attributed[10-11] to carbonyl donor groups involved in an electron exchange (*i.e.* acid-base) process at the interface. The Lewis acid-base description, considered from a molecular orbital point of view, states that the acidic or basic character of a species is only defined by the energetic position of its frontier orbitals (HOMO and LUMO) relative to the energetic position of the frontier orbitals of the second species involved in the interaction. Hence, the decrease of the force constant of the carbonyl valence bond, through electronic delocalization in $n \cdot \sigma^*$ interactions with interfacial aluminol acidic hydroxyl groups, leads to a lower absorption. A complex H-bonded hydroxyl stretching band, in the 3500–3200 cm^{-1} zone, is intensified on the same spectrum and confirms the proposed mechanism of interfacial interaction. The sharp band at 3620 cm^{-1} corresponds to free superficial hydroxyl groups (Al-OH) not involved in electron exchange. The four 3531, 3412, 3241 and 3173 cm^{-1} bands, resolved with curve-resolving OPUS software, are attributed to H-bonded hydroxyls with basic carbonyl groups of the EVA copolymer. The wavenumber of the OH vibration increases when the negative net charge of a considered hydroxyl increases. Therefore, these bands may refer[12-13] to aluminol sites having various environments: when the wavenumber decreases the OH group may be linked to one metallic Al^{VI} atom, to one Al^{IV}, to two Al^{VI} or to one Al^{IV} and one Al^{VI} or bridged on three Al^{VI}. As a consequence, the acidity of the hydroxyl increases from the monobridged to the tribridged cases. Nevertheless, the 3412 cm^{-1} band represents

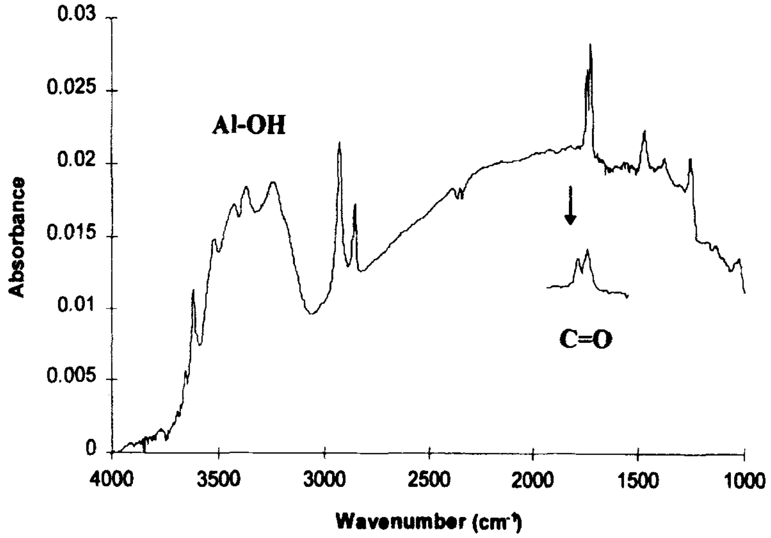

FIGURE 2 IRAS spectrum of 12 nm thick EVA film cast on weakly-hydroxylated aluminum.

82.4% of the integrated absorbance of the four H-bonded hydroxyl bands and would be considered as predominent compared with the cumulative parts of the 3531 (2.7%), 3241 (11.6%) and 3173 cm^{-1} (3.3%) bands.

On the contrary, an IRAS spectrum (Fig. 3) obtained on a 20 mm thick EVA film cast on the second aluminum sheet, highly hydroxylated, shows that the carbonyl stretching frequency is also split into two contributions, the first one at 1735 cm^{-1} (free carbonyls) and the second one, located at 1754 cm^{-1}, attributed to carbonyl acceptor groups. An increase of the absorption frequency implies that the considered carbonyl groups increase their electronic density by an electron exchange process with the oxygen atoms of the aluminol groups (electron donors) (Fig. 4). The experience reveals that the π^* antibonding orbital of the carbonyl oxygen acts as an acceptor. A $\mathbf{n}\cdot\pi^*$ acid-base complex is generated then leading to the increase of the carbonyl infrared absorption frequency. On the same spectrum, the lack of H-bonded hydroxyl bands confirms that the Al-O bond is only involved in the acid-base interfacial mechanism. By increasing the electron donor ability of the substrate, we clearly evidence the amphoteric character of the carbonyl functionality.

Table I gives, for each kind of aluminum, firstly, the intensity ratio I(AB/Free) between acid-base linked and free carbonyls and secondly, the apparent fraction of acid-base bonded entities[14] as a function of the polymer layer thickness, given by[15]:

$$f^{AB}_{\mathrm{C=O}} = 1 - f^{F}_{\mathrm{C=O}} = \frac{A^{AB}_{\mathrm{C=O}}}{A^{AB}_{\mathrm{C=O}} + A^{F}_{\mathrm{C=O}}\dfrac{\varepsilon^{AB}_{\mathrm{C=O}}}{\varepsilon^{F}_{\mathrm{C=O}}}} \tag{5}$$

