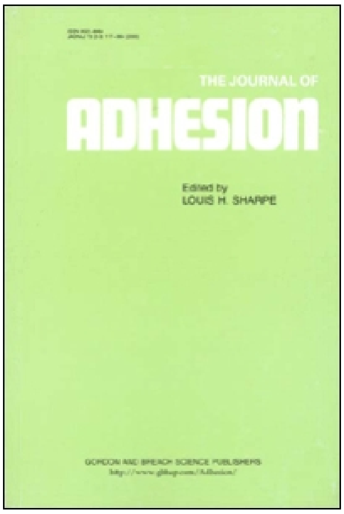

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Reversible and Irreversible Adhesion of Polymers: Possibilities for Measurement and Calculation

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Reversible and Irreversible Adhesion of Polymers: Possibilities for Measurement and Calculation*

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Comparative analysis of existing direct and indirect techniques for estimation of the work of adhesion (W_A) between a polymer and a solid surface - inverse gas chromatography (IGC), wetting, direct adhesion forces measurement - has been carried out. The work of adhesion was calculated from experimental data obtained using different techniques for identical polymer/solid systems. The relationship between the work of adhesion and the bond strength was analyzed, including possible W_A estimations from destructive micromechanical tests. For non-polar polymers, whose adhesion is due to dispersion interaction only, all techniques are in good agreement with each other. However, the estimates of work of adhesion obtained by different techniques considerably differ for polar polymers. The reason for this obviously consists in deficiency of theoretical knowledge about non-dispersion interactions at interfaces. Each of the considered approaches has its own advantages and shortcomings. The problems concerning the estimation of non-dispersion component of the work of adhesion can be solved only by comprehensive use of several different techniques.

Keywords: Work of adhesion; Polymers; Acid - base interaction; Wetting; Inverse gas chromatography; Micromechanical tests; Contact mechanics

INTRODUCTION

Adhesion between polymers and solid substrates determines, to a great extent, bond strength at interfaces and, consequently, mechanical

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[*] This paper is dedicated to the memory of Professor Hans-Jörg Jacobasch.

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strength of joints and composites. Thus, target-oriented variation of interfacial adhesion is an effective way of controlling mechanical properties of polymer composites, coatings, *etc.*

To control interfacial strength (by means of modification of the polymer and/or substrate surface), it is necessary to characterize the adhesion quantitatively. Traditionally, the value of reversible thermodynamic work of adhesion, W_A, is used for this purpose. However, experimental measurement of the work of adhesion between two solid surfaces, a polymer and a substrate, is a rather complicated problem. At present, two techniques are mainly used to determine the work of adhesion between two solids – inverse gas chromatography (IGC) and wetting. They are both indirect; first, "third bodies" (probe liquids) are used to characterize solid surfaces, and then W_A is calculated as a combination of surface characteristic of the two contacting solids (the polymer and the substrate). Besides, the adhesion of polymers is also extensively investigated in recent years by direct methods using surface force apparatuses. Therefore, a comparison of experimental results obtained for identical systems by different techniques would, undoubtedly, be interesting.

Another important issue is to compare "fundamental" adhesion and "adherence", or "practical" adhesion, which is measured by testing adhering solid–solid systems for failure. Numerous investigations revealed correlation between the "practical" adhesion (adhesional strength) and such thermodynamic characteristics of surfaces as surface energy [1–5] and enthalpy of adsorption [1,6,7]. However, it is not enough simply to state a correlation; researchers need a quantitative characteristic of adhesion, a parameter that could be used in models describing loading of adhering systems and predicting their failure. Finding of a functional relationship between adhesion and adhesional strength or, in other words, between interfacial forces and global mechanical response is one of the most challenging problems [8–10]. In spite of the fact that strength of adhering systems is affected by a variety of factors, adhesional interaction is the driving force which governs different processes at interfaces and, in this way, determines the mechanical response [10].

In the recent decade, the relationship between the work of adhesion estimated using different techniques and the adhesional strength at polymer/solid interfaces was studied, for example, by

Berg *et al.* [11, 12], Gutowski [13] and Schultz *et al.* [6, 7, 14]. Comprehensive investigation of surface and adhesional properties of polymers was a subject of permanent interest to Professor H.-J. Jacobasch. Extensive experimental research of adhesional phenomena carried out at the Institute of Polymer Research Dresden, which involved wetting technique, electrokinetic measurements, inverse gas chromatography, direct adhesion force measurement, micromechanical tests, *etc.*, revealed correlation between the results of different experiments and gave a deeper insight into fundamental laws of adhesion [1, 15–25]. The works of Prof. Jacobasch demonstrated an undoubted relationship between the work of adhesion and interfacial bond strength in polymer composites and coatings. Thermodynamics of interfacial interactions was considered by Prof. Jacobasch as the basis of controlling the bond strength and, consequently, mechanical properties of composites and coatings. Another important point of his investigations was comparative analysis of sensitivity and possibilities of different techniques in adhesion characterization.

This paper is a review summarizing the experience of estimation of the work of adhesion between polymers and solid substrates accumulated in various experimental fields. Special attention is given to the relationship between the "fundamental" and "practical" adhesion and a possibility of characterizing adhesion using the results of micromechanical destructive tests.

WORK OF ADHESION: CONTRIBUTION OF ACID-BASE INTERACTION

At present, the approach proposed by Fowkes [26] is generally recognized, that considers the work of adhesion as consisting of two main contributions due to the two principal types of molecular interactions, namely, London – van der Waals (predominantly dispersion) forces and acid–base, or donor–acceptor, interactions, including hydrogen bonding:

$$W_A = W_A^d + W_A^{ab}. \tag{1}$$

In Eq. (1), the dispersion component can be calculated using the geometric mean approach, which is based on the Berthelot's combining rule [27]:

$$W_A^d = 2(\gamma_1^d \gamma_2^d)^{1/2}. \tag{2}$$

The validity of Eq. (2), which also was proposed by Fowkes [16], is reliably established. Therefore, it is not surprising that the values of the dispersion component of the work of adhesion (W_A^d) obtained for polymers using different experimental techniques (IGC, wetting, direct adhesion force measurements) are in good agreement [11, 29–32].

All difficulties of the W_A calculation from Eq. (2) lie in the correct determination of W_A^{ab}. The acid–base (donor–acceptor) interaction between two condensed phases results in the establishment of local bonds (for instance, hydrogen bonds) at the interface. To calculate the work of adhesion, it is necessary to know the surface density of these bonds (*i.e.*, number of bonds per unit area) and their distribution in energy. Such complete information about the interface cannot be easily obtained. Therefore, in practice the surfaces before contacting are characterized by their ability to form acid–base bonds. In existing models, surface density and energies of acidic and basic sites are merged into one unified "acid" or "base" parameter (Saint Flour and Papirer's K_A and K_B [33], or γ^+ and γ^- according to van Oss *et al.* [34]). These parameters are determined experimentally from IGC and wetting, respectively. However, characterization of a surface by a general "acid" or "base" parameter is, to a great extent, an oversimplification. This gives rise to disagreements between the results from different techniques and problems concerning their physical meaning.

Most contradictions arise when estimating the contribution of acid–base interactions. For instance, the work of adhesion estimated from direct adhesion forces measurement is often greater than that from wetting [29, 30, 35]. Inverse gas chromatography also gives greater W_A values than wetting measurements [1, 11, 36]. Different techniques based on contact angle analysis result in the same conclusion: the dispersion contribution is the determining factor, whereas W_A^{ab} acts as a correction parameter [37]. On the contrary, the IGC technique estimates the W_A^{ab} contribution in some polymer/solid substrate systems to be as large as 80% [6]. It was noted many times that contact angles were poorly sensitive to surface modification while other techniques (IGC, XPS) and mechanical testing showed dramatic changes [1, 11, 16].

However, information on the acid–base interaction is present in the results obtained using each technique, because all adhesion phenomena do have a common basis (namely, molecular interactions). Therefore, a point of interest is the comparison of the results from different techniques. Such comparative analysis would reveal restrictions of each technique and, in particular, find the appropriate one to measure adhesion and adhesional strength in polymer composites.

INVERSE GAS CHROMATOGRAPHY

Theoretical Approach

In recent years, inverse gas chromatography (IGC) has been extensively used to investigate surface properties of polymers. It seems to be the most sensitive of all existing techniques to acid–base interactions. This technique is based on adsorpiton of selected low-molecular probe liquids on the investigated solid (stationary disperse phase in a chromatographic column). The knowledge of the retention time or retention volume of these probes allows the determination of the level of the interactions established between the probes and the solid and, thus, the characterization of the solid surface.

The theory of inverse gas chromatography is fully described elsewhere [31, 38, 39]. Here we recount that the dispersion component of the surface energy of the solid can be determined by using a series of *n*-alkanes as probe liquids, and polar liquids used as probes allow the characterization of acid and base properties of the solid surface. According to Gutmann [40], each polar liquid is characterized by an acceptor number (AN) and a donor number (DN). These parameters are determined by means of separate independent measurements; at present, they are known for many liquids. In turn, to characterize solid surfaces, the acid (K_A) and base (K_B) parameters have been introduced [33], which are the analogs of AN and DN, respectively. The IGC technique allows measurement of the enthalpy of interaction between the investigated solid surface and a polar probe. According to the Saint-Flour and Papirer approach [33], the specific (acid–base) part of this enthalpy ($-\Delta H^{ab}$) is related to the AN and DN of the probe as follows:

$$-\Delta H^{ab} = K_A \cdot \mathrm{DN} + K_B \cdot \mathrm{AN}. \tag{3}$$

Having measured $-\Delta H^{ab}$ for several polar liquids with different AN and DN, it is easy to find K_A and K_B for the given solid surface. By analogy with Eq. (3), it is possible to define a specific enthalpy of interaction between two solids, *e.g.*, a fiber and a polymer matrix, as the sum of the cross-products of the coefficients K_A and K_B of both materials:

$$-\Delta H^{ab} = K_A^f K_B^m + K_A^m K_B^f, \tag{4}$$

where superscripts f and m are for the fiber and the matrix, respectively.

This $-\Delta H^{ab}$ value can be converted into the acid–base component of the work of adhesion (W_A^{ab}), if the number of acid–base bonds per unit area, n^{ab}, is known. According to Fowkes [41],

$$W_A^{ab} = -f\Delta H^{ab} n^{ab}, \tag{5}$$

where f is a conversion factor to transform enthalpy values into free energy values, which can be regarded as close to unity [41].

In this paper, we used DN values in kJ/mol as defined by Gutmann [40] and dimensionless AN numbers corrected using the results of Riddle and Fowkes [42]. The values of the work of adhesion, calculated using this approach from experimental data presented in Table I, are shown in Table II.

