Interfacial effects in composites

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Abstract – It is well known that the behavior of diverse multicomponent systems
such as fibrous composites, particle-filled polymers, polymer blends, and
pigmented coatings depends not only on the composition, morphology, and
properties of the constituents, but also on the nature of the interfacial region.
This paper reviews typical examples, with emphasis on interpretation of
interactions between constituents considered in terms of Lewis acids or bases.

INTRODUCTION

With a simple well-bonded composite system, the value of a given property P is determined
by a summation of the constituent properties, usually weighted by the respective volume
fractions. In this limiting case, so-called "perfect" adhesion is assumed (with a sharp
discontinuity in properties at a negligibly thick interface). The value of P may be given
by one of many equations, of which the following upper and lower-bound expressions are the
simplest (1–12):

$$P = P_A V_A + P_B V_B \qquad \text{(upper bound)} \tag{1}$$

$$P = \frac{P_A P_B}{P_A V_B + P_B V_A} \qquad \text{(lower bound)} \tag{2}$$

where the subscripts A and B refer to the two constituents. While a particular equation
may be appropriate for a given system, it should be noted that such continuum-type models
hold in principle for all multicomponent systems, including not only particle and
fiber-reinforced polymers, but also such diverse composites as pigmented coatings,
laminates, polymer blends, and even semicrystalline polymers. Also, models of this kind
can characterize many kinds of properties, from mechanical to transport behavior.
Nevertheless, such models are often excessively simplistic when applied to real systems;
in practice, one must consider real interfaces differently.

This paper reviews briefly implications of the interfacial region with respect to
mechanical and transport behavior. A new approach is also described in which interfacial
interaction is interpreted in terms of the Lewis-acid or Lewis-base character of the
constituents.

The interface

In some cases, typically for elastic behavior, equations 1 and 2 (or variations thereof)
may hold quite well. While good adhesion may be effected chemically, satisfactory
mechanical coupling of stresses and displacements may be obtained due to shrinkage
stresses, though in the latter case, the stress field will depend on temperature.
However, it is often useful to consider that the surface of an actual inclusion contain
asperities, that the state of composition of the matrix may be different at the interface
than in bulk, and that various imperfections and stress gradients or singularities may
exist in the interfacial region (1,4,6,11–18). Hence, the concept of an "interphase" has
been introduced (19) to reflect the presence of an interfacial layer with its own set of
properties, and its own interface (sharp or diffuse) with the bulk polymer (20). To be
sure, even the concept of the interphase is itself simplistic, for the layer may itself
exhibit a gradient of composition or morphology (12,21). (Although an "interphase" should
therefore not be taken to imply the existence of a classically defined homogeneous,
discretely bounded phase, the term is commonly used for the sake of simplicity.) However,
consideration of properties of a binary composite in terms of the two constituents plus an
interphase constitutes a step forward in our appreciation of reality.

Interphases can be developed either deliberately or adventitiously. Indeed coupling agents such as silanes or titanates have long been used to improve mechanical properties (12,22) of composites, and the surfaces of fillers are commonly treated to modify adhesion. Attention has also been given to the use of a polymeric interlayer between a reinforcing fiber or a filler particle and the matrix. For example, a relatively soft interlayer has been claimed to give a useful balance between stiffness and toughness in general composite systems (15,23-28); a controlled crystalline morphology at the interface may also yield improved properties (21,29). Adventitious phenomena include adsorption, chemical reaction (such as copolymerization of the matrix with the coupling agent, or the formation of an interpenetrating polymer network) and interdiffusion (between two polymer phases, or between a coupling agent and the matrix) (1,2,6,9,12).

In view of the diverse and often coupled phenomena involved, it is not surprising that the effects of interfacial adhesion are complex (1,6,12,18). With well-bonded high-modulus inclusions, the modulus, and sometimes the tensile strength and fracture energy (1,30), is increased; the specific properly balance achieved may depend on the modulus of the interphase, as in the case of a deliberately developed interphase (23-28). With respect to large-scale deformation, it has been shown that a silane interphase can change the balance between shearing and crazing (31). Swelling and permeability is usually decreased and the relaxation spectrum is often shifted to higher temperatures or longer times (32). Thus, the T_g of such a system is often, though not always, higher than in the pure matrix (1,18); in fact, the interphase may contain both mobile and immobile components (33). (For reviews on relaxation and transport behavior, see refs. 1 and 18.) Of course, with rubbery inclusions, good adhesion is needed to enable the rubbery phase to generate beneficial delocalized crazing and shear (33a).

In any case, thermodynamic and kinetic factors must be considered. Even though thermodynamics may favor a particular equilibrium state, and hence a particular set of properties, the nature of the interphase will depend on the history of the system, that is, on the conditions of film formation or solidification from the melt (12,18,34,35). For example, the T_g of a polystyrene-silica composite was lower than that of the matrix when first formed, but became higher on annealing (34). Presumably the original interphase was not at equilibrium, and was relatively mobile, while subsequent annealing permitted equilibration to a less mobile conformation. In another example, the blending of a matrix with a filler that had been densely grafted with a matrix-compatible polymer led to poor strength (36), evidently because crowding at the filler surface inhibited interdiffusion with the matrix by creating an unfavorable entropy of mixing.

