A critical review of wetting and adhesion phenomena in the preparation of polymer-mineral composites

J. Drelich and J.D. Miller

Abstract — *The wetting behavior of liquid polymers at solid surfaces and the adhesion forces involved at polymer-filler interfaces should always be considered in the preparation of high-quality polymer composites, including those made with mineral fillers. Spontaneous polymer spreading over the filler surface is a basic condition for the design of polymer-mineral composites. In this regard, the wetting and adhesion characteristics of polymer-mineral systems are reviewed. Based on this review it is clear that several aspects of wetting phenomena at mineral-filler surfaces require further systematic study. Specifically, efforts should be made to determine the wetting characteristics of molten polymers at mineral-filler surfaces in greater detail. Also, the effects of mineral-surface contamination (including surface hydration) on wetting and adhesion phenomena need specific investigation. It is expected that an improved fundamental understanding of wetting and adhesion phenomena for polymer-mineral composites will provide the basis for further technological development.*

Introduction

Polymer (resin) composites often make use of mineral fillers to reduce the overall cost of the final product. Mineral fillers are also used to achieve certain desired properties, such as tensile and flexural strengths, fire retardancy and UV resistance (Mark, 1984; Katz and Milewski, 1987; Seymour, 1991; Harper, 1992). For this purpose, the plastics industry used more than 2.4 million tons of minerals in 1989, and the consumption has probably reached 3.0 million tons in recent years (Katz and Milewski, 1987; Seymour, 1991). Calcium carbonate (as a powder precipitated from a saturated solution or as one of the following minerals: calcite, limestone, dolomite, and marble) is the most popular inorganic filler. It accounts for 75% to 80% (by weight) of all mineral fillers used by the plastics industry (as indicated by data from Katz and Milewski, 1987). Other minerals commonly used as fillers include gibbsite, clay minerals (particularly kaolin and feldspar), wollastonite, talc and pyrophyllite, and quartz and silica (Katz and Milewski, 1987; Seymour, 1991). Antimony oxide, gypsum, barite and mica also serve as fillers for polymer-mineral composites, but their consumption by the plastics industry is very small compared to the previously listed minerals (Katz and Milewski, 1987; Seymour, 1991). Literature reports on the consumption of asbestos by the plastics industry are contradictory. According to Katz and Milewski (1987), the use of asbestos as a mineral filler, although significant at the beginning of the '80s, has dropped drastically in recent years because asbestos has been identified as a carcinogen, and, for that reason, the Occupational Safety and Health Administration has announced limitations and restrictions on its use. On the other hand, the annual use of asbestos in the plastics industry was reported by Seymour (1991) to be 238,000 tons, indicating that asbestos remains in wide demand as a filler.

In addition to cost, several properties of the filler, such as wetting and bonding properties, oil absorption, chemical resistance, strength, modulus, electrical and thermal properties, may be of concern when mineral reinforced plastics are fabricated. Katz and Milewski (1987) proposed that the ideal filler should at least meet the following six requirements:

- low cost,
- availability,
- low oil absorption,
- good chemical resistance,
- high strength, and
- good surface wetting and bonding.

Although all of these properties and features of the filler are important, this discussion is only focused on selected aspects of wetting and adhesion phenomena, which are of critical importance for fabrication of high-quality polymer-mineral composites.

Three requirements for an adhesive (polymer) appear to be of particular significance in the fabrication of composites (Wu, 1982):

- wetting,
- solidification, and
- deformability (to reduce the build-up of stresses at the joint interface).

The formation of an adhesive bond between a mineral and

J. Drelich and **J.D. Miller**, members SME, are research assistant and professor, respectively, with the Department of Metallurgical Engineering, the University of Utah, Salt Lake City, UT. SME Preprint 95–97, SME Annual Meeting, March 6–9, 1995, Denver, CO. Manuscript Feb., 1995. M&MP paper 95–627. Discussion of this peer-reviewed and approved paper is invited and must be submitted, in duplicate, prior to Feb. 28, 1996.