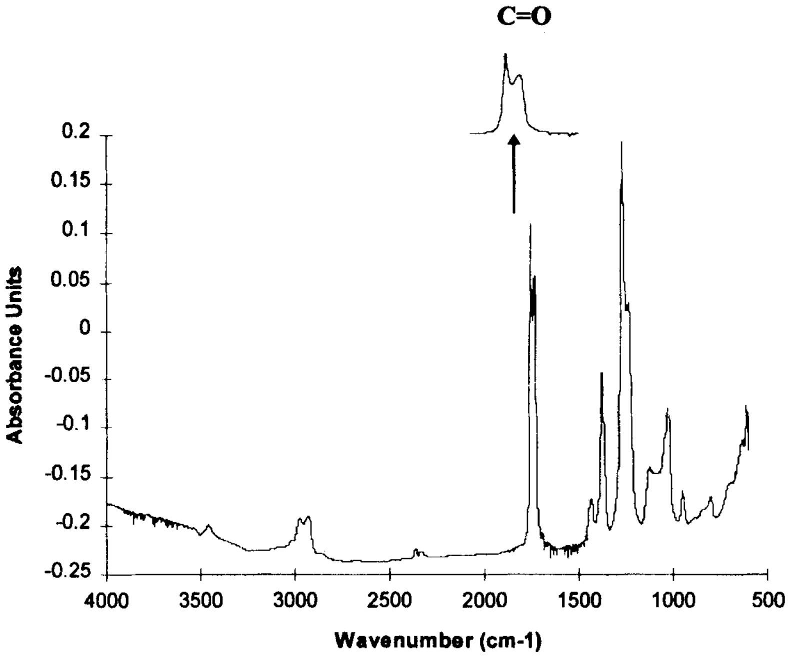

FIGURE 3 IRAS spectrum of 20 nm thick EVA film cast on highly-hydroxylated aluminum.

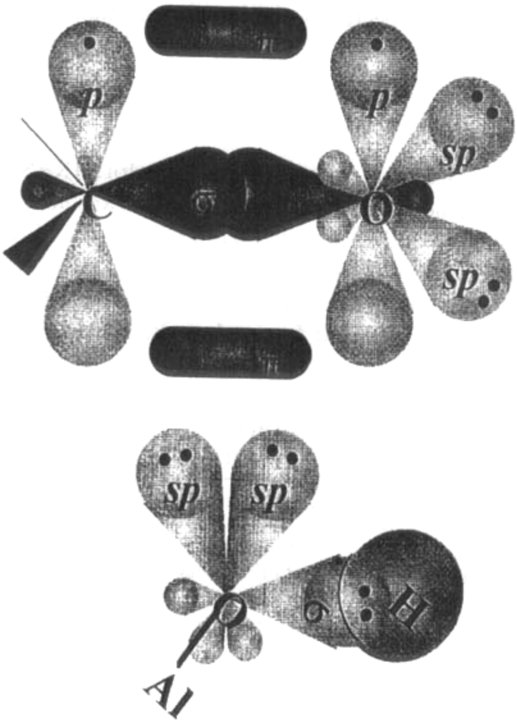

FIGURE 4 Representation of the orbital overlap occuring in n·π* adduct formation.

TABLE I
Quantitative IRAS data of EVA copolymer/aluminum interfaces

Polymer Thickness (nm)	Free C=O Frequency (cm^{-1})	Acid-Base C=O Frequency (cm^{-1})	I(AB/Free)	$f^{AB}_{C=O}$
EVA copolymer/weakly-hydroxylated aluminum substrate				
12	1740	1724	1.40	0.47
15	1740	1724	1.40	0.47
20	1739	1723	1.36	0.46
40	1738	1723	1.08	0.41
60	1738	1722	0.81	0.35
100	1737	1720	0.41	0.21
EVA copolymer/highly-hydroxylated aluminum substrate				
15	–	1749	–	1
20	1735	1749	2.58	0.63
40	1735	1749	1.27	0.47
60	1735	1752	1.11	0.27
100	1736	1754	0.54	0.08

where $A^{i}_{C=O}$ and $\varepsilon^{i}_{C=O}$ are, respectively, the integrated intensity (area) and the molar absorption coefficient of the *i* entity.

EVA*Silica Glass Interface

The silica glass substrate is considered as an acid. Therefore, IRAS spectra show (Fig. 5) that EVA carbonyls interact as electron donor groups with the silanol-type interfacial hydroxyls. The acid-base bonded carbonyl band is located at 1704 cm^{-1}. This result is confirmed (1707 cm^{-1}) by Kawaguchi *et al.*[11] and (1712 cm^{-1}) by Korn and Killmann[16] who have studied the adsorption of EVA on Aerosil silica. But the intensity ratio between acid-base bonded and free carbonyls, given in Table II, is magnified

TABLE II
Quantitative IRAS data of EVA copolymer/silica glass interfaces

EVA copolymer/silica glass substrate				
Polymer Thickness (nm)	Free C=O Frequency (cm^{-1})	Acid-Base C=O Frequency (cm^{-1})	I(AB/Free)	$f^{AB}_{C=O}$
15	1741	1704	1.72	0.54
30	1740	1704	1.64	0.52
40	1739	1705	1.45	0.48
60	1736	1707	1.15	0.43
90	1735	1709	0.81	0.37
120	1735	1709	0.52	0.24

