

Modification of Epoxy Resin with Kaolin as a Toughening Agent

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ABSTRACT: Epoxy resins are widely used as high-performance thermosetting resins for many industrial applications, but unfortunately, some are characterized by a relatively low toughness. In this respect, many efforts have been made to improve the toughness of cured epoxy resins by the introduction of rigid particles, reactive rubbers, interpenetrating polymer networks, and thermoplastics within the matrix. In this work, kaolin as a modifier was added at different contents to improve the toughness of diglycidyl ether of bisphenol A epoxy resin with polyamino-imidazoline as a curing agent. The chemical reactions suspected of taking place during the modification of the epoxy resin were monitored and evaluated with Fourier transform infrared spectroscopy. The glass-transition temperature (T_g) was measured with differential scanning calorimetry. The mechanical behavior of the modified epoxy resin was evaluated in terms of the Izod impact strength (IS), the critical stress intensity factor (K_{IC}), and tensile properties at different modifier contents. Scanning electron microscopy (SEM) was used to elucidate the mechanisms of deformation and toughening in addition to other morphological features. Finally, the adhesive properties of the modified epoxy resin were measured in terms of tensile shear strength (TSS). With the addition of kaolin, the reactivity test revealed that the gel time and temperature, exotherm peak, and cure time were reduced. Infrared spectra showed the existence of a chemical reaction between kaolin and the epoxy resin. The presence of kaolin caused a steady decrease in T_g by about 10°C until 15-phr kaolin was reached prior to leveling off. Most of the tensile properties attained a peak at an approximately 10-phr kaolin content where the toughening reached its maximum. The modulus increased linearly from 1.85 to 2.7 GPa with increasing kaolin content. For both notched and unnotched specimens, a twofold increase in Izod IS was obtained by the addition of just 10-phr kaolin compared to the unfilled resin. On the addition of kaolin, the Izod IS varied from 0.85 to 1.53 kJ/m² for notched specimens and from 4.19 to 8.32 kJ/m² for unnotched specimens, whereas K_{IC} varied from 0.91 to 2.63 MPa m^{1/2} with increasing kaolin content. The adhesive properties, evaluated in terms of TSS, increased from 9.14 to 15.02 MPa. SEM analysis revealed that the prevailing toughening mechanism for the epoxy resin under consideration was localized plastic shear yielding induced by the presence of kaolin particles associated with crack pinning. © 2001 John Wiley & Sons, Inc. *J Appl Polym Sci* 82: 861–878, 2001

Key words: epoxy; kaolin; toughening; K_{IC} ; impact strength

INTRODUCTION

Epoxy¹ resins are considered one of the most important classes of thermosetting polymers and

find extensive use in various fields, including coating, high-performance adhesives, and other engineering applications. Once cured, they are characterized by high chemical and corrosion resistance and good mechanical and thermal properties. However, in many applications they have one major disadvantage: they are very brittle with poor resistance to crack propagation and low impact strength (IS). That is, they exhibit low toughness.¹ The aim

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in toughening brittle polymers is to increase their toughness without significantly decreasing other important properties, such as the modulus and heat-distortion temperature. Most of the reported studies were carried out with glass beads, alumina trihydrate, and silica, and some of the most successful involved the addition of a suitable rubber such as liquid amine-terminated (ATBN), carboxyl-terminated (CTBN), or hydroxyl-terminated (HTBN) copolymers of butadiene and acrylonitrile and, more recently, the use of thermoplastics [polyphenyloxide (PPO)] and interpenetrating polymer network (IPN) structures.