Table 1 — Experimental values of surface free energy for inorganic compounds

Material	Surface free energy, mJ/m^2	Measurement technique	References
LiF (100)*	340 (-196°C)	cleavage experiments	Gilman,1960
MgO (100)*	1200 (-196°C)	ibid.	ibid.
CaF_2 (111)*	450 (-196°C)	ibid.	ibid.
$CaCO_3$ (1010)*	230 (-196°C)	ibid.	ibid.
KCl (100)*	110 (25°C)	ibid.	Westwood and Hitch, 1963
mica	308 (20°C)	ibid.	Bailey and Kay, 1967
CaO	1310 (23°C)	heat of dissolution	Brunauer, et al., 1956
$Ca(OH)_2$	1180 (23°C)	ibid.	ibid.
NaCl	115 (800°C)	surface tension of molten salt	Pandey, et al., 1981
KCl	96 (800°C)	ibid.	ibid.
RbCl	91 (800°C)	ibid.	ibid.
CsCl	79 (800°C)	ibid.	ibid.
Al_2O_3	574 (2050°C)	ibid.	Rasmussen and Nelson, 1971

* Cleavage plane

a polymer begins with interfacial molecular contact, preceded by a spreading of the liquid polymer over the mineral surface. Only after that process can the molecules undergo diffusion and move toward the formation of an interfacial zone with preferential conformations to eventually react chemically and form chemical bonds across the interface. In this regard, the polymer should completely wet the mineral surface to minimize the total free energy of the system. The extent of chemical interaction at the polymer-mineral interface determines the bond strength, i.e., the adhesion between the two phases. Thus, the quality of polymer-mineral composites strongly depends on the interfacial properties of the system. Because several textbooks describe fundamental and practical aspects of wetting and adhesion phenomena (e.g., Wu, 1982; Yosomiya et al., 1990; Vakula and Pritykin, 1991), only a critical review of selected problems related to the quality of fabricated polymer-mineral composites is presented in this contribution.

Surface characterization of minerals

Polymer-mineral interfacial voids and cracks are weak regions of the composite that are due to the concentration of stresses around gas-filled spaces and the reduced contact between the two materials. These can be avoided by achieving both appropriate rheological properties of the polymer during mixing and appropriate wetting conditions at the polymer-mineral interface. To obtain optimal joint strength in a composite, the contact angle (θ) between the liquid polymer and the mineral should be as small as possible, preferably $\theta = 0$. This promotes spontaneous spreading and minimizes the buildup of stress at the joint (Zisman, 1963). The equilibrium contact angle (θ) for the three-phase system (discussed herein as the air-polymer-mineral system) is described as follows by Young's equation:

$$\gamma_M - \gamma_{PM} = \gamma_P \cos\theta \qquad (1)$$

where

γ is the surface/interfacial free energy,
subscript M designates the mineral surface,
subscript P designates the polymer surface, and
subscript PM designates the interface between the polymer and mineral.

Equation (1) is valid for a smooth, homogeneous, isotropic, horizontal and rigid solid surface (a mineral surface in this case). According to Young's equation, the complete spreading of the liquid polymer at the mineral surface should occur when:

$$\gamma_M \geq \gamma_{PM} + \gamma_P \qquad (2)$$

Even perfect spreading of the liquid polymer over the mineral-filler surface does not necessarily guarantee a composite structure free of gas defects. Pores and cracks always exist on the surfaces of minerals and may remain unfilled if the polymer cannot penetrate all of the surface structure defects before polymerizing. This happens especially when the polymer is too viscous at the time of application and/or when the time of mixing the filler with the liquid polymer is too short. In such cases, surface occlusions and gas pockets are frequently formed (Zisman, 1963; 1965). The presence of voids and gas bubbles at a polymer-filler interface reduce the quality of the joint. Stress concentrations build up around these structural defects when a polymer-mineral composite is subjected to external forces (stresses). Consequently, crack propagation may occur from one defect to another and finally the polymer-mineral interfacial joint may break.

The thermodynamic criterion that satisfies the requirement for complete wetting can be defined by a zero contact angle when measured for the polymer at a mineral surface. Minerals are high-energy materials having a surface free energy larger than 100 to 200 mJ/m^2 at room temperature (see Table 1), which is larger than the surface tension of any known liquid with the exception of liquid metals (note that water has the largest surface tension among liquids with a value of 72.9 mN/m at 20°C). In this regard, all pure liquids are expected to spread spontaneously on such high-energy materials (assuming, of course, that their surfaces are smooth

Table 2 — Naturally hydrophobic minerals
(from Fuerstenau et al., 1985)

Mineral	Surface plane	Water contact angle, deg
Graphite	0001	86
Sulfur		85
Molybdenite	0001	75
Stibnite	010	
Pyrophyllite	001	
Talc	001	88
Iodyrite		20

and clean) to minimize the free energy of the system. Although many organic liquids spread freely on high-energy surfaces, exceptions to this behavior are commonly reported and are not limited to polar liquids.