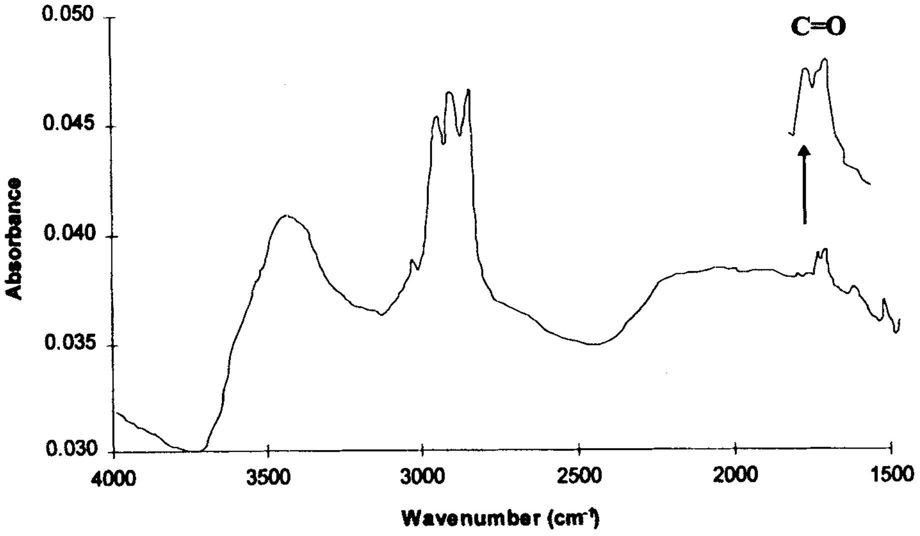

FIGURE 5 IRAS spectrum of 30 nm thick EVA film cast on silica-glass sheet.

compared with the previous results obtained for the EVA/aluminum interface. Hence, by changing the electron acceptor ability of the substrate (SiOH groups are more acidic than AlOH groups), we have experimentaly evidenced that the acid-base character is relative, and may be developed between competitive basic functionalities (aluminols and carbonyls both exhibit a basic character). The acidic or basic character of a species is only defined by the energetic position of its frontier orbitals[17] (HOMO and LUMO) compared with those of the species facing each other.

Terpene-phenol Resin/Aluminum Interface

IRAS spectra show (Fig. 6) that the fundamental vibration band of the aromatic ring (1495 cm^{-1}) is split into two contributions (1493 and 1515 cm^{-1}). In the present case, the phenol hydroxyl cannot exhibit electron donicity towards the aluminum substrate because those hydroxyls are involved in terpene-phenol resin intermolecular associations involving acid-base interactions, namely, phenol hydroxyl groups hydrogen bonded between themselves in vicinal oligomers, forming dimers or trimers.[18] As a consequence, some phenol aromatic rings have electronic deficit, due to the electronic cloud delocalisation. These latter can be considered as potentially electron-acceptor sites. A sketch of the proposed mechanism of orbitals overlap is shown on Figure 7. As a consequence, the π-antibonding orbital of the phenol ring overlaps with the **sp** orbitals of the donor oxygen of superficial aluminol leading to the formation of acid-base **n**·π^* interfacial adducts. The emergence of a strong absorption band at 3240 cm^{-1} is also observed. This latter corresponds to acid-base bonded superficial hydroxyls (through their oxygen atom). This result tends to prove that by changing the acidic character of the organic adsorbate, the aluminol superficial sites can act as acidic sites when facing carbonyl groups or as basic sites when facing phenol groups. Figure 8 shows that the

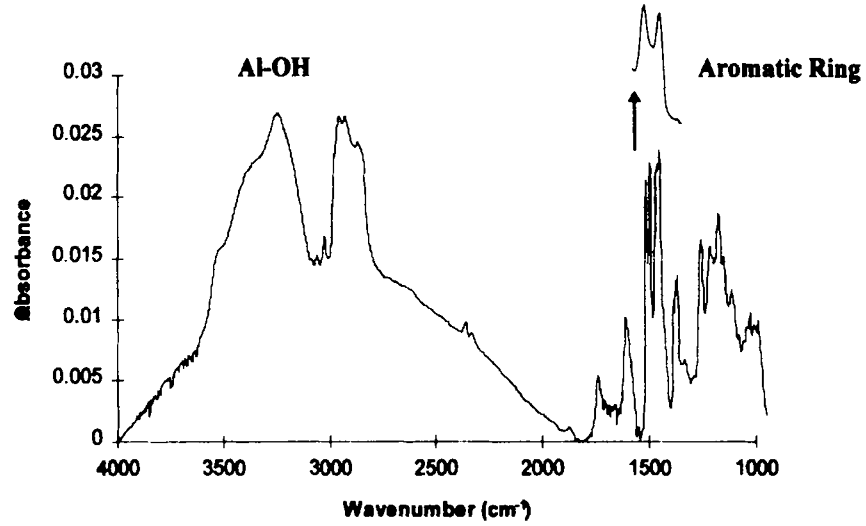

FIGURE 6 IRAS spectrum of 20 nm thick TPR film cast on weakly-hydroxylated aluminum.