The first approach to modifying epoxy resins is rigid particle addition, which generally leads to a significant reduction in cost and a considerable improvement in the resin mechanical, thermal, and electrical properties, namely, the elastic modulus, heat-distortion temperature, and dielectric strength. Considerable work relating to the effect of particulate fillers on the mechanical properties of thermoplastic and thermosetting polymers has been reported in literature. Parameters such as the volume fraction of the filler,²⁻⁶ particle size,^{4,6-8} modulus and strength of the filler,^{3,9} resin-filler adhesion,^{3,10} and toughness of the matrix have been extensively studied. The variation of some of these parameters leads to improved toughness of the filled material while increasing its strength and modulus. Several studies have demonstrated that the fracture energy of filled epoxies reaches a maximum at a specific filler volume fraction.^{2-5,11} Young and Beaumont² used a series of epoxy resin composites with up to 52 vol % irregularly shaped silica particles. The Young's modulus and yield stress both increased, and the critical strain energy release rate, crack-opening displacement, and plastic zone size all reached a maximum at a specific filler volume fraction of about 30% before decreasing at higher volume fractions. However, Moloney et al.³ showed that for the dolomite composite, the relationship between the yield stress and the filler volume fraction was completely different from that of silica and alumina. The yield stress was constant with increasing volume fraction in the case of dolomite, whereas for alumina and silica, the yield stress increased considerably. For dolomite-filled resins and above a certain critical volume fraction (~20%), a plateau was reached, and the stress intensity factor no longer increased. This seemed to be caused by crack propagation through the weak particles, whereas it is highly probable that the plateau was caused by transparticle fracture. Spanoudakis and Young⁴

studied spherical glass particles of two different sizes (4.5 and 62 μm) in an epoxy resin. They showed that values of the critical stress intensity factor (K_{IC}) for both initiation and arrest increased with increasing particle volume fraction, whereas propagation tended to become unstable. However, at high volume fractions, propagation became stable again for the 4.5- μm particles. In contrast, for the resin with the larger (62 μm) particles, there was no tendency for propagation to stabilize at high volume fractions. It was also found that for a given value of the volume fraction, the particle size significantly affected the value of the fracture energy and the nature of crack propagation, whereas the dependence of the modulus on particle size was not particularly strong. The highest values of K_{IC} were found for the composite with the highest volume fractions of the largest particles. Srivastava and Shembekar⁵ used fly-ash particles (with different chemical constituents, i.e., silicon oxide, aluminum oxide, calcium oxide, iron oxide, and magnesium oxide) in an epoxy resin. They found that either the fracture surface energy or the fracture toughness of fly-ash-composite-filled epoxy resins reached a maximum at 6.5% fly ash by volume and the elastic modulus increased with increasing fly-ash percentage. Thus, it can be concluded that an increase in the filler volume fraction increases both the modulus and toughness. Several studies have demonstrated that a change in the filler particle size at a constant volume fraction does not have a significant influence on the modulus of the composite.^{4,6-8} Nakamura and coworkers^{7,8} obtained similar results for another epoxy resin filled with angular-shaped silica particles ranging from 2 to 47 μm in diameter. They concluded that the reason behind the improvement in impact properties with decreasing particle size was that the inherent flaws initiated fracturing in the impact test while decreasing the strength. The particle shape plays an essential role in the determination of the toughness of the composite. In fact, the shape becomes more irregular with increasing particle size, and for this reason, the effect of particle size on toughness with spherical silica particles in the range from 6 to 42 μm was studied.⁶ The values of the stress and strain at break and the impact-absorbed energy increased with decreasing particle size. These phenomena were in accordance with results obtained in the irregularly shaped silica-filled system reported in their previous article,⁸ although it was difficult to distinguish strictly between the effects of size and shape because of the particle agglomeration. An

Table I Materials Used

Materials	Description	Supplier
Epoxy resin	DGEBA Araldite GY 260 weight-average molecular weight (= 381; without diluent) Epoxy index (equiv/kg) = 5.1–5.4 Epoxy equivalent (g/equiv) = 185–196	Schering S.A., Lys-Lez-Lannoy, France
Curing agent	Polyaminoimidazoline (EUREDUR 460) Amine index = 230–260	Schering S.A., Lys-Lez-Lannoy, France
Kaolin	Hydrous alumina silicate: SiO ₂ (45.8%), Al ₂ O ₃ (33.64%) Particle size range (1–15 μm)	EREM, Boumerdes, Algeria
Substrates	Aluminium plates ($l = 100$ mm, $w = 23$ mm, $t = 2$ mm)	

increase in filler modulus increased both the modulus and stress intensity factor of the composite. This was clearly shown by Moloney et al.⁹ for an epoxy resin filled with silica, alumina, and dolomite particles. For an epoxy resin filled with silica and alumina with 94- and 320-GPa moduli, respectively, the K_{IC} values were significantly higher than for the dolomite system (78 GPa). In this case, beyond a certain critical volume fraction (~20%), a plateau was reached.