Work of Adhesion Obtained Using the IGC Approach

During the recent decade, a great variety of polymers have been investigated using inverse gas chromatography. The accumulated data give a possibility of estimation of surface energies of polymers and the work of adhesion between these and various solid substrates. It should be noted that the IGC and other techniques (*e.g.*, wetting) give somewhat similar γ^d values for polymers (see Tab. I).

TABLE I Surface parameters of some materials obtained using the IGC and wetting techniques

Material	γ^d [*mJ/m*^{2}] *from IGC*	K_A	K_B[a] [*kJ/mol*]	*Ref.*	γ^d [*mJ/m*^{2}] *from wetting*	γ^+ [*mJ/m*^{2}]	γ^- [*mJ/m*^{2}]	*Ref.*
Carbon fiber T300 (unsized)	50	0.143	15	[6]	–	–	–	
Carbon fiber Tenax HTA 5000: unsized	84	0.1	20	[1]	37.6	0.4	2.0	[1]
sized	34	1.1	23	[1]	26.2	1.8	30.7	[1]
E-glass fiber: unsized	33.0	0.54	20	[18]	21.6	–	–	[18]
	23	0.34	12.4	[44]				
sized	32.8	0.19	21	[18]	26.3	–	–	[18]
	23	0.5	30.0	[44]				
Cellulose fiber: unsized	44.0	0.31	7.0	[36]	25.5	0.28	24.3	[36, 83]
sized	42.1	0.05	10.2	[36]	27.1	–	–	[36]
Polyethylene	35	0	0	[44]	33	0	0.1	[84]
Polypropylene	32.8	0.01	0.1	[36]	31.7	0.8	0.02	[36, 57]
Polystyrene	37.2	0.085	9.8	[36]	34.8	10.3	0.12	[36, 57]
					42	0	1.1	[84]
Polycarbonate	–	0.088	9.6	[85]	37.0	–	–	[15]
Nylon 6,6	29	0.08	11.5	[44]	34.1	–	–	[15]
Poly(methyl methacrylate)	–	–	–		39–43	0	9.5–22.4	[12, 84]
						20.5	0.15	[57]

[a] Recalculated into energy value (kJ/mol) using the AN–AN^d acceptor numbers by Riddle and Fowkes [42].

TABLE II Work of adhesion (calculated from IGC experiments)[a] and adhesional pressure (data from Ref. [86]) in polymer/fiber systems

Fiber	*Matrix*	W_A^d $[mJ/m^2]$	W_A^{ab} $[mJ/m^2]$	W_A $[mJ/m^2]$	σ_{ult} $[MPa]$
Carbon T300	Nylon 6,6	76.2	17.1	93.3	132.4
E-glass	Nylon 6,6	61.9	46.9	108.8	208.2
E-glass	Polystyrene	70.1	42.0	112.1	192.5
E-glass	Polypropylene	65.8	1.5	67.3	99.8
E-glass	Polyethylene	68.0	0.0	68.0	81.4
E-glass	Polycarbonate	69.9[b]	41.7	111.6	276.6

[a] The IGC data are presented in Table I. For unsized E-glass, data from Ref. [18] were taken.
[b] From wetting data [15].

However, the main advantage of the IGC technique is that it gives a way to calculate the specific (acid–base) component of the work of adhesion between two solids. At present, K_A and K_B values have been determined using the IGC technique for many polymers and reinforcing fibers, which allows the calculation of W_A for a variety of polymer composites. As can be seen from Table II, the technique is very sensitive to the nature of the polymer. For non-polar polymers, the work of adhesion is rather low, but with increasing "polarity" (*i.e.*, K_A and K_B parameters) the contribution of acid–base interactions to the total work of adhesion also increases.

The IGC technique also appeared to be very sensitive to the fiber treatment. We should especially emphasize the obvious correlation between W_A values from the IGC data and "practical" adhesion, or adhesional strength, which was reported in several papers [1, 6, 36, 43]. Table III shows some of these data. We can see that, when complementary acid and base sites are present at interacting surfaces, both W_A and adhesional strength are high. For non-polar polymers, whose adhesion is due to dispersion interaction only, the adhesional strength is rather low and cannot be improved by any fiber treatment [16, 36, 43, 44]. However, simultaneous target-oriented modification of both matrix and fiber can increase the work of adhesion and adhesional strength. As a specific example, we could mention grafting of acrylic acid groups to polypropylene and glass fibers treatment by a base sizing agent, γ-aminopropylsilane [16, 36].

Recently, extensive experiments with different polymer/fiber systems have been carried out, including W_A estimation using the IGC

TABLE III Correlation between the work of adhesion and the strength of macro composites

Fiber	*Matrix*	*Work of adhesion (from IGC) [mJ/m²]*	*Ref.*	*Composite tensile strength [MPa]*	*Ref.*
E-glass unsized	Polyethylene	56.7	[44]	21	[44]
E-glass sized	Polyethylene	56.7	[44]	19	[44]
Cellulose unsized	Polypropylene	76.6	[36]	22	[36]
Cellulose sized	Polypropylene	75.0	[36]	22	[36]
Cellulose unsized	Polystyrene	102.7	[36]	42	[36]
Cellulose sized	Polystyrene	87.3	[36]	37	[36]
E-glass unsized	ABS[a]	109.4	[43]	68	[87]
E-glass sized	ABS[a]	87.8	[43]	48	[87]
E-glass unsized	Nylon 6,6	81.1	[44]	58	[44]
E-glass sized	Nylon 6,6	100.6	[44]	80	[44]

[a] Poly(acrylonitrile - butadiene - styrene).

technique and determination of bond strength by micromechanical techniques [6, 7, 31, 43]. They demonstrated a linear relationship between the work of adhesion and the interfacial shear strength (IFSS).

Critical Discussion

However, absolute W_A values determined using the IGC technique should not be accepted uncritically. For example, Nardin and Schultz [6] obtained for some polymer/fiber systems $W_A = 200 - 350\,\mathrm{mJ/m^2}$. Such figures seem to be physically implausible. Indeed, even if we suppose that the interface is populated by acid - base bonds with the maximum possible density (which is, after Fowkes, about $6 \cdot 10^{-6}\,\mathrm{mol/m^2}$ [41]), then the W_A^{ab} value of 300 mJ/m² will correspond to the mean energy of a single bond of 0.52 eV. At the same time, it is known that the energies of acid - base (hydrogen) bonds range in value from 8 to 42 kJ/mol [45], or 0.08 - 0.43 eV. It comes out that not only is the interface extremely densely covered with hydrogen bonds, but also each individual bond has extremely high energy.

This "non-physical" result is, in all probability, due to an assumption which is implicitly taken every time that the IGC results are treated. (We mean IGC experiments at infinite dilution.) It is usually supposed that the probe liquid adsorbs equiprobably at all acid (or base) sites present at the solid surface. However, any real surface is inhomogeneous, *i.e.*, it is characterized by a wide energy range of acid and base sites. It is clear that an individual molecule of the probe liquid will adsorb, at infinite dilution, predominantly at those sites with highest energies. Therefore, the bond energy value calculated from IGC experiments at infinite dilution characterizes rather its possible maximum, and not the mean value for a given pair of interacting solids. To take into account surface inhomogeneity, measurement of the isotherm of gas adsorption [46, 47] or inverse gas chromatography at finite dilution [48] can be useful.

The second source of possible overestimation of the work of adhesion is the n^{ab} value. The surface density of acid and base sites cannot be obtained within the frames of the IGC technique and requires an independent measurement. However, up to now a simplistic geometric estimation, which assumes active sites packing with maximum possible density, is used.

And lastly, the factor f is not always equal to unity. As follows from the analysis by Berg [12], it can be significantly less when acid–base interactions at the surface are accompanied by considerable entropy changes, and this is the case for adsorption of polar liquids.

Nevertheless, the IGC technique remains, in the present stage, practically the only developed experimental method which is sensitive to the changes of acid–base properties of surfaces and which allows W_A estimation for composites. This provides, of course, the upper estimate, whereas the techniques based on wetting give the lower estimate; true values seem to be in between.

WETTING

The Work of Adhesion Between a Polymer and a Solid

The work of adhesion and the surface energies of solids are traditionally characterized using the wetting technique. For contact between a solid and a liquid, the work of adhesion can be calculated from the Young–Dupré equation:

$$W_A = \gamma_{lv}(1 + \cos\vartheta), \tag{6}$$

where γ_{lv} is the surface free energy of the liquid in the presence of its vapor, and ϑ is the wetting angle.

This technique can be used to good advantage and allows the determination of the work of adhesion of low-molecular-weight liquids to various solids. Problems arise from attempts to use the wetting technique to measure the work of adhesion between two *solids*, *e.g.*, between fibers and matrices in polymer composites. Similarly to IGC, probe liquids are used in the wetting technique to characterize solid surfaces. This approach entails an inevitable question: what set of parameters is sufficient to characterize adequately the capability of a condensed phase for interfacial interaction? For a long time, the surface tension, γ_s, had been considered as the only energy-related parameter of a solid surface. Later, it was split into two components, dispersion and polar:

$$\gamma_s = \gamma_s^d + \gamma_s^p. \tag{7}$$

The polar constituent, γ_s^p, was determined from contact angles of different polar liquids on the solid, using Eq. (6):

$$W_A = \gamma_{lv}(1 + \cos\vartheta) = 2[(\gamma_s^d\gamma_l^d)^{1/2} + (\gamma_s^p\gamma_l^p)^{1/2}]. \tag{8}$$

Equation (8) is known as Owens–Wendt [49] or "geometric mean" approach. A "harmonic mean" approach proposed by Wu [50] is also popular:

$$W_A = \gamma_{lv}(1 + \cos\vartheta) = 4\left(\frac{\gamma_s^d\gamma_l^d}{\gamma_s^d + \gamma_l^d} + \frac{\gamma_s^p\gamma_l^p}{\gamma_s^p + \gamma_l^p}\right). \tag{9}$$

Other approaches have been developed in which the dispersion and polar components were not split explicitly but included in a more complicated manner, *e.g.*, the Good–Girifalco equation [51].

The use of the geometric and harmonic mean approaches appeared to be reasonable when investigating surface modification of solids. There are many examples where the work of adhesion calculated from Eqs. (8) or (9) correlates well with the mechanical strength of composites and coatings. However, in recent papers, the techniques based on wetting are more and more often subjected to criticism. Almost always the work of adhesion between two solids calculated from wetting results is less than that directly measured [29, 30, 35] or estimated using other techniques [1, 11, 36]. This is sometimes attributed to "low sensitivity of the wetting technique to specific interactions" [1, 30].