Most minerals are hydrophilic and have high surface energies. A few minerals exhibit natural hydrophobicity, as shown in Table 2. According to Gaudin (1957), natural hydrophobicity exists for minerals with fracture or cleavage surfaces held together only by residual bonds (van der Waals forces). Although selected surfaces of these minerals have hydrophobic properties (see Table 2 for a specification of the surface planes with natural hydrophobicity), there may also be surface planes of hydrophilic character. Further, the surface free energy of a mineral may depend on the surrounding medium (i.e., environment). For example, a fully hydroxylated quartz or silica surface is hydrophilic, and, when clean, the minerals surface is wetted spontaneously by water. However, quartz and silica plates are progressively rendered hydrophobic when heated to temperatures between 200 and 1000°C (White, 1970; Lamb and Furlong, 1982). The surface siloxane bridges after calcination are weakly dipolar, but they are less hydrophilic than the silanol groups (Kitchener, 1984).

Even hydrophilic minerals may demonstrate "hydrophobic character" during contact-angle measurements. For example, incomplete wetting of high-energy solid surfaces by "autophobic liquids" has been reported by Zisman (1964). An autophobic liquid forms its own adsorbed oriented monolayer at a high-energy solid surface (i.e., octanol on platinum and sapphire), which inhibits the liquid from spreading any further (for more details see Zisman, 1964). Also, hydrolysis of some esters at hydrated surfaces such as hydroxylated silica or sapphire occurs, and the ester is unable to spread upon the adsorbed monolayer of its own hydrolysis product (Zisman, 1964). As another example, volatile compounds from the atmosphere (such as organic contaminants and water) can adsorb physically or chemically on high-energy surfaces (this may happen even in seconds) and change the wetting characteristic of a solid surface completely (i.e., lower the surface free energy of the solid). Further, in several instances, it has been demonstrated that different mineral-surface preparation procedures and different reagents used for mineral-surface cleaning may significantly affect its wetting properties (Somasundaran, 1970; Janczuk et al., 1993). Finally, contact of a high-energy solid with the laboratory environment may initiate chemical changes at the solid surface through, for example, oxidation (Wang et al., 1992).

No paper presenting systematic measurements of contact angles for liquid (molten) polymers at mineral surfaces could be found in the available literature. In this regard, the behavior of liquid polymers at mineral surfaces seems to be presently unpredictable. This area of investigation requires that systematic studies be performed.

In the plastics industry, mineral-filler surfaces are modified with organic compounds before introducing the filler into the polymer matrix in order to enhance interactions at the polymer-mineral interface. Mineral surface modification is required because good wetting of a mineral filler by a polymer is often not sufficient to fabricate a high-quality composite, even though the polymer may spread spontaneously over the high-energy surface of the mineral particles and provide adhesive strength in excess of the cohesive strength of the polymer (Zisman, 1963; from: Plueddemann, 1985). Wetting properties of organic monolayers assembled at mineral and metal surfaces are generally better characterized than unmodified mineral and metal surfaces. Such systems are discussed in a subsequent part of this paper.

Critical surface tension of wetting for minerals

Another criterion satisfying the requirement for complete wetting can be deduced from Zisman's concept of the critical surface tension of wetting (γ_C). Zisman and co-workers (as reviewed by Zisman, 1963; 1964) found a linear relationship between the cosine of the contact angle ($\cos\theta$) and the surface tension (γ_L) of a homologous series of n-alkanes when contact angle measurements were conducted with low-energy solids (polymers). The intercept of this linear $\cos\theta$ vs. γ_L relationship at $\cos\theta = 1$ was termed the critical surface tension of wetting, which can be determined either graphically or by using the linear equation

$$\cos\theta = 1 + b(\gamma_C - \gamma_L) \qquad (3)$$

where b is a constant for a given system.

The values for γ_C may vary depending on the set of liquids used in the contact angle measurements. In particular, liquid solutions such as surfactant or alcohol solutions and hydrogen-bonding liquids are not recommended for use in the determination of the critical-surface tension of wetting (for a recent review see Kloubek, 1992). The preferential adsorption of selected components at a liquid-solid interface from solution or a specific interaction between a liquid and a solid surface can affect the contact-angle values significantly (Bernett and Zisman, 1959; Dann, 1970; Murphy et al., 1972). On the contrary, the concept of a critical surface tension of wetting has been found to be very useful in the analysis of mineral flotation, even when only aqueous surfactants or alcohol solutions are used (Finch and Smith, 1979).