Unfortunately, it is often implied that "good" adhesion is generally to be desired. As indicated, this may be so for some properties, e.g., tensile strength and modulus in the case of fibrous composites, and permeability generally. However, the role of adhesion in other properties and systems is more complex (1,6,30). For example, in many composites maximum fracture energy, impact strength or fatigue resistance [with fibers parallel to a crack (37)] may actually require poor or intermediate adhesion (1,4,5,37). Also, with zinc-filled, corrosion-resisting epoxy coatings, poor interfacial adhesion is required in order to permit the formation of corrosion-inhibiting zinc compounds at the zinc surface and facile diffusion to the steel substrate (38).

As mentioned above, regardless of the inherent interfacial adhesion, good interpenetration between the matrix and interphase [sometimes involving formation of a true interpenetrating polymer network (39)] is generally necessary to avoid weak mechanical coupling between the interphase and the matrix (12,22,20,20a,36). If such weak coupling leads to a brittle interphase-matrix interface, crosslinking or use of a higher-molecular-weight matrix may be advantageous (20a). Good interpenetration will also be favored by inherently good miscibility (see below).

The behavior of composites under especially severe types of loading such as fatigue (40), stress corrosion cracking (41) and simple exposure to an aggressive medium such as water (22) is of particular interest. Indeed, coupling agents such as silanes have long been known to improve the resistance of composites to aqueous media. Nevertheless, even when fibers are treated to enhance adhesion, debonding under stress-cracking (41) or fatigue conditions (42-47) is a major micromechanism of failure; with fatigue loading, water deteriorates performance still further. Thus, fatigue crack propagation resistance in poly(ethylene terephthalate) reinforced with glass fibers disposed in various orientations is increased by fiber treatment to improve adhesion (42); also, overall fatigue life in random-glass-fiber-reinforced polypropylene is increased by the use of an appropriate silane coupling agent (46). Nevertheless, with polypropylene, aligned short glass fibers having enhanced adhesion improved resistance to fatigue when the fibers were perpendicular to the growing crack, but had a deleterious effect when the fibers were parallel (37). In the latter case, the enhanced adhesion was shown to <u>decrease</u> the size of the damage zone, and hence the extent of energy dissipation.

Some models for thermal and mechanical behavior

In order to model the transport and mechanical behavior or real composite systems in which an interphase exists, several approaches have been made. For example, a first approximation has been proposed (8,9,11) in which the interphase is assumed to be a homogeneous and isotropic phase interposed between the two principal phases and well-bonded to each of them. The filled polymer is as an aggregation of many spherical volume elements containing a filler particle and concentric shells consisting of an interphase and matrix, volume fractions being constant. It was possible to estimate the thermal expansion coefficient α_c as follows:

$$\alpha_c = \sum_{j=1}^{N} v_j (K_j/K_c) \, \alpha_j \, [1-a+a(K_j/K_c)]^{-1} \qquad (3)$$

where: N = the number of shells (in this case, 3); v_j is the volume fraction of the jth phase; $a = (1+v_c)/3(1-v_c)$, v being the Poisson's ratio of the composite; and K_j and K_c are the bulk moduli of the jth component and the composite, respectively. Using a suitable computer program the tensile modulus and volume fraction of the interphase were calculated. This model was reported to successfully represent the thermomechanical behavior of resins containing particles of iron, and to permit estimation of the amount of interphase formed (8,9).

In another approach, the van der Poel method (48) for predicting the complex shear and bulk modulus of particulate composites was extended recently to take into account the presence of an interphase (49-51). The bulk modulus K_c was found in terms of bulk and shear moduli for the matrix, interface, and filler. Although no analytical solution was found for the shear modulus G, numerical solutions were found in terms of constituent moduli, composition, and the corresponding values of Poisson's ratio. Complex moduli were estimated by the correspondence principle. Good agreement with prediction was reported for a glass-bead-filled styrene-acrylonitrile copolymer in which the beads had been coated with a layer of an ethylene-vinyl acetate copolymer. Also, the dynamic mechanical spectrum of the interphase (bound polymer) formed in a polyethylene/silica system was characterized, and the dynamic behavior of the composite was successfully predicted in terms of the constituent properties. (Interestingly, the thickness of the interphase and its volume fraction were calculated to be $\sim$ 4 nm and 0.24, respectively.)