The analysis of fundamental equations used for determining the "polar" ability of a solid from the wetting reveals that the problems of this technique are a consequence of the lack of an adequate theory, which can be already seen in Eq. (7). As was shown by Fowkes [41], the contribution of polar (Keesom and Debye) components to the total surface energy value is, as a rule, negligible as compared with the dispersion contribution. The Fowkes opinion is that nearly the whole non-dispersion component of the surface energy of a liquid or a solid is due to acid–base interactions. Therefore, the attempts to combine "polar" components by the laws of "geometric mean", "harmonic mean", *etc.*, are irrelevant. Whereas, for dispersion forces, the geometric mean rule follows from the Lifshitz theory [52], its application to the "polar" interaction is speculation.

The Acid–Base Concept in Wetting

Thus, there is a need for a theory that allows estimation of the energy of acid–base interactions at the interface, taking into account that one surface can carry both acid and base properties. Within this theory, any surface should be characterized by at least three independent parameters: the dispersion component of the surface energy (γ^d), a parameter for acidity, and a parameter for basicity. Such a theory has been recently proposed by van Oss, Chaudhury and Good (vOCG theory, [34]). They introduced the acid and base parameters of the surface, γ^+ and γ^-, respectively, and proposed the following equation to calculate the work of adhesion:

$$W_A = 2[(\gamma_1^d \gamma_2^d)^{1/2} + (\gamma_1^+ \gamma_2^-)^{1/2} + (\gamma_1^- \gamma_2^+)^{1/2}], \qquad (10)$$

where subscripts 1 and 2 indicate two condensed phases (solid or liquid).

It can easily be seen that Eq. (10) resembles Eq. (4) for the ICG technique. The similarity of both approaches is summarized in Table IV; this provides the basis for comparison of experimental results from IGC and wetting.

TABLE IV Estimation of the work of adhesion (W_A) using the wetting and IGC techniques

<table>
<tr><th>Wetting</th><th>Inverse gas chromatography</th></tr>
<tr><td colspan="2">Indirect estimation (using probe liquids)
A surface is characterized by 3 parameters:</td></tr>
<tr><td>$\gamma^d, \gamma^+, \gamma^-$</td><td>$\gamma^d, K_A, K_B$</td></tr>
<tr><td colspan="2">$W_A^d = 2\sqrt{\gamma_f^d \gamma_m^d}$</td></tr>
<tr><td>$W_A^{ab} = 2\sqrt{\gamma_f^+ \gamma_m^-} + 2\sqrt{\gamma_f^- \gamma_m^+}$</td><td>$W_A^{ab} = -f \cdot n^{ab} \cdot \Delta H^{ab}$
$\Delta H^{ab} = K_A^f K_B^m + K_B^f K_A^m$</td></tr>
</table>

Van Oss, Chaudhury and Good suggested relating the experimentally-measured contact angle, ϑ, to adhesion parameters of the liquid and the solid by combining Eq. (10) with the Young–Dupré equation, Eq. (6):

$$\gamma_{lv}(1 + \cos\vartheta) = 2[(\gamma_s^d \gamma_l^d)^{1/2} + (\gamma_s^+ \gamma_l^-)^{1/2} + (\gamma_s^- \gamma_l^+)^{1/2}]. \qquad (11)$$

Having measured ϑ for several liquids at several surfaces, one can determine γ^d, γ^+ and γ^- for all investigated materials. This task becomes still easier in consequence of the fact that the surface energies of liquids (and their dispersion components) are, as a rule, well known. To determine all three components of the surface energy of a solid, it is sufficient to measure its contact angle with three liquids, one non-polar and two polar. In recent years, γ^+ and γ^- for many solids have been calculated using this approach.

Comparison of Experimental Results from Wetting and IGC Approaches

The estimation of the components of the surface energy of solids using the wetting and IGC approaches gave in several cases similar results, especially for γ^d [11,31,32]. It also was noted by Jacobasch *et al.* [1,22] that the variation of the γ^+ parameter of the carbon fiber surface upon its modification correlated with similar variation of K_A (from IGC) and its bond strength to epoxy resin (Fig. 1). The correlation between the results of different techniques for investigating polymer surfaces – electrokinetic measurements, IGC, XPS, wetting, mechanical testing – was demonstrated in numerous papers by

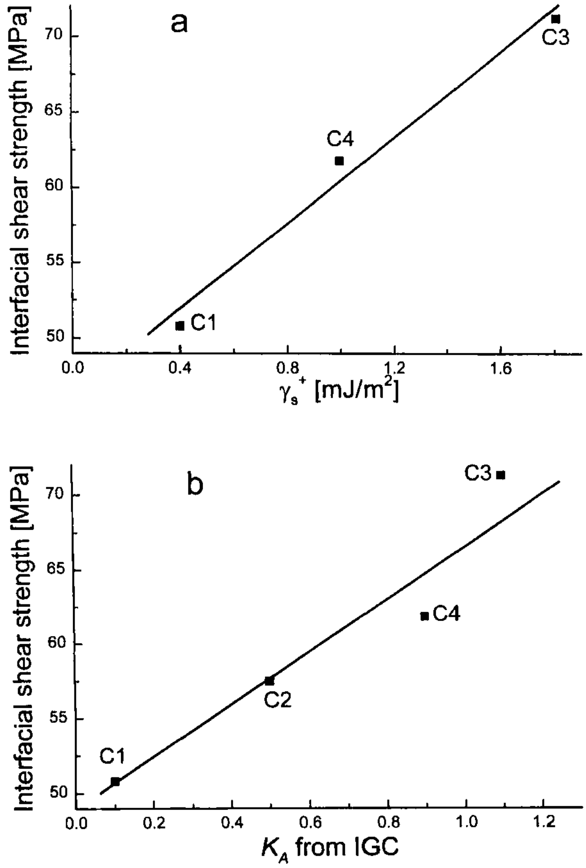

FIGURE 1 Interfacial shear strength, τ, *versus* acceptor parameters of carbon fibers determined by the wetting technique (a) and inverse gas chromatography (b) [1]. Fiber treatment: C1, none; C2, oxidized; C3, acid sizing; C4, base sizing.

Jacobasch with co-workers [1, 15–25]. This confirmed the idea that the basis of all adhesion phenomena is molecular interactions. For instance, flame or plasma treatment of polymer surfaces creates reactive (carboxyl and hydroxyl) groups which can be detected by XPS and which induce changes in the ζ-potential of the surface, increase γ^+, and, as a result, improve the interfacial bond strength [20, 53].

However, the IGC and wetting techniques have not yet been developed to such an extent that the W_A values calculated for a particular system from Eq. (10) and Eqs. (4), (5) should be comparable. The γ^+ and γ^- parameters are still unknown, *e.g.*, for glass fibers and many polymers. If we use a traditional method (for instance, the Owens–Wendt approach) to calculate W_A from wetting data, it appears to give lower values than the IGC technique (Fig. 2). In general, experimental values of the work of adhesion and surface energy from wetting are almost always less than that from IGC. This is true even for the dispersion component, γ^d, especially for inorganic substances (Tab. I). The reason for this probably lies in different experimental conditions intrinsic to these techniques, in particular, different temperatures. Whereas wetting experiments are usually carried out at room temperature, inverse gas chromatography requires several measurements at different temperatures (typically 40–100°C), and common practice is to heat up a chromatographic column to above 100°C and keep it at this temperature for hours before the measurements. This results in desorption of water layers from the solid surface, which can increase γ^d substantially for those solids that have high surface energies, including glass and carbon fibers. Indeed, as was shown in Ref. [48], after drying at 96°C, the γ^d of aluminum trihydrate increased from 33.7 up to 68.4 mJ/m^2, *i.e.*, by more than a factor of two.

This effect was analyzed in detail by Harding and Berg [11] who have shown that for the surfaces most capable of acid–base interaction γ^d from IGC data were larger than those obtained using the wetting technique, which was due to increased adsorption of low

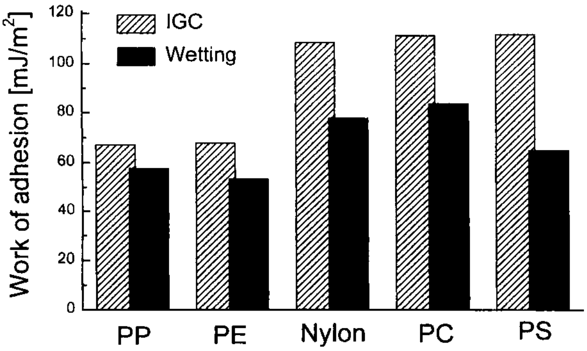

FIGURE 2 Work of adhesion between glass fibers and thermoplastic polymers calculated from IGC and wetting (the Owens–Wendt approach) data.

molecular weight substances. The validity of their suggestion can be seen from Table I. For all types of fibers, the dispersion surface energy component from wetting was considerably less. The possible reason is the presence of adsorbed water layers on the fiber surface in the case of wetting experiments.

Even greater contradictions between the IGC and wetting techniques than the disagreement of the W_A^d values came to light when characterizing acid–base properties of identical solid surfaces using these methods. First, the acid–base contribution to the work of adhesion, measured using the IGC technique, is very large (up to 80% [6]), while the wetting technique estimates it as a rather small "correction to the dispersion component" [37]. Second, most solid surfaces were shown to be bipolar by IGC, *i.e.*, carrying both acid and base sites. On the contrary, characterizing the same surfaces by wetting gave large γ^- values and very small γ^+ (close to zero), *i.e.*, all surfaces appeared to be electron-donating! However, this result often conflicts with the chemical nature of the surfaces. For instance, it is known that the surface of cellulose fibers is covered by OH-groups and is acidic. Nevertheless, the wetting results characterize it as a strong base [32]. Moreover, the vOCG approach resulted, for some polymer surfaces, in negative $\sqrt{\gamma^+}$ values [37, 54]; the physical meaning of this result is so far unexplained. All this gave rise to revision of the vOCG approach by Della Volpe and Siboni [55] and Lee [56]; however, their corrections did not eliminate the shortcomings of the original approach. All surfaces remained predominantly basic (though the γ^- values decreased to some extent), and simultaneous equations still give negative $\sqrt{\gamma^+}$ values for some surfaces.

Critical Discussion

Even if not compared with other techniques, serious problems are within the vOCG approach. In its original version, the characterization of a solid surface involved measurement of contact angles of two liquids (with known γ_l^+ and γ_l^- values) and then calculation of γ_s^+ and γ_s^-. However, the application of different pairs of liquids often resulted in different values of acid and base parameters for the same solid surface. For instance, measurements with water and formamide yielded for sized carbon fibers $\gamma_s^+ = 1.8\,\text{mJ/m}^2$ and $\gamma_s^- = 30.7\,\text{mJ/m}^2$, whereas contact angles of water and dimethylsulphoxide gave for identical fibers, respectively, 4.2 and 4.6 mJ/m^2 [1].