Zisman's criterion predicts that complete wetting of a solid surface by a liquid (it could be a mineral surface wetted by liquid polymer) can be achieved when the surface tension of liquid does not exceed the critical surface tension of wetting of the solid surface, $\gamma_L \geq \gamma_C$. Wetting characteristics, as they relate to the critical surface tension of wetting for low-energy solids (including polymers) are available in several textbooks (i.e., Wu, 1982; Kinloch, 1987). For example, Table 3 presents critical surface-tension data for selected polymers. Based on these data, the wetting behavior of a liquid at a polymer surface can be predicted. A liquid spreads over the polymer surface when the surface tension of the liquid is less than the critical surface tension of wetting for the polymer. When $\gamma_L > \gamma_C$, the liquid forms a lens with a contact angle of $\theta > 0$. Such a clear understanding of the wetting characteristics for high-energy surfaces (inorganic minerals and metals) does not exist, and any generalization of liquid behavior at high-energy solids may fail.

As discussed in a previous section, the complications of the wetting characterization of high-energy solids arise from the following problems:

- Almost every organic liquid spreads freely over smooth, clean, high-energy surfaces, and, for this reason, the critical surface tension cannot be determined based on contact-angle measurements for a homologous series.
- "Autophobic liquids" form their own adsorbed oriented monolayers at high-energy solid surfaces, and these monolayers inhibit further spreading of the liquid.

Table 3 — Surface tensions and critical surface tensions of wetting for selected polymers at 20°C (data from Wu, 1982; Zisman, 1964)

Polymer	Surface tension, mN/m	Critical surface tension, mN/m
Polytetrafluoroethylene	21.5–23.9	18.5
Polyethylene	33.7–36.8	31
Polystyrene	39.3–40.7	33
Poly(methyl methacrylate)	41.1	39
Poly(vinyl chloride)	41.9	39
Poly(ethylene terephthalate)	44.6	43
Poly(hexamethylene adipamide)	46.5	46

Table 4 — Critical surface tension of wetting of selected minerals (experimental data collected by Ozcan, 1992)

Mineral	Critical surface tension, mN/m
Molybdenite	26.0-50.0
Galena	31.0-49.0
Chalcocite	24.0-44.0
Pyrite	26.5-42.0
Stibnite	26.0-43.0
Talc	29.0-41.0
Calcite	>70-73
Quartz	73.7*

(* as reported by Yarar, 1988)

- The wetting characteristics of many high-energy surfaces change when exposed to the environment. This is because of the adsorption of organic contaminants and/or water or because of a chemical interaction with oxygen, water or other gas (air) components.

The values of the critical surface tension of wetting have been determined for a few minerals and are presented in Table 4. Alcohol-in-water solutions and liquids with high surface tension (but no homologous series!), i.e., water, diiodomethane, formamide, etc, were used in contact-angle measurements. Assuming that the concept of the critical surface tension of wetting is applicable for polymer-mineral composites and that the γ_C values from Table 4 are representative values for the listed minerals, a simple analysis of the wetting behavior of polymers at mineral surfaces can be performed based on these data. (Unfortunately, contact-angle data for molten polymers at high-energy surfaces are rarely published (Dettre and Johnson, 1970), and, thus, no systematic analysis of such systems could be performed for this contribution—this area of investigation needs further research.) The surface-tension values for polymers were presented in Table 3. It follows from the concept of the critical surface tension of wetting that molten polytetrafluoroethylene should spread spontaneously over the surface of any mineral listed in Table 4. (The temperature coefficients of surface tension were assumed to be the same for the polymer and the mineral in order to simplify our discussion.) Calcite and quartz should be covered easily by all of the polymers specified in Table 3. Polyethylene, polystyrene, poly(methyl methacrylate) and poly(vinyl chloride) may or may not spread at molybdenite, galena, chalcocite, chalcopyrite, pyrite, stibnite and talc, depending on the value of the critical surface tension of wetting, which is selected for this analysis from the range of data presented in Table 4. Evidently, much more experimental work must be done to determine the γ_C values more precisely and to examine the wetting behavior of polymers at mineral surfaces.

The experimental γ_C data vary widely (see Table 4) according to the method of measurement, mineral-surface preparation and the liquids used for the contact-angle measurements (methanol-in-water solutions and pure liquids with the surface tension $\gamma_L > 40$ mN/m). Due to scatter in the experimental data (Table 4), the values of the critical surface tension of wetting for these minerals seem to be uncertain.