To model composites containing unidirectional fibers, the 3-phase concentric shells of Fig. la (8,9) can be replaced by concentric cylinders in which the fiber, matrix, and interphase bear tensile, tensile, and shear stresses, respectively (12). A still more realistic model was developed (52) in which the interphase was considered as a collection of an infinite number of cylinders, each having its own modulus; thus, the modulus E(r) was taken to decrease continuously with the distance r from the fiber:

$$E(r) = E_f (r_f/r)^{2k_1} + E_m \, [1-(r_f/r)^{2k_2}] \qquad (4)$$

where f and m refer to the filler and matrix respectively, and k_1 and k_2, which can be measured experimentally (53,54), are parameters characterizing the quality of adhesion. When $k_1/k_2 = 1$, perfect adhesion would exist and E(r) would decrease continuously from E_f to E_m; when $k_2/k_1 < 1$, E(r) would exhibit a minimum at or close to $r = r_o$, and then rise to E_m. Values of the volume fraction of the interphase can also be calculated (11). The modulus of the composite is given by the following rule of mixtures:

$$E_c = E_m + (E_f-E_m) \, u_f + u_f \, [E_f/(1-k_1) \, (u_f^{k_1-1}-1) - E_m/(1-k_2) \, (u_f^{k_2-1}-1)] \qquad (5)$$

where $u_f = r_f^2/r_m^2$ is the filler volume fraction. Other models that have been proposed to take into account phase mixing in polymer blends (55,56) may be adaptable to deal with the interphase.

The Nielsen model for permeability

The simplest expression relating the permeability coefficient of a composite, P_c, to the volume fraction of a spherical filler v, v_f, and the permeability coefficient ^{c}of the matrix, P_p, is (57):

$$P_r = P_c/P_p = v_p/(1 + v_f/2) \tag{6}$$

where P_r is the relative permeability, and the term $(1 + v_f/2)$ corresponds to the tortuosity τ of the diffusion path. Deviations from sphericity can be allowed for by taking τ to be $[1 + (Lv_f/W)]$, where L/W is the length-to-width ratio of the filler (58). While such equations constitute limiting cases at low v_f, they hold reasonably well for many composite systems, including semi-crystalline polymers (1), they assume good interfacial adhesion and do not take account of poor adhesion, phase mixing or the presence of an interface. When the latter phenomena are involved, more general equations are necessary (59,60,61; for reviews, see references 1,2 and 61). For the purpose of this paper, the Nielsen equation (58) is particularly useful because it explicitly treats the properties of an interphase;

$$P_r \overset{\sim}{=} \frac{P_i}{P_p^n v_f + P_i(-v_f^n)} \quad \frac{v_{\ell i}}{\tau} + \frac{v_p + v_{\ell p}}{\tau} \tag{7}$$

where: $v_{\ell i}$ and $v_{\ell p}$ are the volume fractions of liquid permeant dissolved in the interphase and polymer, respectively; P_i is the permeability coefficient of the interphase; $\tau*$ is the tortuosity of the interphase ($\sim \tau$ in many cases); and n is a geometrical factor ranging between zero and unity for thin plates perpendicular and parallel, respectively, to the membrane. (It is assumed that v_i is small with respect to v_p.) Although Equation 7 is an approximation, it is said to hold well for many systems (58). If, as in the example discussed below, poor adhesion exists, P_i will become appreciable with respect to P_p and the value of $\underline{n}$ may approach zero. Equation 8 can also be modified to deal with aggregated filler particles (58).

Direct characterization of interfacial interaction

In addition to the mechanical and transport measurements discussed above, many other experimental methods have been used to characterize the implications of interfacial interactions as well as composition, especially in terms of miscibility. Useful methods are based on such properties as density, viscosity, viscoeleastic relaxation, thermooptical behavior, morphology, scattering or diffraction behavior, solution behavior, inverse gas chromatography, and the various types of spectroscopy (for a review, see reference 63). With insoluble inclusions such as inorganic fillers, classical techniques have, of course, long been used to characterize wetting and adsorption (18), and direct information about the interphase has been deduced from methods based on, for example, dilatometry (64), dynamic mechanical response (65), and nuclear magnetic resonance (66). Recent developments using improved instrumentation have made it possible to conveniently obtain direct thermodynamic evidence about the interface, as well as about miscibility; in some cases, conformational data can be obtained as well (18,67,68). Such methods include standard and Fourier transform infrared spectroscopy (FTIR) (12,12a,12b,67-72), microcalorimetry (72-75), and inverse gas chromatography (IGC) (76-81). The identity, nature, and concentration of surface atoms or functional groups is also of interest. For this purpose, both traditional techniques such as titration with acids or bases (82), and contemporary instrumental techniques such as FTIR (12), x-ray photon spectroscopy (27), and IGC (76-78), are useful. For example, such measurements can be used to determine what functional groups in a given coupling agent (applied in a given way) are actually presented to the matrix, and what kind of sites are available for adsorption on a bare inorganic surface. (Sometimes the findings are unexpected.) Clearly, a combination of fundamental thermodynamic information (e.g., enthalpies of interaction and polymer-polymer or polymer-solvent interaction parameters) with evidence for the number, nature, and identity of adsorptive or reactive sites at an interface constitutes a powerful tool for investigation.