Recently, Good and Hawa [57] proposed a new ("absolute") approach. Having measured contact angles of *three* different liquids ($l1, l2, l3$) on *three* solids ($s1, s2, s3$), one obtains 9 equations in 9 variables, $\gamma_{l1}^+, \gamma_{l2}^+, \gamma_{l3}^+, \gamma_{s1}^+, \gamma_{s2}^+, \gamma_{s3}^+, \gamma_{s1}^-, \gamma_{s2}^-, \gamma_{s3}^-$. The authors believed that the solution of this system would provide values of all the γ^+ and γ^- parameters for investigated solids and probe liquids, including water if it is used for contact angle measurements. These values would be really *absolute*, *i.e.*, not requiring any conventions and assumptions concerning γ^+ and γ^-.

However, the first attempt to apply this approach also ran into difficulties. Solving the system of 9 *non-linear* equations in 9 variables seems to be too complicated even for a powerful computer equipped with modern software [57]; besides, this approach involves purely mathematical problems, as was noted by Della Volpe and Siboni [55]. Preliminary results obtained appeared to be physically implausible. For example, on the basis of chemical structure, PMMA and polystyrene would be expected to be Lewis bases, not acids; but the computer solution gave for these polymers very large values of the acid parameter (20.5 and 10.3 mJ/m^2, respectively). The same solution estimated interfacial tension between water and formamide $\gamma_{\text{water/formamide}} =$ 6.8 mJ/m^2. However, formamide and water are miscible in all proportions, and the interfacial tension must be negative or zero! The authors note, "the theory of hydrogen bonds at interfaces is still in its infancy" [57]. The analysis of the current state of this field of science shows that the problem lies in the very nature of interfacial interactions. The following question inevitable arises: can all non-dispersion interactions be regarded as "hydrogen bonds"? Moreover, are they acid–base interactions in the sense of Lewis? The common idea that a polymer surface is uniformly and densely covered with acid as well as base groups capable of interaction with any other base (acid) groups seems to be a rough oversimplification. Many researchers noted the "chemical paradox": both wetting and IGC provide information on donor and acceptor properties of a polymer which cannot be explained from the viewpoint of its chemical structure. For example, it is not obvious from the molecular structure of PVC which sites contribute to its basicity, or why PVA should be more basic than

PMMA [32]. Many polymers, like polystyrene, do not contain any groups capable of hydrogen bonding but, nevertheless, both wetting and IGC indicate a large non-dispersion contribution to their surface energy.

Thus, the problem reduces to the true nature of the non-dispersion (specific) component. It is known that the total energy of interatomic interaction is composed of several contributions of different physical nature: electrostatic, polarization, exchange repulsion, charge transfer, and coupling [58]. The minimum in the resulting energy–distance curve corresponds to interatomic bonding; its depth and its very existence depend on the nature of both contacting atoms and their surroundings, *i.e.*, the nature of the surfaces in contact. The range of possible interactions can be very wide, from strong covalent bonds to no bonding at all.

The above consideration indicates that the basic assumption of existing acid–base adhesion theories – that any surface can be characterized by two constant parameters for acidity and basicity (K_A and K_B, or γ^+ and γ^-) – is, in all probability, incorrect. Actual interaction of two solid surfaces is very complicated and cannot be described by a simple law like a geometric mean. As was noted in Ref. [37], solid surfaces are not bipolar (*i.e.*, acidic and basic simultaneously), but behave either predominantly basic or predominantly acidic, depending on the nature of the contacting liquid. This can result from even a slight difference in the energy levels of the lowest unoccupied molecular orbitals of the two liquids. The concept of a constant nature of solid surfaces that can be characterized by three constant parameters (γ^d, γ^+ and γ^-) entails confusion and disagreement.

Considering that the exact quantum mechanics analysis of wetting is an extremely complicated task, there is a need for simpler approaches taking into account the individual nature of contacting atoms and molecules. It is most probable that the problems of wetting cannot be solved within the framework of this very approach. As was proposed by Jacobasch [1, 15, 22], the problem of the work of adhesion and surface energy can be solved only by comprehensive investigation using a combination of different experimental techniques, including calorimetry and spectroscopy. For instance, the flow sorption calorimetry technique was developed to characterize quantitatively specific interactions at solid–liquid interfaces [21]. Further development of this and other techniques could give one an insight into the nature of specific interactions and, on this basis, a correct treatment of contact angles.

DIRECT ADHESION FORCES MEASUREMENT

Theoretical Remarks

As is clear from the previous sections, indirect estimations of the work of adhesion from the IGC and wetting techniques are complicated by a series of both theoretical and experimental problems. Therefore, direct measurement of adhesion forces may seem to be a reasonable alternative. The measured adhesion force is related to the work of adhesion by the Derjaguin–Muller–Toporov (DMT) [59] and Johnson–Kendall–Roberts (JKR) [60] theories. For solid particles having sufficiently low elastic moduli and relatively large size (*e.g.*, polymer spheres of radius $R \geq 30\,\mu\mathrm{m}$) the JKR theory is valid [61–63]. When two spherical particles or a particle and a flat surface in contact are under external load, P, the contact radius, a, can be obtained from the following equation:

$$a^3 = \{P + 3\pi W_A R + [6\pi W_A PR + (3\pi W_A R)^2]^{1/2}\}R/K, \qquad (12)$$

where $R = R_1\ R_2/(R_1 + R_2)$, R_1 and R_2 are the radii of the particles, K is the elastic constant, and W_A is the work of adhesion per unit interfacial area. From Eq. (12) we can see that the separation of the particles occurs when the external load becomes negative and equal to

$$P_0 = -\frac{3\pi R}{2} W_A. \qquad (13)$$

All recently developed techniques of the determination of the work of adhesion between two solids from direct adhesion force measurements are based on the JKR theory, in particular, on Eqs. (12) and (13). For instance, the force required to separate two crossed cylinders (surface force apparatus, SFA [64–66]) or two spherical particles (MASIF device (Measurement and Analysis of Surface and Interfacial Forces) [67]) is measured and then converted into the work of adhesion. It should be noted that the separation force is independent of the elastic moduli, as can be seen from Eq. (13). In a JKR apparatus, a contact between a spherical particle and a flat surface is loaded by variable external force, and the function $a(P)$ is recorded. Then W_A is determined from the best fit of the experimental relationship by the theoretical function from Eq. (12) [29, 30].

Polymer/Polymer Contact

Most of the data obtained by direct adhesion force measurements characterize inorganic materials having a smooth surface at the molecular level, such as mica, quartz, or some metals. There are rather little data available for polymers; the application of direct methods is limited by the difficulties of obtaining polymer surfaces with sufficiently low roughness. As can be seen from Table V, the directly-measured work of adhesion between two polymers is sometimes less than its possible minimum, *i.e.*, the dispersion component of W_A calculated using the geometric mean rule. For example, many researchers

TABLE V Work of adhesion in some polymer/solid systems obtained using direct adhesion force measurements

Polymer	*Solid*	P_0/R [mN/m]	W_A [mJ/m^2]	*Device*	*Ref.*
PE	PE	314	66.6	SFA	[30]
PE[a]	PE[a]	264	112	SFA	[71]
PET	PE	364	77.3	SFA	[30]
PET	PET	577	122.4	SFA	[30, 72]
PMMA	PMMA	500	106	SFA	[29]
PS	PS	265[b]	56[b]	MASIF	[17]
PS	PS	415	88	SFA	[29]
PS	PS	–	84	JKR	[29]
PS	PS	329[b]	69.8[b]	MASIF	[88]
PVP-PI copolymer	PVP-PI copolymer	518	110	SFA	[35]
PVP-PS copolymer	PVP-PS copolymer	236	50	SFA	[35]
PS	Mica	~700	148.5	AFM	[89]
PU	Glass	~800	170	JKR	[90]
PS	Glass	403[b]	85.5[b]	MASIF	[88]
Epoxy	Glass OTE[c] SIZED	270[b]	57.3[b]	JKR	[91]
Epoxy	Glass APS[d] SIZED	392[b]	83.1[b]	JKR	[91]

[a] Corona treated polymer.
[b] Maximum measured values.
[c] Octadecyltriethoxysilane.
[d] γ-aminopropyltriethoxysilane.

investigated the adhesion between two identical polystyrene surfaces (see Tab. V). For two PS droplets obtained by melting [17], the measured W_A values scattered strongly; the maximum value, $W_A = 56\,\mathrm{mJ/m^2}$, was less than the calculated, $W_A^d = 2\gamma^d = 74.4\,\mathrm{mJ/m^2}$ [68]. The authors attributed this to the surface roughness. Similar scatter of the measured values seems to be typical; it was also reported for other systems [17, 35]. It can be concluded at once that direct techniques give a lower estimate for W_A and are close to the true values only in the case of molecularly-smooth contact. The achievement of such contact is the main experimental difficulty of this technique.

One of the possible solutions to this problem can be deposition of thin polymer layers onto molecularly smooth surfaces such as mica or quartz. In recent years, smooth polymer surfaces were actually obtained in this way [35, 69]. However, it should be noted that polymer layers obtained by means of this procedure can substantially differ in their properties from "natural" ones, formed by solidification of molten polymers. First, if the thickness of the adsorbed layer is not greater than tens of nanometers, the results of direct force measurement are affected by the dispersion interaction between the substrates. Second, orientation of macromolecules in thin layers results in substantially-different physical properties [69, 70].

Tirrell, Mangipudi and co-workers [29, 30, 71, 72] have developed a very good experimental technique to obtain smooth and, at the same time, sufficiently thick (2 – 6 μm) polymer layers. It consists in extrusion of a relatively thick (~ 50 μm) polymer film followed by biaxial stretching to achieve the required thickness. This technique allowed them to measure, for the first time, the work of adhesion between various polymers. The values obtained are quite reasonable and range between 56 and $126\,\mathrm{mJ/m^2}$. It is interesting that for the contact of two non-polar polymers the results of the direct measurement are in accord with the W_A values calculated from wetting. For instance, both techniques gave $W_A = 66\,\mathrm{mJ/m^2}$ for PE/PE contact [30], which evidences good agreement between them when only the dispersion interaction is of interest. Disagreements arise for contacts of two polar polymers. In this case, the work of adhesion from direct measurements appeared to be greater than that from wetting (Tab. VI). Trying to match the results obtained using these techniques, the authors used different approaches (critical surface

TABLE VI Comparison of W_A values calculated from wetting data and obtained using direct adhesion force measurements

		Wetting			*Direct measurements*	
Polymer	*Solid*	W_A [mJ/m^2]	*Calculation method*[a]	*Ref.*	W_A [mJ/m^2]	*Ref.*
Polyethylene	Polyethylene	68	1	[29]	66.6	[30]
		66	2	[29]		
		66	3	[29][b]		
Polystyrene	Polystyrene	82	1	[29]	88	[29]
		80	2	[29]		
		79	3	[29][b]		
Polystyrene	Mica	122	1	[29, 70][b]	148.5	[89]
Polystyrene	E-glass	86.6	1	[18, 29][b]	85.5	[88]
Poly(methyl methacrylate)	Poly(methyl methacrylate)	88	1	[29]	106	[29]
		84	2	[29]		
		81	3	[29][b]		
Poly(ethylene terephthalate)	Poly(ethylene terephthalate)	88	1	[29]	122.4	[30]
		86	2	[29]		
		87	3	[29][b]		

[a] 1, geometric mean approach; 2, Good–Girifalco equation; 3, van Oss–Chaudhury–Good method.