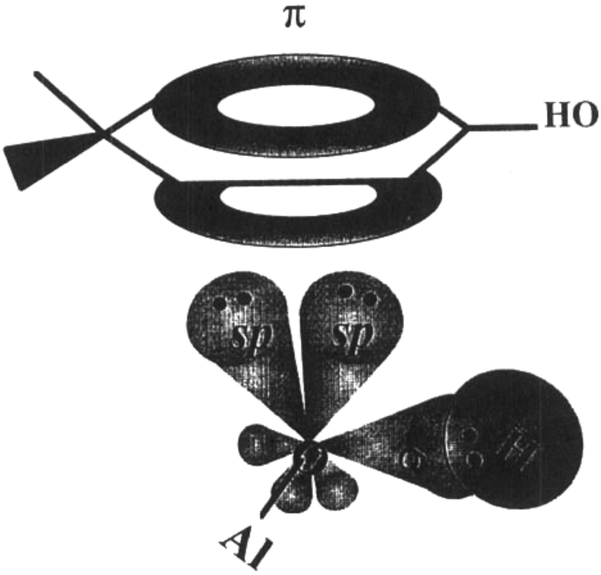

FIGURE 7 Representation of the orbital overlap occuring in $n\text{-}\pi^*$ adduct formation.

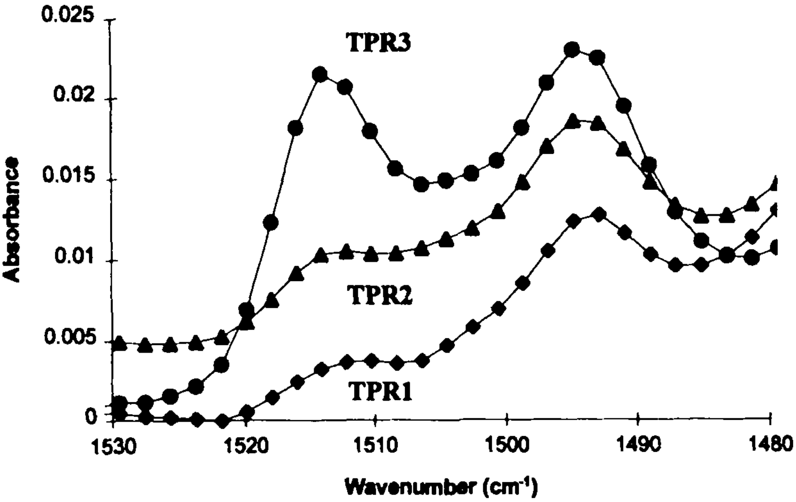

FIGURE 8 Aromatic ring vibration mode of TPR1, 2 and 3 cast on weakly-hydroxylated aluminum.

1515 cm^{-1} band increases as the phenol group density of the resin increases. Calculation of the integrated intensities shows that the 1515 cm^{-1} band represents 12%, 40% and 46% of the aromatic rings total integrated intensity, respectively, for molecules supporting an average number of phenol equal to 0.7, 1.1 and 1.4. Nevertheless, no further quantitative calculation can be done due to the unknown values of the molar absorption coefficient of both free and acid-base bonded phenols.

Enthalpy of Acid-base Interaction

The knowledge of the variation of enthalpic strength of a valence bond per unit of infrared frequency shift for the carbonyl,[19] 0.99 kJ/mol/cm^{-1}, or for the hydroxyl,[20] 0.0805 kJ/mol/cm^{-1}, absorption bands, allows us to estimate the enthalpy of acid-base interactions for all the systems described. The obtained values are summarized in Table III. The average enthalpy of acid-base interaction for the EVA/weakly-hydroxylated aluminum is equal to − 15.9 kJ/mol. This value is confirmed by Kunath and Schulz.[21] They reviewed the correlations between infrared absorption vibration of surface hydroxyl groups and adsorption enthalpies: a value of − 15.6 kJ/mol is found for the absorption of ethyl acetate. On the highly-hydroxylated aluminum surface, this enthalpy reaches − 18.8 kJ/mol and reveals that a shift from a basic species to an acidic species for the EVA carbonyl group may be associated with an enthalpic gain. In the case of EVA cast on silica glass sheet, the substrate acidity increases relative to the weakly-hydroxylated aluminum sheet, thus leading to a high value of the interfacial enthalpy of interaction: − 35.6 kJ/mol.

EVA-TP Resin Blend/Aluminum Interface

In order to reveal interaction selectivity at the metal oxide/polymer blend interface, binary EVA/TPR hot-pressed blends/aluminum assemblies obtained by dissolution in $CHCl_3$, are analysed. Enthalpic considerations, based on the comparison of the n·σ* interaction strength (− 15.9 kJ/mol) for the EVA/Aluminum interface and the n·π* interaction strength (− 30.7 kJ/mol) for the terpene-phenol resin/aluminum interface, tend to prove that the weakly-hydroxylated aluminum oxide would exhibit electron donicity when covered by EVA-TPR blends. IRAS spectra (Fig. 9) reveal, firstly, the selective adsorption of the terpene-phenol resin at the interface through, on the one hand, the splitting of the 1495 cm^{-1} band into two contributors at 1495 and 1515 cm^{-1} and, on the other hand, the emergence of a strong absorption band at 3250 cm^{-1}. This latter corresponds to acid-base bonded superficial hydroxyls (through their oxygen atom). Interfacial interactions (n·π* type) between the electron donor oxygen of the aluminol groups (Al-O band) and the electron acceptor aromatic ring of the phenol groups of the resin are observed. This selectivity is explained from pure enthalpic considerations and confirms previous predictions. The frequency shift, Δν(OH), equal to 370 cm^{-1}, leads to an enthalpy of adduct interaction of − 29.8 kJ/mol, in good agreement with the previously calculated n·π* interaction strength (− 30.7 kJ/mol). Secondly, the 3400 and 3460 cm^{-1} H-bonded bands due to intermolecular EVA/TPR