It is interesting to note that a similar range of γ_C values (γ_C = 25 to 46 mN/m), shown in Table 4, were reported by Zisman (1975) for several metals, glasses, alumina and metal oxide (Fe_3O_4) when these surfaces were covered with adsorbed water. Zisman's experiments clearly indicated that, for some systems, the measured value of γ_C reflects the nature of the surface contamination rather than the nature of the substrate (mineral in our case). The large difference between the γ_C values obtained for the same mineral (as presented in Table 4) are due to, among other factors, mineral surface contamination.

Also, molten metals have been used to examine the wetting properties of inorganic compounds. But recent analysis of such experimental data indicates that Zisman's relationship does not appear to be valid for the metal-mineral systems (Asthana, 1994). These results also suggest that Zisman's concept of the critical surface tension of wetting, although useful for a characterization of polymer surfaces, might not necessarily be applicable for all minerals.

Problem of surface contamination

For optimum adhesion of filler and polymer, the mineral surface must be kept free of organic contaminants, dust and moisture. A freshly prepared mineral surface, when exposed to the laboratory environment, tends to achieve its lowest-energy (most stable state) by instantaneous changes at the surface, e.g., adsorption of organic contaminants or water. In this way, contamination of mineral surfaces and consequently a reduction of surface energy occurs naturally for many high-energy materials.

Over a long time, the problem of contamination of high-energy surfaces with organic compounds had been ignored in many laboratories. For example, contact angles as high as 55 to 85° were reported in the literature for water at gold surfaces (Wu, 1982). After the work of Bewig and Zisman (1965) and Schrader (1970, 1974), it became clear that pure water spreads (exhibiting a zero contact angle) over the surface of a freshly prepared clean metal such as gold, platinum, copper or silver. Not much work, however, has been done to examine the adsorption of contaminants at mineral surfaces and their stability in the laboratory environment. Contamination of mineral surfaces is a significant problem when describing the wetting characterization of these materials, and this problem should receive more attention (see, for example, discussion by Somasundaran, 1970).

The phenomenon of contaminant adsorption at high-energy surfaces was examined many years ago by Bartell and Bristol (1940) (probably for the first time). They showed that the wetting characteristics of quartz and glass depend on the state of the solid surface. Also, White (1970) reported the kinetics of contact-angle change for water drops placed at the surfaces of mica and oxidized surfaces of nickel, aluminum and nichrome when these materials were exposed to laboratory air. He observed a systematic increase in contact angles to a certain plateau value, and he concluded that these changes were affected by the adsorption of contaminants from the surrounding atmosphere.

De Bruyne (after Zisman, 1963) formulated an empirical rule which states that strong bonds can never be formed between polar adhesives and nonpolar adherends (note that this rule was further extended by Wu (1982), who proposed, based on the analysis of wettability, that polarities of the adhesive and the adherend should be equal for optimum adhesion). However, according to Zisman (1963) de Bruyne's rule is correct for the polar adhesive-nonpolar adherend pair. This is because a polar adhesive has a larger surface tension than the critical-surface tension of wetting for a nonpolar adherend. On the other hand, poor wetting and spreading of the nonpolar adhesive may occur at the polar adherend due to the presence of moisture at a hydrophilic surface (polar adherend), and such pairs may form weak bonding.

Hydrophilic surfaces adsorb water even from the laboratory environment. Water at the polymer-mineral interface has a deteriorating influence on the composite adhesion. Although the phenomenon of formation and stability of water films at mineral surfaces is also important in many other areas of science (e.g., mineral processing), not enough research has been done to study the properties of adsorbed water films (including adsorbed monolayers). It is generally accepted that, under ordinary atmospheric conditions, hydrophilic minerals such as oxides adsorb at least a monolayer of water (Plueddemann, 1985). For example, a clean glass surface is covered with a monolayer of adsorbed water at relative humidities of around 30% to 50% at 20°C (Razouk and Salem, 1948). Formation of a water film composed of as many as 20 molecular layers, or more, may occur at the clean surface of high-energy solids, especially at high relative humidities (i.e., >90% to 95%)(Zisman, 1965; Jones, 1989). For example, Rhykerd et al. (1991) measured ellipsometrically the thickness of the adsorbed water film on a fused-silica surface and found it ranged from 24 to 90Å, depending on the water-vapor pressure. Staszczuk (1985), using gas chromatography to determine the water-adsorption isotherm on quartz at 20°C, found that about 16 statistical water layers adsorbed on quartz from a gas phase saturated with water vapor. Also, similar experiments using the chromatographic technique showed that about 15 statistical water layers may adsorb onto a marble surface (Janczuk et al., 1983). Water films with thicknesses from 10 to 80Å were also reported for muscovite mica (Perevertaev et al., 1979).