[b] Calculated by us using the data from corresponding references.

tension after Zisman, interfacial interaction parameter proposed by Good and Girifalco, geometric mean approach according to Owens–Wendt and harmonic mean approach according to Wu). Poor correlation of all these models with experimental results brought them to the conclusion that splitting the work of adhesion into dispersion and polar components does not correspond to physical reality [30]. The authors also found that the results obtained from the wetting technique using different polar liquids did not agree with each other, which was attributed to specific interactions (in particular, hydrogen bonding) between the liquids and polar polymer surfaces.

Data Reduction: the Concept of Acid–Base Interaction

Acid–base interactions affect not only adhesional contact between a liquid and a solid, but also contacts between two polar solids, thus contributing to measured W_A values. Direct adhesion force measurement technique is very sensitive to changes of the state of the surfaces. For instance, the work of adhesion between two polyethylene surfaces doubled upon corona treatment of the polyethylene [71]. However, the calculation of the acid–base adhesion component by the treatment of data from direct adhesion force measurement is not yet developed in existing practice. Traditionally, for two identical surfaces, the work of adhesion determined using the JKR approach is divided in half, and the value obtained is supposed to be the surface energy, γ, of the investigated material. This procedure implicitly includes into γ all types of possible interactions, including specific ones. We already noted above that γ, as a sole scalar parameter, cannot be a satisfactory characteristic of a surface's ability to interact with another medium. Therefore, it is not surprising that γ values obtained for polar polymers from direct measurements are high as compared with other techniques (up to 65 mJ/m^2, Tab. VI).

The description of a contact between two *different* polar polymers is even more problematic. For instance, direct adhesion force measurement gave the value of the work of adhesion in a PE/PET pair as $W_A = 77.1\,\text{mJ/m}^2$, whereas for PE/PE and PET/PET contacts the values of 66.0 and 122.4 mJ/m^2, respectively, have been obtained [30]. The formal application of the Dupré equation yielded $\gamma_{\text{PET/PE}} = 17\,\text{mJ/m}^2$. The authors noted that this value of interfacial energy was extremely high but could not find a satisfactory explanation for it. We would like to propose another interpretation of their result. As can easily be seen, of the three polymer pairs investigated, acid–base interactions are possible only in the PET/PET system (since PE

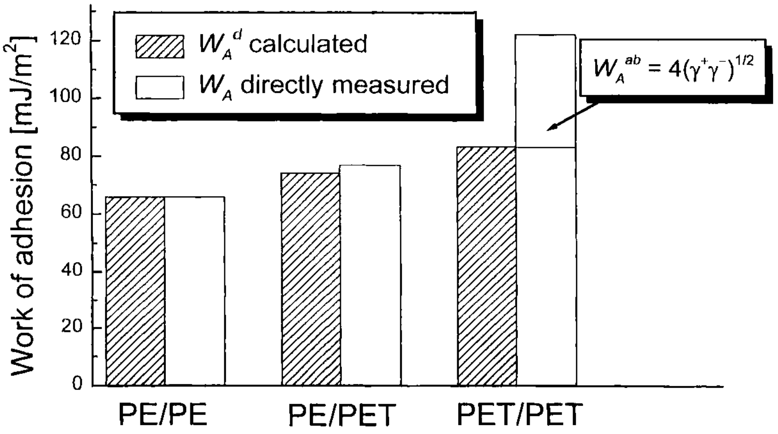

FIGURE 3 Work of adhesion and its dispersion component for PE/PE, PE/PET and PET/PET contacts (calculated using the results of direct adhesion force measurements by Mangipudi *et al.* [29, 30]).

does not contain any polar groups). Thus, low W_A values in the two other systems resulted from the fact that only dispersion forces acted between the polymer surfaces. In contact with PE, polar groups at the PET surface are idle and do not contribute to the total work of adhesion. Independent calculation of the dispersion component of the work of adhesion using the geometric mean approach (assuming $\gamma^d_{\text{PE}} = 33\,\text{mJ/m}^2$ [30] and $\gamma^d_{\text{PET}} = 41.8\,\text{mJ/m}^2$ [70]) gives $W^d_A = 74.3\,\text{mJ/m}^2$, which is in good agreement with the experimental value of $77.1\,\text{mJ/m}^2$. Thus, the traditional approach causes confusion in the interpretation of data obtained using contact mechanics. Probably, the data treatment can be revised in a way that connects it to other techniques (wetting and IGC). For instance, similarly to the vOCG approach for wetting, the surface of each contacting particle can be characterized by the same three parameters proposed by Good *et al.*, γ^d, γ^+ and γ^-. In the spirit of the vOCG approach, we can conclude that the difference between the experimental W_A value in the PET/PET system and its dispersion component ($W^d_A = 2\gamma^d_{\text{PET}} = 86.6\,\text{mJ/m}^2$) is nothing but $4(\gamma^+\gamma^-)^{1/2} = 38.8\,\text{mJ/m}^2$ (Fig. 3).

Polymer/Inorganic Solid Contact

The range of values of the work of adhesion between polymers and inorganic surfaces, obtained using direct adhesion force measurements, is wider than that for polymers only. In polymer-inorganic surface adhesion, adsorbed water layers play a considerable role. High energy surfaces readily adsorb water, which results in substantial decrease of the dispersion surface energy component, γ^d. For example, γ^d value for pure quartz silica (measured using inverse gas chromatography) is about $250\,\text{mJ/m}^2$ [11], while for glass fibers $\gamma^d = 33\,\text{mJ/m}^2$ from IGC data [18] and even less, $21.6\,\text{mJ/m}^2$, from wetting [18]. As can be seen in Table V, measured W_A values between polymers and high energy surfaces such as mica and glass are very large – 148.5 mJ/m^2 for PS/mica and $170\,\text{mJ/m}^2$ for PU/glass systems. However, adsorbed water deteriorates adhesion considerably. This can be illustrated by the data on the polystyrene/glass pair using the MASIF device [17]. Random fluctuations of the roughness at the contact point resulted in wide variation in measured W_A values. The maximum value obtained, $W^{\max}_A = 85.5\,\text{mJ/m}^2$, obviously approaches the true value.

The measurements with MASIF appeared to be extremely sensitive to the state of the surfaces; in particular, to the moisture adsorbed on the glass surface. For instance, after washing the glass sphere and following drying at 60°C for 5 min the work of adhesion between PS and glass decreased dramatically to 5.3 mJ/m^2. Drying the sphere in vacuum at 110°C for 3 hours resulted in partial recovery of the work of adhesion. One of possible causes of lower polystyrene adhesion to wet glass is a sharp decrease of the dispersion component of the surface energy of glass (for dry glass, γ^d is about 250 mJ/m^2; for water, $\gamma^d = 21.8$ mJ/m^2) and, consequently, a much lower W_A^d value. As was noted above, a similar effect is responsible for the lower W_A^d obtained from wetting than from IGC. However, this cannot explain such low W_A values as the measured 5.3 mJ/m^2. More probably, disjoining pressure plays the determining role here. As was shown by Derjaguin *et al.*, the presence of adsorbed water on high energy surfaces can produce a disjoining pressure which decreases adhesion between these and can even fully eliminate it (*i.e.*, the interaction force is *repulsive* for any separation distance) [47].

The described drawbacks of the direct adhesion force measurement technique (strong sensitivity of measured W_A values to surface roughness and adsorbed moisture) can be turned into its advantages. These effects, as well as kinetics of interaction and interdiffusion of polymer chains [17, 35], can be directly investigated using this technique. It seems especially important when we take into account that indirect techniques, which only calculate the work of adhesion from component properties, cannot predict all phenomena occurring at direct contact. This illustrates that each separate technique is insufficient for studying adhesion phenomena; on the other hand, results from one method *can* and *should* be used in other methods, thus forming a unified "field" of adhesion science.

MICROMECHANICAL TESTS

"Fundamental" and "Practical" Adhesion

The issue of the connection between the "fundamental" and "practical" adhesion has been extensively discussed during the last few years. Though there is no doubt that these two quantities, the work of adhesion and the bond strength, are both determined by molecular interactions, their relationship remains still unknown. Two opposite opinions can be found in the literature. On the one hand, the interfacial bond strength measured by means of destructive tests is often referred as "adhesional strength" or simply "adhesion". On the other hand, the existence of a variety of processes accompanying interfacial failure (matrix yielding, crazing, cohesive failure, *etc.*) provides a ground for the opinion that the results of, *e.g.*, micromechanical tests have nothing in common with adhesion.

Nevertheless, correlation has been found between the W_A and the strength of adhering systems. Many papers reported a linear relationship between the work of adhesion and the bond strength [6, 14, 19], as well as between the bond strength and the surface energy of the solid substrate [3–5].

The direct proportionality between the work of adhesion and the "practical" adhesion was shown by Andrews and Kinloch [2]:

$$G = W_A \cdot \phi, \tag{14}$$

where G is the measured fracture energy, and ϕ is a temperature and rate dependent viscoelastic term.

It is important that this proportionality has been revealed for macroscopic composites, which allowed the prediction and control of the strength of composite materials using the results of surface characterization by means of the wetting or IGC techniques [19].

However, for target-oriented interfacial design, a more accurate quantitative relationship is required, not simply a correlation. Obtaining such a relationship is possible only in consideration of local failure processes, in order to minimize the effect of side phenomena in which energy is dissipated. In this approach, the energy required for the separation of adhering surfaces can be estimated separately.

For polymer composites, this approach can be used in micromechanical tests. Having investigated many polymer/fiber systems, Nardin and Schultz [6, 14] reported a linear proportionality between the interfacial shear strength (τ) measured using the fragmentation technique and W_A from IGC data. They suggested that the relationship between W_A and τ can be written simply as

$$W_A = \delta^{-1}\left(E_f/E_m\right)^{1/2}\tau, \tag{15}$$

where E_f and E_m are elastic moduli of the fiber and the matrix, respectively, and δ^{-1} is equal to about 0.5 nm and corresponds to an equilibrium center-to-center distance involved in physical interactions, such as van der Waals and acid – base interactions. The term $(E_f/E_m)^{1/2}$ was considered by the authors as "a normalizing factor allowing all composite systems to be compared with each other". Thus, the Nardin – Schultz approach allows one to determine the work of adhesion from the results of destructive tests. A similar approach was used to estimate the work of adhesion of SiO_x coatings on PET films by means of the scratch test and coating fragmentation [73].