At the same time, interpretation requires an adequate rationale. In this respect, an increasing number of research groups, including our own, is finding the concept of (donor-acceptor interactions of which H-bonding interactions constitute a sub-set) to be very useful in both rationalizing behavior in many multicomponent systems, and in selecting combinations of constituents (72,73,83-86). The approach is quite general and soundly based on thermodynamics, and avoids theoretical and practical problems associated with, for example, the use of solubility parameters (see below). In many cases, this concept has already proved applicable to questions of both adsorption (obviously a sine qua non for adhesion) and miscibility. A discussion of principles follows, as well as specific examples.

INTERFACIAL INTERACTION: A NEW LOOK AT AN OLD CONCEPT

Whether one is dealing with the miscibility of polymer blends, with polymer solutions, or with interphase formation and interpenetration with the matrix in filled or reinforced polymers, it is useful to consider the fundamental basis for the interaction of phases. In the most general case (63, 72,73,83-95), the interaction of two phases involves some combination of dispersion or London forces, "polar" or dipole-dipole forces, and specific interactions such as proton transfer in acid-base reactions or hydrogen bonding. Although many investigators of interfacial phenomena combine the dipole-dipole and specific interactions into one "polar" contribution, it is now known (83-86, 87) that the specific interactions usually dominate in both solution and the solid state. It is also useful to treat hydrogen bonding as a Lewis acid-base interaction and to consider all specific interactions as involving a donor-acceptor relationship, whether or not charge transfer actually occurs.

For many years the concept of the solubility parameter has found much use in predicting heats of mixing of two components that interact primarily through dispersion forces. The scientific adage "like dissolves likes" has also been a popular, though often uncertain, guide to practice. In spite of the facts that the solubility parameter has long been known not to take account of specific interactions (63,83-86), and that specific interactions are much more common than has been generally believed, the solubility parameter is still commonly used in cases in which it is basically inapplicable. Although attempts have been made to include a polar or hydrogen-bonding component, these involve a fundamentally incorrect evaluation, as shown below, and computer-forced correlation of heat of mixing with work of adhesion are necessary. Such fitting, however, can lead to incorrect conclusions, e.g., finite polar terms for nonpolar polymers, and false predictions of miscibility or immiscibility (89,90).

The concept described here is based on extensive research by Drago et al. (87, 87a), who correlated enthalpies of interaction of more than 30 acids and bases in neutral solvents. To make the correlations, Drago expressed the acid-base interaction H_m^{ab} with two constants for each base and acid (E_B and C_B, and E_A and C_A, respectively):

$$-\Delta H_m^{ab} = C_A C_B + E_A E_B \tag{8}$$

The two constants for both the acid and the base reflect the idea that the strength of interaction of a pair of groups depends not only on the donor/acceptor characteristics but also on the polarizability (E refers to the former, and C to the latter). The ratio C/E is a measure of the relative ease of deforming outer electron orbitals by an electric field; the greater C/E the "softer" the acid or base. Thus, iodine and Bronsted acids behave as soft and hard acids, respectively, while sulfur and oxygen behave as soft and hard bases, respectively. It is believed that maximum interaction occurs between soft acids and soft bases, or hard acids and hard bases. Drago et al. were able to predict values of ΔH_m^{ab} for many systems involving hydrogen bonds and both Bronsted and Lewis acids and bases with good accuracy. In addition, they found a most interesting result: good correlations could be made assuming the existence of only dispersion and acid-base interactions (the contribution of dipole-dipole interactions being usually very small or negligible).

Turning to interfacial phenomena, Fowkes proposed long ago (91,92) that the work of adhesion W_A can be expressed as follows:

$$W_A = W_A^d + W_B^p + W_A^h + \ldots \tag{9}$$

where the superscripts $\underline{d}$, $\underline{p}$, and $\underline{h}$ refer to dispersion forces, dipole interactions, and hydrogen bonds, respectively. (In principle, any other kinds of interactions could be added to Equation 10.) By analogy, the surface tension γ would be given by

$$\gamma = \gamma^d + \gamma^p + \gamma^h \ldots \tag{10}$$

Several interfacial properties were successfully calculated using the geometric-mean expression:

$$W_A^d = 2\sqrt{\gamma_1^d \gamma_2^d} \tag{11}$$

An analogous geometric mean expression for W_A^p is also correct:

$$W_A^p = 2\sqrt{\gamma_1^p \gamma_2^p} \tag{12}$$

However, it is quite incorrect to use a similar geometric mean to calculate W_A^h; γ^h is zero for hydrogen-bond acceptors such as ethers, or aromatics that cannot form hydrogen bonds with themselves, even though W_A^h with a hydrogen donor may be large. Also, some hydrogen donors, e.g., chloroform, have $\gamma^h = 0$, but large values of W_A^h. Note that because $\gamma^h = 0$ in such cases, one cannot calculate a solubility parameter contribution to the enthalpy of mixing due to hydrogen bonding.