Water, if not already present at the mineral surface during the preparation of mineral-reinforced plastics, may also penetrate and diffuse to the polymer-mineral interface, attack the adhesive bond and progressively reduce the interfacial-joint strength (Kinloch, 1987; Plueddemann, 1985). For example, water was found to desorb organic adhesives from metal-oxide surfaces, particularly from those surfaces that were not protected with an organic film (Kinloch, 1987). Although it is possible to modify the mineral surface with organic compounds in order to decrease its tendency to adsorb water, such surface treatment also affects the wetting and adhesive properties of the filler. This important issue of mineral-surface modification is discussed in the next section.

Modification of mineral surfaces

The surface treatment of minerals with organic compounds of varying functionality improves the compatibility of the mineral-filler surfaces with polymers, increases the adhesion and strength of the polymer-mineral joint and reduces water adsorption at the mineral surface, which reduces its destructive effect on the polymer-mineral interfacial bonding. The chemical agents commonly used to alter the organophilic nature of the filler surface are known as primers or surface modifiers. A function of these surface-reactive compounds is to promote coating and eventually coupling with the polymer. The bifunctionality of these surface modifiers (coating and coupling) obviously makes these compounds more attractive for the plastics industry than monofunctional coating compounds. Almost all available $CaCO_3$ fillers in the market are coated with stearic acid or calcium stearate to make the surface hydrophobic and to improve the dispersion of $CaCO_3$ particles in resins (Katz and Milewski, 1987; Miller et al., 1994). Initially, the research effort in this area was primarily directed toward changing the wetting characteristics of the mineral from hydrophilic to hydrophobic and toward improving the dispersibility of filler particles in polymer matrices. Most recent studies have led to enhanced adhesion between polymer and mineral by changing the functionality of the organic monolayers. Coupling agents of varying chemical composition and functionality, such as silanes, titanates, zirconates, zircoaluminates, orthosilicates, chrome complexes, phosphates, phosphonates and sulphonates, have been proposed in the literature as mineral-surface modifiers (Katz and Milewski, 1987; Kinloch, 1987; Yosomiya et al., 1990). Organofunctional silanes remain the most popular coupling agents in the fabrication of polymer-mineral composites (Plueddemann, 1985). On the other hand, consumption of titanates by the plastics industry seems to have increased in recent years (Katz and Milewski, 1987). Coupling agents of other chemical composition have received only limited industrial attention.

Bonding of a mineral surface covered by an organic monolayer with a polymer is often complicated and may involve several phenomena (e.g., interdiffusion, copolymerization and crosslinking) depending on the system and functionality of the coupling agent. The changes in the interfacial zone at a molecular scale are extremely complex and practically each particular primer-polymer system requires a separate theoretical analysis, and this discussion exceeds the goal of this review. Readers are referred to the specific literature discussing this aspect of adhesion (Wu, 1982; Yosomiya et al., 1990).

Zisman (1963) believed that an increase in the joint strength between the adhesive and adherend can be accomplished by chemical modification of the adherend surface, as a result of the increased critical surface tension of wetting for these modified surfaces. Although the adhesion between the polymer and coupling agent involves complex mechanisms, for many systems, Zisman's concept still seems to be attractive for predicting the polymer spreading behavior on the organic monolayer film (assembled at the mineral surface). The values of the critical surface tension of wetting for several organic functional groups are shown in Table 5. A full spectrum of the γ_C values for varying functionality of coupling agents is not available in the literature at this time. So far, such full-wetting characterization based on the γ_C values exists only for polymers (Wu, 1982).

Some important conclusions can be drawn from the data presented in Table 5. Fluorocarbon surfaces, followed by hydrocarbon surfaces, are the most hydrophobic materials with very low γ_C values. Thus, a limited variety of polymers are able to spread spontaneously at such surfaces. For example, no known liquid spreads over the condensed monolayer of a fluorinated fatty

Table 5 — Critical surface tensions of wetting of selected low-energy organic surfaces (Zisman, 1963)

Functionality of organic surface	Critical surface tension γ_c, mN/m
$-CF_3$ (monolayer)	6
$-CF_2H$ (monolayer)	15
$-CF_2-CF_2-$ (polymer)	17
$-CH_3$ (monolayer)	22-24
$-CH_2-CH_2-$ (polymer)	31
$-C_6H_5$ (polymer)	35
$=CCl_2$ (monolayer)	43
$-CH_2ONO_2$ (polymer)	40-45
$-C(NO_2)_3$ (monolayer)	42