TABLE III
Experimental enthalpies of acid-base interaction

Polymer	Substrate	ΔH^{ab}(kJ/mol)
EVA copolymer	Weakly-hydroxylated aluminum	− 15.9
EVA copolymer	Highly-hydroxylated aluminum	− 18.8
EVA copolymer	Silica glass sheet	− 35.6
Terpene-phenol resin	Weakly-hydroxylated aluminum	− 30.7

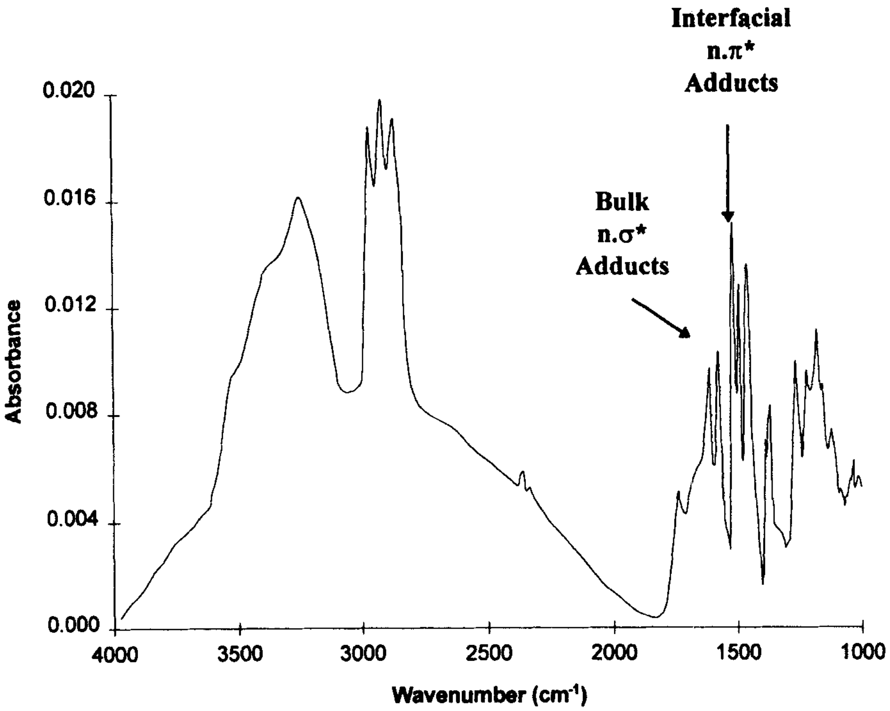

FIGURE 9 IRAS spectrum of 30 nm thick EVA/TPR3 (50:50 w/w) film cast on weakly-hydroxylated aluminum.

adducts (see full description in Ref. 14) are observed. They were absent on Figure 6. The C=O stretching band is thus logically split into free (1738 cm^{-1}) and acid-base bonded (1710 cm^{-1}) bands. The system is then defined as having phenol groups which interact, on the one hand, as a Lewis acid with C=O groups of the copolymer, thus leading to the miscibility of the system and, on the other hand as a Lewis base with superficial aluminol basic sites. It is of major importance to notice that for all the EVA/TPR blend/aluminum interfaces analysed, the enthalpy of adduct interaction was equal to −29.8 kJ/mol.

PEEL ENERGY

The second part of this work is devoted to an original explanation of adhesive behaviour of polymer blends/aluminum joints through practical adhesion measurements and also by refering to the previously calculated enthalpies of adduct formation.

In that way, the consequence of the establishment of interfacial polymer blends/metal oxide bonds was measured by a series of peel experiments conducted on various EVA-TPR/weakly-hydroxylated aluminum joints, for which the locus of failure is clearly interfacial. As an example, Figure 10 shows the behaviour of an EVA (50% w/w)/TPR3 (50% w/w) based assembly, the separation being performed in air