Adhesional Pressure in Micromechanical Tests

Recently, the Nardin – Schultz approach has been substantially revised [43, 74]. One of its major drawbacks was that it related the work of adhesion to interfacial *shear* stress, whereas it is done against *normal* stresses at the interface, *i.e.*, in the case of fiber/matrix system, radial interfacial pressure, σ_{rr}. This normal interfacial stress is produced by molecular forces responsible for the adhesion between two surfaces. Therefore, the work of adhesion can be calculated as the integral of the normal interfacial stress (adhesional pressure) over the separation distance. The problem is to extract this adhesional pressure from the results of a destructive test; to do this, one should pay special attention to local processes that occur at the interface. However, the analysis of local stresses is a rather complicated task even in the case of model composites with well-defined simple geometry, for instance, in specimens for micromechanical tests.

Fortunately, recent investigations of the mechanisms of interfacial failure in micromechanical tests gave a possibility of correct estimation of the work of adhesion between a fiber and a polymer. Piggott [75] and Marotzke [76] showed that crack initiation in the pull-out and microbond tests occurred in normal tension (Mode I), as illustrated in Figure 4. The variational mechanics analysis carried out by Scheer and Nairn [77] confirmed this observation theoretically. Moreover, they derived a set of equations which can be used to calculate the normal interfacial stress at the moment of crack initiation, *i.e.*, adhesional pressure in fiber-matrix systems.

To estimate the work of adhesion, the exact integral of interfacial normal stress over the separating distance can be approximated

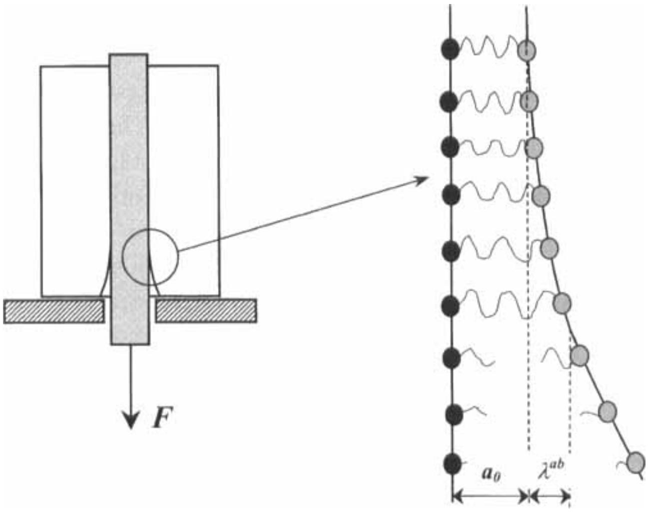

FIGURE 4 Schematic view of crack propagation in a microbond test. The equilibrium interatomic distance is labelled as a_0, and the elongation-to-break of acid–base bonds as λ^{ab}.

by a product

$$W_A = \sigma_{\text{ult}} \cdot \lambda, \tag{16}$$

where σ_{ult} is the adhesional pressure and λ is a characteristic displacement over which the work of adhesion is done. For acid–base interactions, it is the bond elongation-to-break (λ^{ab} in Fig. 4). The σ_{ult} value is determined by means of a micromechanical test, and λ can be estimated theoretically and experimentally. There are different approaches understandings of the physical meaning of λ. Nardin and Schultz demonstrated that the λ value varied in accordance with the contribution of acid–base interactions to the total work of adhesion [14]. However, it seems more natural to introduce *two* different ranges of adhesional forces, namely, λ^d for dispersion forces and λ^{ab} for acid–base interactions [43, 74]. In this approach, λ^d and λ^{ab} can be considered as nearly constant for all polymers, and the work of adhesion is estimated as

$$W_A = \sigma^d_{\text{ult}} \cdot \lambda^d + \sigma^{ab}_{\text{ult}} \cdot \lambda^{ab}. \tag{17}$$

Experimental σ_{ult} values from micromechanical tests and W_A measured independently by the IGC technique are in good agreement with Eq. (17) (Fig. 5). Estimation of the λ's from these data gave $\lambda^d \approx 7.0$ Å and $\lambda^{ab} \approx 3.2$ Å, which is close to typical theoretical values [74]. Nardin and Schultz [14] found that λ varied between 2 and 5 Å in accord with the contribution of acid–base interactions; however, they understood λ as an equilibrium *interatomic distance* rather than the *range of action* of adhesional forces. It is obvious that, *e.g.*, the range of action of dispersion forces is larger than the equilibrium interatomic distance.

Estimation of the Work of Adhesion from Micromechanical Tests

This technique can be very useful for estimating the work of adhesion from destructive micromechanical tests. First, σ_{ult} is determined by means of the microbond or pull-out test, and then W_A is calculated from Eq. (17). Table VII presents the results of calculations for several polymer-fiber systems. It should be noted that this approach (as well as inverse gas chromatography) is very sensitive to the nature of interacting surfaces, *e.g.*, fiber surface treatment and matrix modification. The W_A values calculated for all systems are in good agreement with the strength data for macro composites.

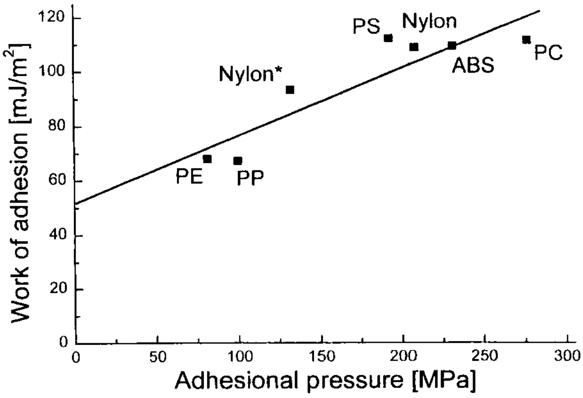

FIGURE 5 Correlation between the adhesional pressure (from micromechanical tests) and the work of adhesion (from IGC data) [88]. The point marked Nylon* is for a Nylon 6,6/carbon fiber system, and all other points for polymer/glass fiber pairs.

TABLE VII Work of adhesion for some polymer/fiber systems estimated from micromechanical tests

Fiber	*Matrix*	σ_{ult} [*MPa*]	W_A [mJ/m^2]	*Composite strength* [*MPa*]	*Ref.*
E-glass γ-APS sized	Polypropylene	99.8	69.7	11.0[a]	[16]
E-glass γ-APS sized	Polypropylene MA grafted	147.0	84.8	19.7[a]	[16]
E-glass unsized	Epoxy resin	153	86.7	27.3[b]	[92]
E-glass γ-APS sized	Epoxy resin	326	142.1	72.9[b]	[92]
E-glass γ-APS sized with PU film former	Epoxy resin	232	112.0	49.2[b]	[92]
E-glass with PVAc film former	Epoxy resin	185	97.0	24.1[b]	[92]
Aramid unsized	Epoxy resin	180	95.4	–	

[a] Compression shear strength.
[b] Transverse tensile strength.

The estimation of the work of adhesion from micromechanical tests is especially valuable, in spite of possible partial irreversibility of the process (for instance, breaking of covalent bonds in the case of epoxy resins). For thermosetting resins, the IGC technique can predict a decrease in fiber-matrix adhesion upon surface treatment, while micromechanical tests reveal considerably improved interfacial bonding [18, 78]. This is quite reasonable, because amino groups present in γ-APS act as additional hardener of the epoxy resin by chemical bonding at the interface. Drzal *et al.* [79] showed that even a small amount of interfacial covalent bonds substantially increases the bond strength. However, covalent bonding cannot be predicted using the IGC technique.

Another important advantage of the technique proposed is its sensitivity to the conditions of the composite formation. It is known that kinetic factors determine, to a high degree, interfacial adhesion in fibrous polymer composites formed from a polymer melt [80–82]. The number of local bonds in real composites is usually far from thermodynamic "saturation"; nevertheless, it affects the measured F_d value and, as a consequence, the estimated work of adhesion. Thus, destructive micromechanical tests allow W_A measurement even under non-equilibrium conditions. This distinguishes them from the IGC and wetting techniques, which can yield only thermodynamic reversible work of adhesion at the given temperature.

Finally, this approach eliminates "third bodies" (probe liquids) and, in this way, makes unnecessary extensive intermediate measurements. We need not characterize each of contacting bodies by three parameters, as in IGC and wetting approaches; direct measurement of the debond force will suffice.

W_A VALUES FROM DIFFERENT TECHNIQUES: HOW CAN THEY BE COMPARED?

Comparative analysis of different experimental techniques shows that the dispersion component of the work of adhesion (W_A^d) can be reliably measured by each of them. As can be seen in Table VIII, for non-polar PP and PE all W_A values are in good agreement. No doubt this is due to the fact that the dispersion interaction is non-local; it is a superposition of many non-specifics, long-range forces acting between individual molecules occupying considerable volume. The dispersion interaction does not require overcoming any energy barrier: its intensity is not zero even when two bodies are separated by a broad gap, and it increases monotonically with approach of the bodies. Besides, dispersion forces only marginally depend on temperature; therefore, the good agreement between the results of different methods (for non-polar polymers) can be expected.

In contrast, for polar polymers different techniques give inconsistent results, as can be seen for PS in Table VIII. Of course,

TABLE VIII Work of adhesion obtained using different techniques

	Direct measurements		*Wetting*		*IGC*		*Micromechanical tests*	
System	W_A [mJ/m^2]	*Ref.*	W_A [mJ/m^2]	*Ref.*	W_A [mJ/m^2]	*Ref.*	W_A [mJ/m^2]	*Ref.*
PE/PE	66.6	[30]	66	[30]	70.0	[44][a]	–	
PE/glass	–		57.1	[15][a]	68.0	[18, 44][a]	63.8	[43]
PP/glass	–		56.6	[18][a]	67.3	[18, 36][a]	69.7	[74]
PS/PS	88	[29]	82	[29]	84.4	[36][a]	–	
PS/glass	85.5	[88]	86.6	[18, 29][a]	112.1	[9, 62][a]	99.4	[74]

[a] Calculated by us using the data from corresponding references.

this inconsistency is, to a certain extent, due to insufficient theoretical knowledge about specific (non-dispersive) interactions at interfaces. All existing theories involve simplifying assumptions; as a result, the calculated acid–base components of the work of adhesion differ from each other. For instance, due to the basic assumptions of the IGC approach, the data obtained using this technique is always to a certain degree overestimated (and refer rather to the thermodynamic limit of interaction for the given system). On the other hand, direct adhesion force measurements (contact mechanics) often give underestimated values, which may be attributed to surface roughness.