Fowkes then proposed that the heat of mixing, ΔH_m, should be given by

$$\Delta H_m = P\Delta V_M + V_M \phi_1 \phi_2 (\delta_1^d - \delta_2^d)^2 - X_p(C_A C_B + E_A E_B) + \Delta U_M^P \tag{13}$$

where δ_1 and δ_2 are the solubility parameters, V_M is the volume of mixing, ϕ_1 and ϕ_2 are the volume fractions, X_p is the mole fraction of acid-base pairs per mole of components, and ΔU_M^P is the change of internal energy of mixing associated with dipole-dipole interactions. Similarly, the work of adhesion becomes:

$$W_A = 2\gamma_A^d \gamma_B^d - f(C_A C_B + E_A E_B) \times \frac{\text{moles acid-base pairs}}{\text{unit area}} + W_A^P \tag{14}$$

where W_A^P refers to dipole-dipole interaction. The fact that interfacial interactions appear to be dominated by dispersion forces and specific acid-base or hydrogen bonding behavior not only simplifies the picture considerably but also clarifies the significance of the vague term "polar". Moreover, C and E constants can be determined for both substrate and matrix materials (85).

Determination of C and E values

Values of $-\Delta H_m^{ab}$ can be predicted for many acid-base pairs using Equation (8) and tabulated values of C and E (87,87a). Although the C and E values provided are for small molecules, the latter can often serve as approximate models for polymers, e.g., chloroform for poly(vinyl chloride) and ethyl acetate for poly(vinyl acetate) (73). Direct measurement of $-\Delta H_m^{ab}$ can be effected calorimetrically or spectroscopically. The latter is suitable for many polymers because groups such as hydroxyl and carbonyl are ubiquitous and shifts in their spectral frequency are readily measured. Thus, for example, the carbonyl stretching frequency is decreased by acid-base ($\Delta \nu^{ab}$) and dispersion force interaction ($\Delta \nu^d$); the latter is proportional to the dispersion contribution to surface tension (γ^d). For poly(methyl methacrylate) (PMMA)

$$\nu^{ab}(C=O) = 1757 - 0.70 \gamma^d \tag{15}$$

$\Delta \nu^{ab}$ can also be calibrated in terms of ΔH_m^{ab} (measured calorimetrically); for PMMA

$$\Delta \nu^{ab}(C=O) = (1.0 \text{ cm}^{-1} \cdot \text{kJ}^{-1} \cdot \text{mol}^{-1}) \Delta H_m^{ab} \tag{16}$$

Values of C_A and E_A, or C_B and E_B, are determinable for acidic or basic components, respectively, from ΔH_m^{ab} with a complementary component whose C and E values are known. Procedures are described elsewhere (72).

$$E_B' = -\Delta H_m^{ab}/E_A - C_B'(C_A/E_A) \tag{17}$$

For PMMA, C_B and E_B are about 1 and 0.7 (kcal·mol)$^{\frac{1}{2}}$, respectively. This procedure should be useful for other polymer systems as well.

In a similar manner, C and E values for filler surfaces can be estimated from heats of adsorption or from spectral shifts. Thus, silica (an acidic filler) has been found to exhibit C_A and E_A values of 1.1 and 4.4 (kcal·mol^{-1})$^{\frac{1}{2}}$, respectively (93) and α-iron oxide values of 1.1 and 0.5-1.0 (kcal·mol^{-1})$^{\frac{1}{2}}$ (75). Using these constants, one can then predict the heat of adsorption for any base of known C_B and E_B; with C_B and E_B constants for a basic filler, a similar prediction can be made for any acid of known C_A and E_A.

IMPLICATIONS AND APPLICATIONS

Miscibility

Until recently, it was thought that in general pairs of polymers tend to be immiscible (or "incompatible") because of the combination of a low (though favorable) entropy of mixing with an often zero or negative charge (94). Whereas many pairs are in fact immiscible on

a segmented scale, it is now clear that many more systems are wholly or partially miscible than may have been thought earlier. Thus the role of specific interactions leading to negative (favorable) enthalpies of mixing is invoked more and more often to explain miscibility (63,94). Such interpretations are also consistent with the increasing number of systems found to exhibit <u>upper</u> rather than <u>lower</u> critical solution temperatures. The former are predicted by newer theories that admit specific interactions, while the latter are predicted by older theories, which also lead to the traditional solubility parameter, whose limitations have been discussed above.