Table 6 — Bond types and their energies (Kinloch, 1987)

Bond type	Bond energy, kJ/mol
Primary bonds	
Ionic	600-1100
Covalent	60-700
Metallic	110-350
Donor-acceptor bonds	
Bronsted acid-base interactions	≤1000
Lewis acid-base interactions	≤80
Secondary bonds	
Hydrogen bonds	≤40
van der Waals interactions	≤40

acid with exposed terminal $-CF_3$ groups, and a similar behavior of liquid polymers is expected at these modified $-CF_3$ surfaces. Practically no polymer would demonstrate a zero contact angle at modified surfaces with terminal $-CF_3$ and $-CF_2H$ groups. Strong hydrophobicity and oleophobicity of fluorinated surfaces makes the adhesion of these materials to another substrate (mineral, metal or polymer) impossible without chemical modification of the fluorinated terminal groups. Further, only dimethyl silicones and highly fluorinated polymers are able to spread spontaneously on a surface coated with close-packed methyl groups. In this regard, as discussed earlier, calcium carbonate coated with stearic acid or calcium stearate may be wetted spontaneously by only a few polymers. Of course, many common polymers will spread over surfaces modified with organic monolayers having polar terminal groups, especially when the value of the critical surface tension of wetting is larger than 40 mN/m (compare the γ_C values from Table 5 with the surface tension values for polymers in Table 3). Again, this analysis, based on Zisman's concept of the critical surface tension of wetting, cannot be supported with experimental results. No systematic examination of contact angles for molten polymers placed at self-assembled or deposited organic monolayers was found in the literature.

Mechanisms of adhesion

Although good wettability of mineral surfaces by polymers is strongly desired for the preparation of high-quality mineral-reinforced plastics, the strength of the polymer-mineral particle interfacial joint only rarely can be described in terms of the surface free energy. Spontaneous polymer spreading over the mineral surface does not necessarily cause strong adhesion. The wettability of a mineral-filler surface by the polymer is only one of the conditions desired, and other determinant factors of interfacial bonding should be taken into consideration, such as chemical reaction between these phases in the interfacial zone, diffusion of phase components or chain segments into the interfacial zone, electrostatic interactions across the interface, residual interfacial stress after polymer solidification and mineral surface topography (roughness) (Wu, 1982; Kinloch, 1987; Allen, 1988; Yosomiya et al., 1990). A complete discussion of all these factors is beyond the scope of this review.

The following four main mechanisms of adhesion have been discussed extensively in the literature:

- adsorption theory,
- mechanical interlocking theory,
- diffusion theory, and
- electronic theory.

The *adsorption theory* states that adhesion between two phases with intimate contact is achieved because of various intermolecular and interatomic forces of attraction across the interface in a joint. Van der Waals forces and hydrogen bonds are referred to as secondary force interactions. Chemical bonds such as ionic attractions, covalent or metallic bonds are referred to as primary force interactions. Also, donor-acceptor interactions, which are typically intermediate in strength between secondary and primary forces, occur at the polymer-mineral interface. All these forces are effective over a short distance (a few tens of angstroms at most), but the interaction across the interface has an effect on various properties of the composite. The typical bond energies are shown in Table 6.

The adhesive joint strength may be enhanced significantly by a roughening of the mineral surface. According to this concept, known as the *theory of mechanical interlocking*, an increased surface area and irregularities of the adherend surface may promote wetting and provide mechanical overlapping of the two phases. A popular example that demonstrates the use of this adhesion mechanism is the filling of tooth cavities by mercury amalgams.

The *diffusion theory* states that long-chain molecules, or at least their segments, are able to diffuse across the interface improving the adhesion strength, which is of particular significance in the fabrication of strong polymer-polymer joints. This mechanism has little significance in the preparation of polymer-mineral composites. Polymer penetration into the fine structure of the mineral-filler surface has been considered as a diffusion mechanism in such systems (Allen, 1988). However, penetration of the mineral-surface structure by the polymer could be attributed to mechanical interlocking. Interface diffusion between segments of the long-chain coating/coupling agents at the mineral surface and polymer molecules seems to be the obvious case for such a mechanism. However, a satisfactory description of interface-diffusion mechanisms for such systems appears to be lacking in the literature.

Finally, Russian researchers proposed the *electronic theory of adhesion*, which assumes that a double layer of electrical charge is formed at the interface when the adhesive and adherend have different electronic-band structures (Deryaguin and Smilga, 1960; Kinloch, 1987). This electrical charge may be of particular concern in metal-semiconductor systems, but electrostatic double-layer forces have probably no practical contribution to adhesion at polymer-mineral interfaces.