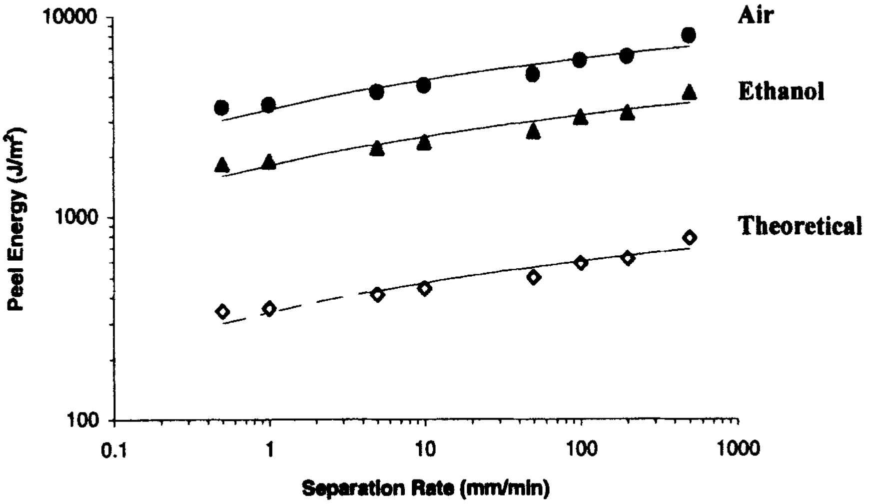

FIGURE 10 Practical adhesion results (EVA:TPR (50:50 w/w)/weakly-hydroxylated aluminum).

and in ethanol, respectively. By examining the variation of the peel adhesion strength (failure energy), G^A and G^L, with the peel rate, R_s, the following comments can be made: The curve in air and in ethanol are parallel on a logarithmic scale, verifying that the ratio G^L/G^A (Eq. (2)) is constant and independent of the peel rate. Therefore, the viscoelastic dissipative function, Φ, is not modified by the presence of the liquid. Secondly, the dotted curve shows the theoretical values of G^L:

$$G^L_{Th} = G^A \frac{W^L_0}{W^A_0} \tag{6}$$

W^L_0 and W^A_0 were calculated from the surface properties of the solids and of the liquid according to Equations (3), and (4). All these calculations suppose that only physical interactions take place during the solid/solid and solid/liquid contacts.

Surface properties of the solids and liquid used are gathered in Table IV. Figure 10 reveals that theoretical values of G^L are greatly different from experimental values, for the considered assembly. Values of the reduction of peel adhesion strength, due to the

TABLE IV
Surface energies of solids and liquid

	γ(mJ/m^2)	γ^D(mJ/m^2)	γ^P(mJ/m^2)	W^{ND}_{PL}(mJ/m^2)	W^{ND}_{SL}(mJ/m^2)
Ethanol	22.8	17	5.8	–	–
Weakly-hydroxylated aluminum	63	39	24	–	23.6
EVA/TPR1 62.5/37.5% w/w	41.5	40	1.5	5.5	–
EVA/TPR1 50/50% w/w	40.1	39	1.1	3.8	–
EVA/TPR2 62.5/37.5% w/w	41.7	40	1.7	6	–
EVA/TPR2 50/50% w/w	44.8	39	5.8	11.2	–
EVA/TPR3 62.5/37.5% w/w	42	40	2	6.8	–
EVA/TPR3 50/50% w/w	46	39	7	12.5	–

presence of the liquid, obtained either experimentally ($G^A - G^L/G^A$) or by calculation ($W_0^A - W_0^L/W_0^A$), are collected in Table V, for all the assemblies. Assuming that only physical interactions take place at the solid/solid interace, experimental and calculated values should be equal. Table V tends to prove that practical and theoretical values differ as the degree of adduct inter-association in the bulk adhesive between EVA copolymer and terpene-phenol resin increases.[14] A London-Van der Waals interfacial force field is not able to explain the experimental results. Therefore, acid-base or chemical bonds must be developed at the polymer/metal interface in order to explain practical adhesion results.

IRAS experiments, previously conducted on hot-pressed laminates, clearly show that no pure covalent bonds are formed at the polymer blends/aluminum oxide interface, whatever the blend composition. In all cases, only electron-donor/electron-acceptor adducts were evidenced. Thus, we suggest that interfacial acid-base bonds may contribute to intrinsic adhesion forces and may explain our experimental results. This hypothesis is consistent only if the liquid medium, ethanol, does not affect interfacial acid-base bonds. This assumption is obviously true, as both the Drago acidic constants[22] (related to the acid strength) and the Gutmann acceptor numbers[23] of phenol are greater than those of ethanol. Then, the ($W_0^A - W_0^L/W_0^A$) value is calculated in order to be equal to the ($G^A - G^L/G^A$) experimental value, for each assembly. As previously mentioned, $W_{\mathrm{PL}}^{\mathrm{ND}}$ and $W_{\mathrm{SL}}^{\mathrm{N}}$ are determined by wettability measurements performed with apolar liquids (α-bromonaphtalene and tricresylphosphate) and with ethanol. The non-dispersive component of the work of adhesion, $W_{\mathrm{PS}}^{\mathrm{ND}}$, equal to $W_{\mathrm{PS}}^{\mathrm{AB}}$, equal to $W_{\mathrm{PS}}^{\mathrm{AB}}$ to a first approximation, is calculated in order to satisfy Eq. (2). Corresponding results are gathered in Table VI. Results range from 13 to 118 mJ/m^2. These original values agree with literature data. As an example, Fowkes[24] has determined an acid-base work of adhesion equal to 100 mJ/m^2 for silica glass/PMMA interfaces.