As mentioned above, hydrogen bonding appears to play an important role in polymer-polymer miscibility. For example, poly(vinyl chloride) tends to be miscible with polymers containing carbonyl groups. The former acts as a hydrogen donor to the electron-rich carbonyl; non-H-bonded interactions may exist as well (63,69-71,94,95). Such interactions provide the basis for the use of polycaprolactone, for example, as a miscible polymeric plasticizer. Whereas many miscibility studies have used infrared spectral shifts for correlation, calorimetric measurement have been useful also, e.g., in the prediction of miscibility in hydrogen-bonding polymers from the behavior of low-M analogues (96). A recent example of a miscibility study (72) involved 1:1 blends of poly(methyl methacrylate) (PMMA) (a basic polymer) with the following acidic polymers: poly(vinyl fluoride) (PVF), poly(vinylidene fluoride) (PVF$_2$), postchlorinated PVC (Cl-PVC), and poly(vinyl butyral) (PVB). Calculations of values of ΔH^{ab} based on carbonyl spectral shifts (after correction for the dispersion contribution) were in the order PVB > PVF$_2$ > PVF > Cl-PVC.

The implications of the Drago-Fowkes approach with respect to miscibility are quite clear. Once C and E values are determined for a polymer, it will be possible to predict the heat of mixing with any other polymer whose solubility parameters C and E values are known.

Solution and swelling can also be predicted better using the donor-acceptor concept in combination with the solubility parameter; the advantages of such an approach have been recently discussed and demonstrated (89,97). Polystyrene (a basic polymer) provides an interesting example. Of 14 good solvents described in the literature, 9 are acidic, including 2 of the lowest, and three of the highest, δ. Whereas the range of δ for nonacidic (essentially neutral) solvents was 8.6 - 10.0, the range for acidic solvents was significantly greater, 0.4 - 10.7. Thus acid-base interaction broadened the range of δ values corresponding to good solvation with an acidic polymer, poly(vinyl butyral) (δ = 9.2 - 9.5), in which internal, intermolecular hydrogen bonding exists. Solubility was found to depend on acid-base interaction with strongly basic solvents ($\Delta H^{ab} << 0$) such as cyclohexanone (δ = 10.4) and pyridine (10.6). However, the polymer was insoluble in the more strongly basic amines such as tributylamine ($\delta^d = 7.8$). Evidently, in agreement with a traditional rule-of-thumb, the strong basicity cannot overcome the fact that δ^d is about 2 units below the value for the polymer. The need to consider δ as well as specific interaction was also seen in studies of the solubility of postchlorinated PVC (δ ∿ 8.65) in esters. With equally basic esters (same ΔH^{ab} ∿3.4 kcal·mol^{-1}), maximum solubility was found when δ was in the range 8.6 - 8.7, lower than the value for a nonbasic solvent like dichloromethane (δ = 9.9). It was suggested that the acid-base interaction resulted in the orientation of hydrocarbon groups away from the polymer so that the complexed polymer interacted with additional solvents more like a hydrocarbon. In any case, when acid-base interactions were present, the solubility and intrinsic viscosity showed a negative temperature coefficient (consistent with the existence of upper critical solution temperatures).

Adsorption and adhesion

The phenomenon of surface-bound polymer has long been known in composites such as reinforced elastomers (1,64). While actual chemical bonding may occur in a reinforced elastomer, even relatively weak interactions such as those involved in hydrogen bonding may suffice if the surface area of the filler, and hence number of active sites, is very large. In any case, both typical carbon blacks and silica contain significant numbers of acidic sites. Indeed, the fraction of bound rubber tends to increase with increasing unsaturation in the rubber (increasing concentration of electron-rich sites) (1). In acrylonitrile-containing elastomers reinforced with silica (acidic), the bound rubber fraction was found to increase with an increase in the acrylonitrile content (i.e., with the concentration of basic comonomer units) (98). Hysteresis also varied with acrylonitrile content, as would be expected if deformation in values the movement of oppositely charged (or partially charged) units past each other. While in these cases the possibility of acid-base interactions was not explicitly considered, such interactions appear to constitute a reasonable explanation for at least some of the phenomena.

About a decade ago, explicit consideration of acid-base interactions and their role in dispersion of pigments, adsorption, and adhesion began to occur. In 1966, it was proposed that the adsorption of a basic polymer on an acidic filler involved protonation of the adsorbate, which could then desorb, leaving the polymer and filler with a positive and

negative charge, respectively (99). The consequent development of a <u>negative</u> zeta potential has since been confirmed (90,100), as has the development of a <u>positive</u> zeta potential when an acidic polymer is dispersed in a basic medium (90). Independently, and later, it was shown that empirical observations of pigment-binder compatibility in coatings (as measured by gloss) could be correlated with the Lewis acidity or basicity of the pigment, binder, and solvent (101). Thus stability in colloidal dispersions requires the development of significant electrostatic interactions.