The second method used to improve the toughness of epoxy resins involves an addition to the uncured epoxy resin of suitable rubbers that are copolymers with variable acrylonitrile contents. The effects of the acrylonitrile content of the copolymer type, the molecular weight, the concentration, and the solubility parameter of the rubber and its functional end groups on the fracture toughness or on the IS of the epoxy resin have been studied. In these studies, epoxy resins were modified with CTBN,^{12–23} ATBN,^{21,24} HTBN,²⁵ or epoxy-terminated^{24,26–27} copolymers of butadiene and acrylonitrile.

The degree to which a highly crosslinked epoxy resin can be toughened by rubber particles is very limited because its ability to deform by shear yielding is reduced with increasing crosslink density; therefore, a third technique has emerged. Recently, highly crosslinked thermosetting has been toughened by tough, ductile, and chemically and thermally stable engineering thermoplastics such as polyethersulfones,^{28–30} polyetherimides,^{31,32} phenolic hydroxyl-terminated bisphenol A polysulfone,³³ and PPO.³⁴

Finally, IPNs are a novel type of polymer alloy intended, in the case of epoxy resins, to modify impact resistance. Interpenetration, or permanent entanglement, usually leads to improved

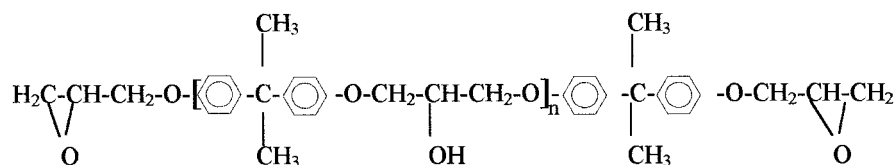
compatibility, which means that a decreased degree of phase separation is attained. Morphology, which plays a major role in affecting IPN properties, is controlled by the chemical compatibility of the polymers, interfacial tension, crosslinking densities of the networks, polymerization method, and IPN composition.^{35–38}

In this study, we attempted to improve the toughness of diglycidyl ether of bisphenol A (DGEBA) epoxy resin cured with polyaminoimidazoline using kaolin with a distribution of particle diameters ranging from 1 to 15 μm as a modifying agent. The chemical reactions that possibly took place during the modification of the epoxy resin were monitored with Fourier transform infrared (FTIR) spectroscopy, and the glass-transition temperature (T_g) was measured with differential scanning calorimetry (DSC). The mechanical behavior of the modified epoxy resins was evaluated in terms of the Izod IS (high speed of crack propagation), K_{IC} (low speed of crack growth), and tensile properties [stress and strain at break, tensile modulus (E), and energy at break (U_B)] at different modifier contents. The fractured surfaces were studied with scanning electron microscopy (SEM) to elucidate the mechanisms of deformation and toughening and other morphological features. Finally, the adhesive properties of the modified epoxy resins were evaluated in terms of tensile shear strength (TSS).

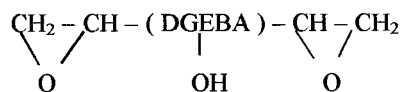
EXPERIMENTAL

Materials

The materials used and their chemical structures are illustrated in Table I and Scheme 1, respectively.



This structure will be reduced to



Scheme 1 Chemical structures of epoxy and curing agent.

Sample Preparation

Epoxy/Kaolin/Curing Agent System

Samples of the epoxy/kaolin (5–30 phr) composites were prepared first by the addition of dry kaolin to DGEBA resin. This mixture was heated to approximately 60°C for 5–15 min in a water bath and degassed while it was stirred with a mechanical stirrer. After the mixture had cooled below 60°C, the curing agent, which was heated to approximately 40°C, was added, and the mixture was hand-mixed for 1–2 min. Next, the resin mixture was poured into a polytetrafluoroethylene-coated mold, cured for 24 h at room temperature, and postcured at 120°C for 3 h. At this stage, the cured specimens of epoxy composite were allowed to cool slowly in the mold at room temperature.