Considering the mole number of functional carbonyl [C=O] and hydroxyl [OH] entities present in a given blend–these numbers are deduced from the molar vinyl acetate content of EVA and from the average number of phenol groups per TPR molecule – we are able to express the degree of acid-base inter-associations between phenol and carbonyl groups, D^{AB}, as:

$$D^{AB} = \frac{2 f_{\mathrm{C=O}}^{AB}[\mathrm{C=O}]}{f_{Blend}^{EVA}[\mathrm{C=O}] + f_{Blend}^{TPR}[\mathrm{O-H}]} \tag{7}$$

TABLE V
Experimental and calculated liquid peel strength reduction factors

Resin	EVA Content (%)	$\frac{G^A - G^L}{G^A}$ (%)	$\frac{W_0^A - W_0^L}{W_0^A}$ (%)
TPR1	37.5	90.8	96.1
TPR1	50	93.2	97.6
TPR2	37.5	65.4	95.8
TPR2	50	85.4	91.1
TPR3	37.5	75.6	95.2
TPR3	30	47.7	90.2

TABLE VI
Estimation of fundamental adhesion data

Resin	EVA Content (%)	D^{AB} (%)	ΔH^{AB}(kJ/mol)	W^{AB} (mJ/m^2)	n^{AB} (μmol/m^2)
TPR1	37.5	43	−29.7	17	0.6
TPR1	50	37	−29.7	13	0.45
TPR2	37.5	44.5	−29.7	55	1.9
TPR2	50	40	−29.7	30	1
TPR3	37.5	43.5	−29.7	38	1.3
TPR3	50	56	−29.7	118	4

where f^{EVA}_{Blend} and f^{TPR}_{Blend} are the weight fraction of EVA and TPR in the blend. Table VI shows that the estimated acid-base work of adhesion seems to be related to the degree of adduct inter-association, D^{AB}, in the bulk adhesive.[14] This trend is not surprising because as the EVA/TPR adducts formed in the bulk adhesive increase, the probability that a phenol aromatic ring (π electrons) may be involved in an electron exchange process increases, even if this phenol is stabilized by n.σ^* interaction through its hydroxyl. On the contrary, low D^{AB} values imply that either EVA copolymer or TPR are in excess. In the first case, excess of EVA induces the development of crystalline entities[14] that may nucleate at the interface (heterogeneous nucleation) and hinder accessibilty to basic AlOH superficial sites. On the other hand, excess of TPR induces the formation of molecular resin dimers or trimers.[14] The geometrical area of adsorption of such complexes is highly increased (compared with monomolecular entities) leading, firstly, to a reduction of the number of interfacial interacting sites and, secondly, to the development of a weak boundary layer enriched in TPR entities; thus, the peel adhesion strength is strongly reduced as well as the corresponding acid-base work of adhesion.

The knowledge of both the enthalpy of interaction at the interface and the reversible acid-base work of adhesion allows us to estimate the number of acid-base interacting sites at the interface. Fowkes *et al.*[19] have suggested that the contribution of the polar (dipole-dipole) interactions to the thermodynamic work of adhesion could be neglected compared with both dispersive and acid-base contributions, as was previously experimentally confirmed. They have also considered that the acid-base component of the adhesion energy can be related to the variation of enthalpy due to acid-base interfacial adducts interaction, as follows:

$$W^{AB} = f(-\Delta H^{AB})n^{AB} \tag{8}$$

where f is a dimensional factor that converts enthalpy into free energy and is taken equal to unity, and n^{AB} is the number of acid-base bonds per unit interfacial area, close to[25] about 6 μmol/m^2, *i.e.* 3.6 sites/nm^2. ΔH^{AB} values were previously determined by IRAS measurements on hot-pressed laminates. Values of n^{AB}, estimated according to Equation (8), are collected in Table VI and range from 0.45 to 4.0 μmol/m^2. The fact that our results are lower than Fowkes' value is not surprising. First, Fowkes' value (6 μmol/m^2) is an average value for polymers in general and may be considered as a scale value. Secondly, the dimensional factor, f, when taken equal to unity, neglects

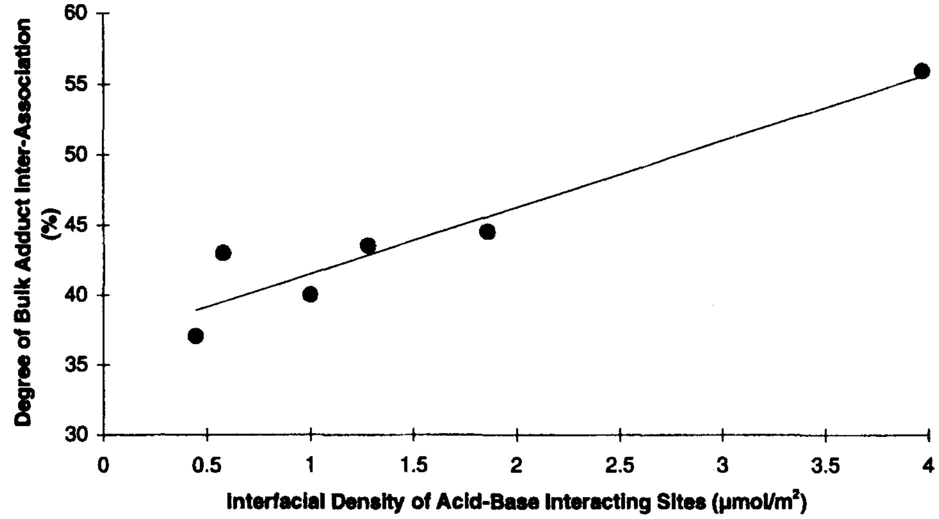

FIGURE 11 Evolution of n^{AB} with the bulk degree of adduct inter-association, D^{AB}.