The concept of acid-base interaction in determining dispersion stability can be very helpful in understanding and solving industrial problems (72). For example, PMMA and chlorinated PVC were used as basic and acidic polymer probes, respectively, to investigate reasons why three pigments (uncharacterized with respect to surface chemistry) gave good dispersion with a complex polymeric binder solution, while a fourth, which had otherwise desirable properties, posed serious problems. As shown in Table 1, significant differences in adsorption were noted (102). The first three pigments adsorbed PMMA well from an essentially neutral solvent, while the fourth did not. Thus, the first three pigments behaved as Lewis acids, and the fourth as a Lewis base;

TABLE 1. Adsorption of acidic and basic polymers in pigments (102)

Pigment	Adsorption of PMMA[a]		Adsorption of Cl-PVC[a]	
A	30	($\sim$ 100)	0.1	(0.3)
B	97	(98)	1.7	(2)
C	35	(80)	8.5	(20)
D	6	(9)	61	(91)

[a]First number, mg/g; number in parenthesis, % adsorbed

the polymeric binder solution evidently behaved essentially as a Lewis base. [Of course, it should not be expected that a filler surface contain <u>only</u> acidic or basic sites.]

The effect of acid-base interaction on dispersibility is not confined to solutions. For example, blends of barium titanate (basic) with polycarbonate (basic) were found to possess undesirably low electrical resistivity (103); this would be expected with poor dispersion, which favors agglomeration and the formation of chains. However, when the titanate was treated with aluminum sulfate to make the surface acidic, much more uniform dispersion was obtained. More recently (76), in a study of the mixing of PVC with calcium carbonate (plain and treated to endure a predominantly acidic or basic surface) the critical mixing time necessary for the torque to drop to a constant level was much shorter with the basic filler (Table 2). With polyethylene (essentially neutral), the times were in fact somewhat increased by surface treatment of the filler. These results, i.e., the tendency of an essentially electrostatically neutral phase to be incompatible with a polar one, may be consistent with the established practice of coating fillers with a hydrophobic layer for use with polyolefins.

TABLE 2. Critical mixing times for polymer with calcium carbonate (76)

Polymer	Ω(polymer)[a]	Filler Surface	Ω(filler)[a]	Crit. mixing time, s
PVC	0.5	acidic	0.6	255
		no treatment	1.3	90
		basic	2.0	35
		more basic	2.8	15
Polyethylene	1.1	acidic	0.6	145
		no treatment	1.3	75
		basic	2.0	105
		more basic	2.8	118

[a]Ω is a measurement of relative acidity from inverse gas chromatography; $\Omega < 1$ for an acid and > 1 for a base.

At the same time, it has been reported that the maximum torque developed during the melt mixing of an ethylene-vinyl acetate copolymer with various silicas varied directly with the concentration of acidic silanol groups available for interaction with the basic acetate groups (104).

Confirmation of the competitive role of polymer-polymer, filler-polymer, filler-solvent, and polymer-solvent interactions (90) was provided by a study of the adsorption of an acidic and basic polymer (postchlorinated PVC and PMMA, respectively), from solutions in acidic, basic, and neutral solutions (90). Significant adsorption occurred only when the filler and polymer constituted an acid-base pair, and when the solvent was either neutral or a much weaker acid or base than the polymer. Such selectivity of adsorption has provided the basis for the use of PMMA and postchlorinated PVC as model probes to supplement titration and dye techniques in the characterization of the relative acidity and basicity of several fillers, including zinc particles and wollastonite (calcium metasilicate) (105,106). Of course, while acidic or basic sites may dominate on the surface of a pigment or filler, the surface may be amphoteric (101,105).

All these findings are consistent with earlier observation of the tendency of carbonyl-containing polymers to adsorb on acidic surfaces (for reviews, see 18,74, and 75).

Recent research in our laboratory

During an early study, explanation of the transport and mechanical behavior of some glass-bead-filled epoxies requires postulation of an interphase (107,108); others also examined effects of inclusion on viscoelasticity (109; 1, ch.12). When awareness of the research by Fowkes et al. developed (90), it seemed reasonable to extend the adsorption studies by investigating the implication of adsorption with respect to mechanical properties and morphology (110) of films chlorinated PVC and polycarbonate filled with barium titanate, calcium carbonate or silica, and cast from tetrahydrofuran (THF) (basic), or methylene chloride (acidic).