However, close study of all four techniques shows that their results *should not* be in agreement. The reason is that in the different approaches *the experimental conditions* are substantially different. For one instance, there is direct contact between two solid surfaces at room temperature, but the polymer-fiber interface in a composite is formed from a melt. It is also difficult to compare inverse gas chromatography at elevated temperatures and at infinite dilution with wetting where the interaction occurs between two condensed phases. These processes differ in the purely thermodynamic sense, and their kinetics are also different. This is especially important in the case of polymers. This can be illustrated by an example represented in Figure 6. In the contact of two solids (contact mechanics) the local bond formation is determined by the arrangement of acid and base sites at the moment of contact, Figure 6(a), whereas mobility in a polymer melt, Figure 6(b) results in increasing number of acid–base bonds, and consequently, interfacial adhesion, with time.

In general, there is some confusion about the work of adhesion. For example, it is often implicitly assumed that the work of adhesion is a universal characteristic of two given interacting phases. However, even the thermodynamic (reversible) work of adhesion depends on pressure, temperature, and chemical activity of the system. Figure 7 presents an energy barrier that must be overcome to form a local adhesional bond. It is obvious that the populations of levels 1 (no bond) and 2 (local bond formed) are functions of temperature.

For polymer adhesion it is much more important to realize that thermodynamic equilibrium is almost never achieved. For example, in the case of direct adhesion force measurement there is simply little time to achieve the equilibrium. On the contrary, fast cooling of

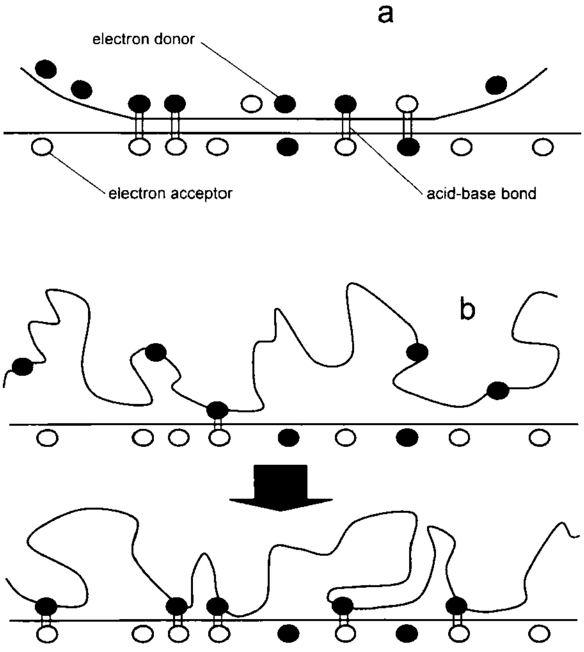

FIGURE 6 Formation of acid – base bonds between two solids (contact mechanics, a) and a solid and a polymer melt (b).

the composite after its formation from a polymer melt results in "freezing" of a state which could be equilibrium at the formation temperature but is substantially non-equilibrium at the testing conditions. To break such a "frozen" bond, it is not sufficient to do the work equal to the thermodynamic energy of the bond ($-\Delta G$, Fig. 7); the energy barrier, ε_B, should be overcome.

Moreover, there can be several energy barriers, corresponding to different types of bonds, for one pair of contacting solids. As an example, consider the interaction between an epoxy resin and a glass surface. Discounting the universal dispersion interaction, formation of hydrogen bonds (transition 1 → 2, Fig. 8) is possible in this system even at room temperature. However, an increase in temperature can activate another process – covalent bonding between epoxy and glass. For this transition (1 → 3 or 2 → 3, a higher energy barrier, ε_A, should be overcome, but the work needed to break the adhesional contact, ε_B, is also greater (Fig. 8).

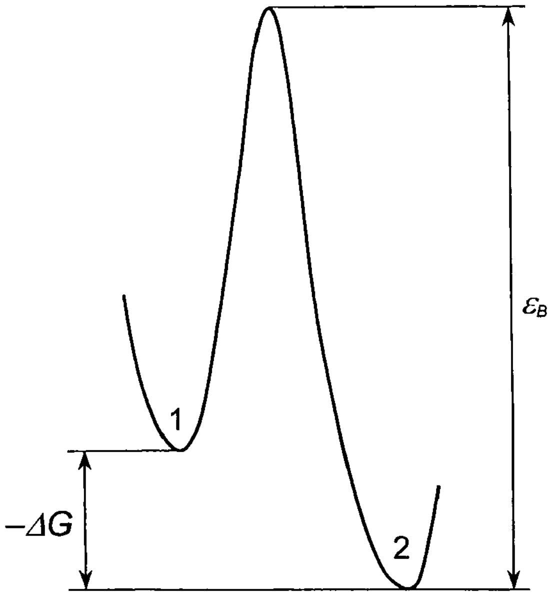

FIGURE 7 Energy diagram for acid–base bonding: (1) unbonded state; (2) bonded state.

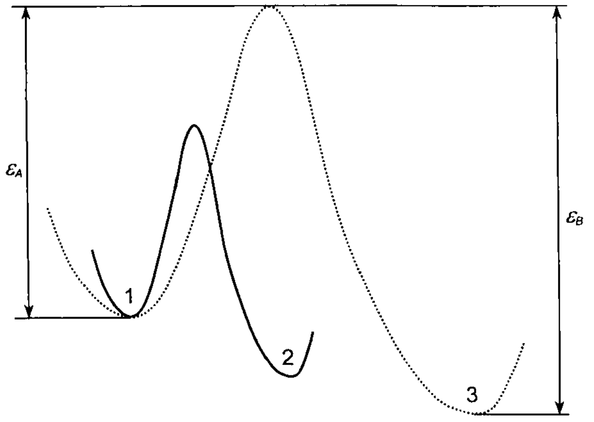

FIGURE 8 Energy diagram for acid–base and covalent bonding: (1) unbonded state; (2) acid–base local bond; (3) covalent bond.

The work of adhesion for the same system can be different, if adhesional contact is formed differently. In this concern, micromechanical measurements can give information about the real adhesion level in the composite, *i.e.*, these tests can estimate the irreversible work of adhesion.

From the above discussion, we can conclude that detailed information about adhesion in a polymer-solid system, and its variations with different conditions of composite formation and testing, can be obtained only by comprehensive use of various techniques, both direct and indirect. For instance, the IGC technique gives the thermodynamic limit of adhesion in a given system. Besides, its important advantage is the possibility of prediction of adhesion variations in the system upon surface modification of one or both components. A simple calculation shows that coating of glass fibers with a basic sizing agent (γ-APS) will deteriorate its adhesion to electron-donor polymers, *e.g.*, PS and ABS [78]. To confirm this result using the micromechanical tests [78] or testing of macro composites, extensive and labor-consuming experimental work should be done. It should also be mentioned that the IGC technique can give more correct W_A values, if the experiments are performed at finite concentrations of probe liquids rather than at infinite dilution, which, however, requires much more time [48].

While micromechanical techniques characterize adhesion contact formed at high temperatures, the wetting and contact mechanics approaches can be successfully used to determine W_A at lower temperatures. These two techniques are valuable for studying fine surface effects, *e.g.*, chemical surface heterogeneity or the presence of adsorbed layers. Additional information can be obtained using direct adhesion force measurement. The advantage of this technique is that it measures adhesion directly, without using any third bodies.

CONCLUSION

We have compared existing direct and indirect methods of estimation of the work of adhesion in polymer-solid systems. For non-polar polymers, the data obtained using all these approaches are in good agreement. The difference between the results of these techniques in the case of polar polymers is, in all probability, due to different estimations of the non-dispersion contributions some of which may be due to acid–base interaction. In the most fully developed method, inverse gas chromatography, the acid and base parameters are semi-empirical; besides, this method is principally related to the sites with the highest energies, which results in overestimated W_A values. The IGC estimate can be regarded as the thermodynamic limit characteristic of a given system.

For the wetting technique, there are several contradictory theories whose aim is to take into account the specific (non-dispersion) component of interaction. As a rule, these theories are not sufficiently justified theoretically and mostly try to fit experimental results. This is rarely successful, and W_A values derived from the wetting technique are often underestimated.

Contact mechanics, or direct adhesion force measurement, as a rule, underestimates the work of adhesion between two solids, which is primarily due to the roughness of contacting surfaces. However, in the cases when molecularly smooth contact has been achieved, this technique appeared to be very informative. Contact mechanics and micromechanical tests have the advantage that they do not need third bodies (probe liquids, as in the IGC and wetting techniques) and directly consider interfacial failure. We demonstrated the possibility of W_A estimation from micromechanical tests. This approach is based on the measurement of the critical normal interfacial tension corresponding to crack initiation (adhesional pressure).

In general, one system can be characterized by more than one value of the work of adhesion. The number of local bonds depends substantially on the formation conditions and is determined by both thermodynamics and kinetics of the process. Therefore, the full picture of the adhesion in a particular system can be obtained only by using a comprehensive approach involving different experimental techniques.

References

[1] Jacobasch, H.-J., Grundke, K., Uhlmann, P., Simon, F. and Mäder, E., *Composite Interfaces* **3**, 293 (1996).

[2] Andrews, E. H. and Kinloch, A. J., *Proc. R. Soc. Lond.* **A332**, 385 (1973).

[3] Wagner, H. D., Gallis, H. E. and Wiesel, E., *J. Mater. Sci.* **28**, 2238 (1993).

[4] Sheu, G. S. and Shyu, S. S., *J. Adhesion Sci. Technol.* **8**, 1027 (1994).

[5] Lui, F. P., Wolcott, M. P., Gardner, D. J. and Rials, T. G., *Composite Interfaces* **2**, 413 (1994).

[6] Nardin, M. and Schultz, J., *Composite Interfaces* **1**, 177 (1993).

[7] Nardin, M., Asloun, E. M. and Schultz, J., *Surface Interface Anal.* **17**, 485 (1991).