entropic effects at the interface.[26] A recent study[27] has proved that f may differ from unity. However, these results, consistent with the literature, confirm the good estimation of the acid-base work of adhesion. As mentioned for W^{AB}, the estimated number of interfacial interacting sites is related to the bulk degree of adduct inter-association (Fig. 11). Such a relation proves that acid-base adduct formation in polymer blends determines the thermodynamic and morphological properties of the blend[14] and, on the other hand, governs the adhesive behaviour of the blend. The originality of the study lies in the explanation of interfacial properties of the polymer blends through the description of molecular mechanisms of interaction. Therefore, fundamental adhesion data such as the acid-base work of adhesion and the number of interfacial interacting sites are estimated.

CONCLUSION

IRAS spectroscopy has proven to be a helpful tool for the determination of both the nature and the free energy of interfacial adduct formation in polymer/metal oxide systems. Changes in the electron donor ability of the substrate reveal the amphoteric character that a given substrate may exhibit. Therefore, acidity and basicity should be discussed on a "relative" scale: it is shown that functionalities of competitive basicity can be involved in an acid-base interacting process. Finally, an original correlation between IRAS and practical adhesion results leads, through thermodynamic considerations, to the estimation of fundamental adhesion data such as the acid-base contribution to the work of adhesion and the number of interfacial interacting sites. Synergical properties of the blending process are finally highlighted.

References

1. W. B. Jensen, in *The Lewis acid-base concepts* Ed. (J. Wiley & Sons, New-York, 1979).
2. A. M. Bradshaw, J. Pritchard and M. L. Sims, *J. Chem. Soc., Chem. Commun.*, 1519 (1968).
3. K. Naknishi, in *Infrared absorption spectroscopy* Holden Day Inc., Nankodo Co. Ltd., Tokyo, 1969).
4. R. Greenler, *J. Chem. Phys.*, **44**, 310 (1966).
5. H. Pearce and N. Sheppard, *Surf. Sci.*, **118**, 415 (1982).
6. A. N. Gent and J. Schultz, *J. Adhesion*, **3**, 281 (1972).
7. M. L. Williams, R. F. Landel and J. D. Ferry, *J. Am. Chem. Soc.*, **77**, 3701 (1955).
8. A. Carré, and J. Schultz, *J. Adhesion*, **18**, 171 (1984).
9. F. M. Fowkes *Ind. Ing. Chem.*, **56**, 40 (1964).
10. M. Kawaguchi, A. Inoue and A. Takahashi, *Polym. J.*, **15**, 537 (1983).
11. M. Kawaguchi, A. Funayama, A. Takahashi and T. Kato, *J. Colloid Interface Sci.*, **121**, 130 (1988).
12. H. Knözinger and P. Ratnasamy, *Catal. Rev. Sci. Eng.*, **17**, 1, 31 (1978).
13. C. Monterra V. Bolis and G. Magnacca, *Langmuir*, **10**, 1812 (1994).
14. M. Brogly, M. Nardin and J. Schultz, submitted to *J. Polym. Sci., Part B: Polym. Physics.*
15. M. M. Coleman F. Graf and P. C. Painter, *Specific interactions and the miscibility of polymer blends* (Technomic Pub., Basel, 1991), p. 257.
16. M. Korn and E. Killmann, *J. Colloid Interface Sci.*, **76**, 19 (1980).
17. I. Fleming, *Frontier Orbitals and Organic Chemical Reactivity* (J. Wiley & Sons, Chichester, 1987).
18. K. B. Whetzel and J. H. Lady, in *Spectrometry in Fuels*, Friede, Ed. (Plenum Press, London, 1979), p. 259.
19. F. M. Fowkes, D. O. Tischler, J. A. Wolfe, L. A. Lannigan, C. M. Ademu-John and M. J. Halliwell, *J. Polym. Sci., Polym. Chem.* Ed., **22**, 547 (1984).
20. A. S. M. Murphy, C. N. R. Rao, *Appl. Spect. Rev.*, **2**, 69 (1968).
21. D. Kunath and D. Schulz, *J. Colloid Interface Sci.*, **66**, 3, 379 (1978).
22. R. S. Drago, G. C. Vogel and T. E. Needham, *J. Am. Chem. Soc.*, **99**, 3203 (1977).
23. V. Gutmann, *The Donor-Acceptor Approach to Molecular Interactions* (Plenum Press, New York, 1978).
24. F. M. Fowkes, *J. Adhesion Sci. Tech.*, **1**, 7 (1987).
25. M. Nardin and J. Schultz, *Composite Interfaces* **1**, 177 (1993).
26. H. Haidara, M. F. Pinhas and J. Schultz, *C. R. Acad. Sci. Paris*, **315**, Série II, 521 (1992).
27. M. D. Vbranac and J. C. Berg, *J. Adhesion Sci. Tech.*, **4**, 255 (1990).