In general, the best films were obtainable from pigment-binder pairs that constituted an acid-base couple cast from methylene chloride, and that exhibited adsorption (confirmed by microscopy). Two exceptions were noted: silica and chlorinated PVC, and calcium carbonate and polycarbonate, were compatible when cast from THF and methylene chloride, respectively; the solvent of the opposite electrostatic character appeared to act as a coupling agent. Strengths and moduli tended to exceed predicted bounds with appropriate acid-base coupling, and the tendency to retain solvent was clearly related to the propensity for acid-base interaction with the matrix. Solvent complications were avoided by the milling of ethylene-vinyl acetate (EVA) copolymers (0 to 32 wt % acetate) with silicas containing various concentrations of silanol groups, as determined by titration (104). Adsorption was favored with a given acetate content when the silanol concentration was high, and adsorption was correlated with tensile strength and modulus. The role of dispensibility has already been mentioned (72,102). Adsorption studies have also been useful in correlating interfacial effects with mechanical and transport behavior (105,106). Zinc powders adsorbed PMMA but not chlorinated PVC, and hence acidic sites predominated; adhesion to polystyrene (basic) was much stronger than to the chlorinated PVC or an epoxy (acidic). Wollastonite adsorbed both PMMA and chlorinated PVC, the latter to a lesser extent. Tensile and compressive fracture energy varied with the extent of adsorption (Fig. 1). Although the data for Fig. 1 are not corrected to account for particle size differences, a similar trend is seen after such correction.
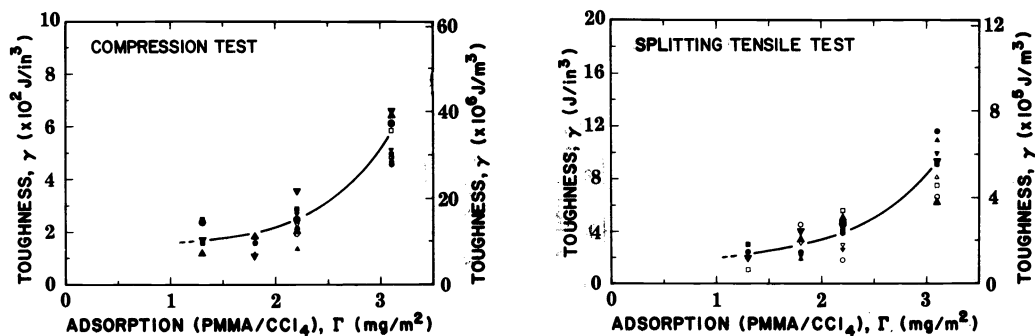

Fig. 1. Fracture Energy (stress-strain curves for wollastonite as a function of adsorption of PMMA).

Current studies with treated and untreated glass beads (both acidic and basic) are in progress; the use of IGC has been discussed above. So far, good adhesion is seen with an acidic polymer (phenoxy or epoxy) when cast from a not-too-basic solvent, but not with a basic polymer (PS or PMMA) (Fig. 2) (79). Good adhesion also reduces the permeability to water vapor, though not to the value predicted for perfect adhesion; behavior can be modelled using Equation (7); assuming a more or less permeable interphase.
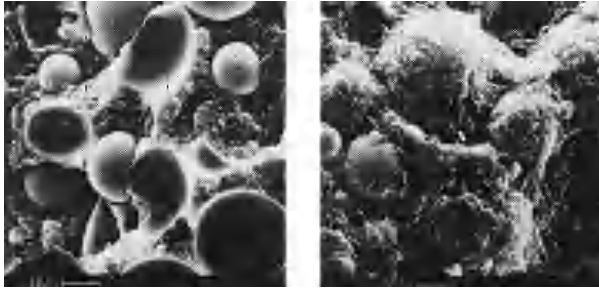

Fig. 2.

Improvement of adhesion to epoxy (acidic) when acidic glass (L) is made basic (R)

Research is also in progress with the characterization and treatment of glass and carbon fibers (111). As shown by IGC (Fig. 3), both E-glass and carbon fiber tend to be acidic; the glass can also be made more acidic by treatment with aluminum sulfate. Heats of adsorption are being obtained, and will be correlated with the mechanical behavior (including fracture) of composites with acidic and basic polymers [e.g., PMMA, poly(phenylene oxide), phenoxy, and epoxy].
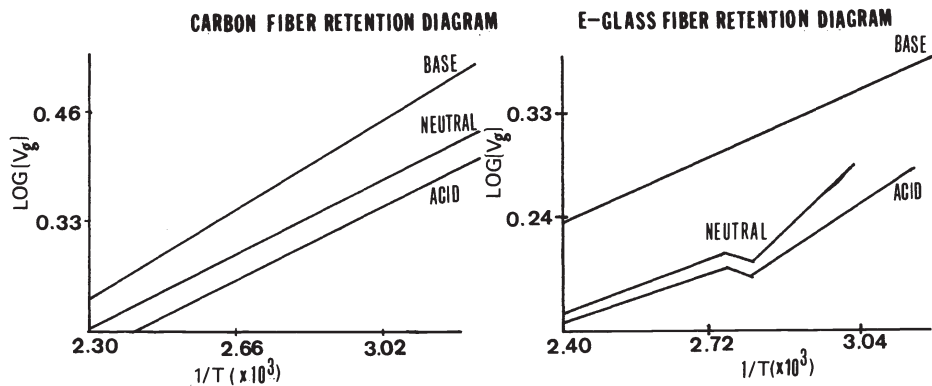

Fig. 3.   Retention volumes for acidic, basic and neutral
          probes with glass (b) and carbon (a) fibers.

CONCLUSIONS

By considering acid-base interactions, much behavior of composite systems can be rationalized. By appropriate matching of the electrostatic nature of a substrate (e.g., a filler, reinforcement, interphase, or plain polymer) with a second phase (matrix or diluent) it should be possible to design composites or other multicomponent systems more expeditiously and effectively.

ACKNOWLEDGEMENTS

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