[8] Kendall, K., *Composite Interfaces* **4**, 299 (1997).
[9] Packham, D. E., *Int. J. Adhesion and Adhesives* **16**, 121 (1996).
[10] Sharpe, L. H., *J. Adhesion* **67**, 277 (1998).
[11] Harding, P. H. and Berg, J. C., *J. Adhesion Sci. Technol.* **11**, 471 (1997).
[12] Berg, J. C., In: *Wettability*, Berg, J. C. Ed. (Marcel Dekker, New York, 1993), p. 75.
[13] Gutowski, W., In: *Controlled Interfaces in Composite Materials*, Ishida, H. Ed. (Elsevier, New York, 1990), p. 505.
[14] Nardin, M. and Schultz, J., *Langmuir* **12**, 4238 (1996).
[15] *Interfaces, Surfactants and Colloids in Engineering* (*Progress in Colloid and Polymer Science*, Vol. 101), Jacobasch, H.-J. Ed. (Springer-Verlag, Heidelberg, 1996).
[16] Mäder, E., Jacobasch, H.-J., Grundke, K. and Gietzelt, T., *Composites Part A* **27A**, 907 (1996).
[17] Schmitt, F.-J., Ederth, T., Weidenhammer, P., Claesson, P. and Jacobasch, H.-J., *J. Adhesion Sci. Technol.* **13**, 79 (1999).
[18] Jacobasch, H.-J., Grundke, K., Mäder, E., Freitag, K.-H. and Panzer, U., *J. Adhesion Sci. Technol.* **6**, 1381 (1992).
[19] Mäder, E., Grundke, K., Jacobasch, H.-J. and Wachinger, G., *Composites* **25**, 739 (1994).
[20] Grundke, K., Jacobasch, H.-J., Simon, F. and Schneider, St., *J. Adhesion Sci. Technol.* **9**, 327 (1995).
[21] Schneider, S., Simon, F., Pleul, D. and Jacobasch, H.-J., *Fresenius J. Anal. Chem.* **358**, 244 (1997).
[22] Simon, F., Jacobasch, H.-J., Pleul, D. and Uhlmann, P., *Progr. Colloid Polym. Sci.* **101**, 184 (1996).
[23] Spange, S., Simon, F., Heublein, G., Jacobasch, H.-J. and Börner, M., *Colloid Polym. Sci.* **269**, 173 (1991).
[24] Weidenhammer, P. and Jacobasch, H.-J., *J. Colloid Interface Sci.* **180**, 232 (1996).
[25] Jacobasch, H.-J., *Macromol. Chem., Macromol. Symp.* **75**, 99 (1993).
[26] Fowkes, F. M., In: *Adhesion and Adsorption of Polymers*, Lee, L. H. Ed. (Plenum Press, New York, 1980), **A**, 43.
[27] Berthelot, D., *Compt. Rend.* **126**, 1703 (1898).
[28] Fowkes, F. M., *Ind. Eng. Chem.* **12**, 40 (1964).
[29] Mangipudi, V. S., Intrinsic Adhesion Between Polymer Films: Measurement of Surface and Interfacial Energies, *Ph.D. Thesis*, Univ. of Minnesota (1995).
[30] Mangipudi, V., Tirrell, M. and Pocius, A. V., *J. Adhesion Sci. Technol.* **8**, 1251 (1994).
[31] Schultz, J., Lavielle, L. and Martin, C., *J. Adhesion* **23**, 45 (1987).
[32] Shen, W., Sheng, Y. I. and Parker, I. H., *J. Adhesion Sci. Technol.* **13**, 887 (1999).
[33] Saint Flour, C. and Papirer, E., *Ind. Eng. Chem. Prod. Res. Dev.* **21**, 666 (1982).
[34] van Oss, C. J., Good, R. J. and Chaudhury, M. K., *J. Colloid Interface Sci.* **111**, 378 (1986).
[35] Watanabe, H. and Tirrell, M., *Macromolecules* **26**, 6455 (1993).
[36] Felix, J. M., Gatenholm, P. and Schreiber, H. P., *Polymer Composites* **14**, 449 (1993).
[37] Dalet, P., Papon, E. and Villenave, J.-J., *J. Adhesion Sci. Technol.* **13**, 857 (1999).
[38] Conder, J. R. and Young, C. L., *Physicochemical Measurements by Gas Chromatography* (Wiley Interscience, New York, 1979).
[39] Papirer, E., Balard, H. and Vidal, A., *Eur. Polym. J.* **24**, 783 (1988).
[40] Gutmann, V., *The Donor-Acceptor Approach to Molecular Interactions* (Plenum Press, New York, 1978).
[41] Fowkes, F. M., *J. Adhesion Sci. Technol.* **1**, 7 (1987).
[42] Riddle, F. L. Jr. and Fowkes, F. M., *J. Amer. Chem. Soc.* **112**, 3259 (1990).
[43] Dutschk, V., Pisanova, E., Zhandarov, S. and Lauke, B., *Mech. Compos. Mater.* **34**, 431 (1998).

[44] Ulkem, I. and Schreiber, H. P., *Composite Interfaces* **2**, 253 (1994).
[45] Lee, L.-H., In: *Fundamentals of Adhesion*, Lee, L.-H. Ed. (Plenum Press, New York, 1991), p. 1.
[46] Papirer, E., Li, S., Balard, H. and Jagiello, J., *Carbon* **29**, 1135 (1991).
[47] Derjaguin, B. V., Churaev, N. V. and Muller, V. M., *Surface Forces* (Nauka, Moscow, 1985).
[48] Balard, H. and Papirer, E., *Progress in Organic Coatings* **22**, 1 (1993).
[49] Owens, D. K. and Wendt, R. C., *J. Appl. Polymer Sci.* **13**, 1741 (1969).
[50] Wu, S., *Polymer Interface and Adhesion* (Marcel Dekker Inc., New York and Basel, 1982).
[51] Girifalco, L. A. and Good, R. J., *J. Phys. Chem.* **61**, 904 (1957).
[52] Lifshitz, E. M., *J. Exper. Theor. Phys.* **29**, 94 (1955).
[53] Song, Q. and Netravali, A. N., *J. Adhesion Sci. Technol.* **12**, 957 (1998).
[54] Good, R. J., In: *Contact Angle, Wettability and Adhesion*, Mittal, K. L. Ed. (VSP, Utrecht, The Netherlands, 1993), p. 3.
[55] Della Volpe, C. and Siboni, S., *J. Colloid Interface Sci.* **195**, 121 (1997).
[56] Lee, L.-H., *J. Adhesion* **67**, 1 (1998).
[57] Good, R. J. and Hawa, A. K., *J. Adhesion* **63**, 5 (1997).
[58] Lee, L.-H., *J. Adhesion Sci. Technol.* **7**, 583 (1993).
[59] Derjaguin, B. V., Muller, V. M. and Toporov, Yu. P., *J. Colloid Interface Sci.* **56**, 314 (1975).
[60] Johnson, K. L., Kendall, K. and Roberts, A. D., *Proc. R. Soc. Lond.* **A324**, 301 (1971).
[61] Muller, V. M., Yushchenko, V. S. and Derjaguin, B. V., *J. Colloid Interface Sci.* **77**, 91 (1980).
[62] Muller, V. M., Yushchenko, V. S. and Derjaguin, B. V., *J. Colloid Interface Sci.* **92**, 92 (1983).
[63] Maugis, D., *J. Colloid Interface Sci.* **150**, 243 (1992).
[64] Tabor, D. and Winterton, R. H. S., *Proc. R. Soc. Lond.* **A312**, 435 (1969).
[65] Israelachvili, J. N. and Tabor, D., *Proc. R. Soc. Lond.* **A331**, 19 (1972).
[66] Israelachvili, J. N. and Adams, G. E., *J. Chem. Soc. Faraday Trans. I* **74**, 975 (1978).
[67] Parker, J. L., *Progress in Surface Sci.* **47**, 205 (1994).
[68] Qin, X. and Chang, W. V., *J. Adhesion Sci. Technol.* **10**, 963 (1996).
[69] Israelachvili, J. N., *Intermolecular and Surface Forces* (Academic Press, London, 1991).
[70] Kinloch, A. J., *Adhesion and Adhesives* (Chapman and Hall, London, 1987).
[71] Mangipudi, V., Tirrell, M. and Pocius, A. V., *Langmuir* **11**, 19 (1995).
[72] Merrill, W. W., Pocius, A. V., Thakker, B. V. and Tirrell, M., *Langmuir* **7**, 1975 (1991).
[73] Pitton, Y., Hamm, S. D., Lang, F.-R., Matthieu, H. J., Leterrier, Y. and Manson, J. A., *J. Adhesion Sci. Technol.* **10**, 1047 (1996).
[74] Zhandarov, S., Pisanova, E. and Schneider, K., *J. Adhesion Sci. Technol.* **14**, 381 (2000).
[75] Piggott, M. R., *Composites Sci. Technol.* **55**, 269 (1995).
[76] Marotzke, C., *Composite Interfaces* **1**, 153 (1993).
[77] Scheer, R. J. and Nairn, J. A., *J. Adhesion* **53**, 45 (1995).
[78] Pisanova, E. and Mäder, E., *J. Adhesion Sci. Technol.* **14**, 415 (2000).
[79] Drzal, L. T., Sugiura, N. and Hook, D., *Composite Interfaces* **4**, 337 (1997).
[80] Pisanova, E., Zhandarov, S. and Schneider, K., *J. Macromolecular Sci. Part B: Physics* **B38**, 945 (1999).
[81] Pisanova, E. V., Zhandarov, S. F. and Dovgyalo, V. A., *Polymer Composites* **15**, 147 (1994).
[82] Zhandarov, S. F., Pisanova, E. V. and Dovgyalo, V. A., *J. Adhesion Sci. Technol.* **8**, 995 (1994).

[83] van Oss, C. J., *Interfacial Forces in Aqueous Media* (Marcel Dekker, New York, 1994).

[84] Good, R. J., Chaudhury, M. K. and van Oss, C. J., In: *Fundamentals of Adhesion*, Lee, L. H. Ed. (Plenum Press, New York, 1991), p. 153.

[85] Panzer, U. and Schreiber, H. P., *Macromolecules* **25**, 3633 (1992).

[86] Zhandarov, S., Pisanova, E. and Schneider, K., *ICCM-12: Proc. 12th International Conference on Composite Materials*. Paris, 5–9 July, 1999.

[87] Fu, S. Y. and Lauke, B., *J. Mater. Sci. Technol.* **13**, 1 (1997).

[88] Pisanova, E., Dutschk, V., Zhandarov, S. and Mäder, E., *J. Adhesion Sci. Technol.* (in press).

[89] Biggs, S. and Spinks, G., *J. Adhesion Sci. Technol.* **12**, 461 (1998).

[90] Rimai, D. S., DeMejo, L. P. and Bowen, R. C., *J. Adhesion Sci. Technol.* **8**, 1333 (1994).

[91] Woerdeman, D. L., Amouroux, N., Ponsinet, V., Jandeau, G., Hervet, H. and Léger, L., *Composites Part A* **30**, 95 (1999).

[92] Mäder, E., Mai, K. and Pisanova, E., *Composite Interfaces* (in press).