Thermodynamic work of adhesion

The work of adhesion (W_A) is a thermodynamic parameter that refers to equilibrium energies associated with the reversible process of separation of the interface between two bulk phases. W_A is expressed by the following Dupré equation

$$\frac{W_A}{A_{PM}} = \gamma_P + \gamma_M - \gamma_{PM} \tag{4}$$

where

A is the interfacial area of the joint;
γ describes the surface or interfacial free energy; and
subscripts M and P correspond to mineral and polymer, respectively.

It is important to recognize that this equation is applicable to systems with secondary force interactions (no chemical bonds across the interface) and with no mechanical interlocking. Also, other important restrictions must be noted in the case of polymer-mineral-filler systems: the shrinkage stresses at the polymer-mineral interface should be negligible and the polymer surface free energy should not change drastically after polymer solidification.

A difficulty in the application of the Dupré equation is that there are two interfacial parameters, γ_M and γ_{PM}, which cannot be measured directly, and, thus, this fundamental equation has no practical utility. But after substitution of Young's equation, Eq. (1), into Eq. (4), the work of adhesion is as follows:

$$\frac{W_A}{A_{PM}} = \gamma_P(1 + \cos\theta) \tag{5}$$

with two parameters, γ_P and θ, which can be determined experimentally. Eq. (5) holds for liquids with $\theta > 0$ and for systems in which Eqs. (1) and (4) apply.

The thermodynamic work of adhesion should correlate with the strength of the adhesive joint as long as the system satisfies the conditions dictated by the thermodynamic relations of Eqs. (4) and (5). A lack of such correlation may appear, but it is probably due to the fact that the test methods for measuring the strength of adhesive joints are not well suited for the confirmation of theoretical models. Particularly, this happens when contributions from intrinsic adhesion forces and from viscoelastic/plastic energy losses in the polymer and mineral are not well identified (Kinloch, 1987). On the other hand, it should be recognized that the shrinkage stresses at the interface after polymer solidification may completely change the adhesion joint.

Several new equations for the calculation of the work of adhesion have been proposed in the literature. These equations were based on the concept of the additivity of surface tension/surface free-energy components (Wu, 1982; Hata et al., 1988; Yosomiya et al., 1990). These concepts have no practical significance for the polymer-mineral composites, at this time. First, the surface free-energy components remain unknown for the minerals of interest and their determination is difficult because of the high surface free energy of mineral surfaces, at which most liquids spread spontaneously. Second, these models are semiempirical. The empirical treatment of natural phenomena is allowed as long as our knowledge of surface/interfacial forces is incomplete, but such an approach is always an approximation and may limit the development of this important area of technology.

Concluding remarks

This review has discussed the various aspects of wetting and adhesion phenomena that may occur during the fabrication of polymer-mineral composites. The wetting behavior of a polymer at the filler surface and the adhesion forces involved at the polymer-filler interface should always be considered for the fabrication of polymer composites of high quality, including the composites made with mineral fillers. A review of the available literature indicated that, although conditions for good surface wetting and bonding are well recognized, no systematic characterization of the wetting and adhesion properties for minerals, particularly with regard to various polymers, has been conducted. Zisman's concept of the critical surface tension of wetting has been extensively adopted. However, no experimental support of its validity could be found in the literature for polymer-mineral systems. It seems that this area of research requires further study before new technological advances will be made.

The issue of contamination of the mineral surface requires additional studies. For example, mineral surface contamination by organic impurities from the air has received insufficient attention at research centers, even though it has been demonstrated several times that organic contaminants totally change the surface characteristics of high-energy solids. The stability of water films at the surface of selected minerals has been examined in several laboratories. However, this work has been limited almost exclusively to quartz and silica. The formation and stability of water films, including the monolayer level, at many mineral surfaces cannot be predicted with existing knowledge.

Several different mechanisms of adhesion between phases have been proposed in the literature. The mechanism of adsorption (including interfacial chemical reactions) seems to be the main mechanism responsible for intrinsic adhesion between the two phases. However, in many systems, two or more mechanisms can be involved in one joint. It is not always correctly recognized that thermodynamic relations describing three-phase systems are applicable to systems with secondary force interactions. For example, the thermodynamic work of adhesion may correlate with the strength of the adhesive joint if there are no chemical bonds across the interface and no mechanical interlocking occurs. Generally, these theoretical concepts and theories must be confirmed for polymer-mineral filler composites, and this research area needs to receive our dedicated attention.

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