Adhesive Preparation

The adhesive preparation was carried out as indicated previously. The aluminum specimens (the substrate) were immersed for 10 min at 65–70°C in a 25% sulfuric acid and 2.5% sodium dichromate solution before they were washed with water and acetone successively before bonding.³⁹ Then, about 0.1 g of adhesive was manually spread as uniformly as possible on both surfaces of the substrates (4.6 cm²). After deposition of the adhesive on the substrate surfaces and the forming of an adhesive layer, a 1500-g weight was placed over the overlap area of the sample to ensure continuous contact for 24 h at room temperature; The sample was then postcured at 120°C for 3 h. Before curing, the excess of adhesive was cleaned off the joint with a knife.

Testing

Characterization Methods

Reactivity. When used in a resin, the filler has a direct influence on the curing parameters, such as

gel time, cure time, gel temperature, and cure temperature. For exothermic curves, 15 g of epoxy resin was cured with a stoichiometric content of curing agent in a glass beaker. This beaker was immersed in an oil bath (80°C), and the temperature was recorded with a thermocouple. Finally, the cure conditions were determined from the exothermic curves, that is, the temperature as function of time.

FTIR Spectroscopy. FTIR spectroscopy was used to monitor the extent of cure of the DGEBA/hardener epoxy resin system and the reactions that occurred when such modifiers were used. A small portion of the cured epoxy was ground to a fine powder, mixed with potassium bromide (KBr) powder, and pressed into a pellet. FTIR spectra were recorded on a PerkinElmer 1000 PC spectrometer (Norwalk, CT).

DSC. T_g of the cured and modified DGEBA resins with kaolin was measured. The matrix and dispersed-phase transition temperatures were measured at a heating rate of 10°C/min with a PerkinElmer DSC7 differential scanning calorimeter (Norwalk, CT).

Mechanical Properties Evaluation

Tensile Properties. The load–elongation curve was obtained directly from the extensometer with an Instron mechanical tester (Canton, MA) with a crosshead speed of 10 mm/min. All tests were performed at room temperature according to BS 2782 method 302 A. The tensile strength and modulus of elasticity with different contents of kaolin were obtained (E was taken at 0.2% extension).

Izod IS. Izod IS was measured according to ASTM D256 with a standard notched (1 mm) specimen. Tests were run in a TM Inc. N 431

impact tester-type machine (Alberville, NY) equipped with a hammer. The Izod IS was calculated as follows:

$$IS = \frac{U_1 - U_2}{(w - a) \cdot t} \text{ (kJ/m}^2\text{)}$$

where w is the specimen width (in meters), t is the specimen thickness (in meters), U_1 is the impact energy (in kilojoules), U_2 is the residual energy (in kilojoules), and a is the precrack length (in meters).

Six samples from each formulation were broken. Average IS values along with the standard deviations are reported. Samples were prepared by casting into rectangular-shaped cavities ($65 \times 15 \times 4$ mm).

K_{IC} . The fracture toughness was measured in terms of K_{IC} . Fracture toughness values were determined with precracked, single-edge-notched specimens in three-point bending with a span of 50 mm. These tests were performed with an Instron tensile machine type 1185 at a crosshead speed of 5 mm/min at room temperature. K_{IC} was determined according to ASTM E 399-78, with the following relationship:⁴⁰

$$K_{IC} = \frac{3PSa^{1/2}Y}{2tw^2}$$

where P is the critical load for crack propagation (in newtons), S is the length of the span (in millimeters), a is in millimeters, t is in millimeters, w is in millimeters, and Y is a geometrical factor given by

$$Y = 1.93 - 3.07(a/w) + 14.53(a/w)^2 - 25.11(a/w)^3 + 25.80(a/w)^4$$

Adhesive Properties (TSS). The TSS test was carried out on an Instron tensile testing machine at a crosshead speed of 10 mm/min at room temperature. The TSS was calculated as follows:

$$TSS = F/A \text{ (N/m}^2\text{)}$$

where F is the force at fracture (in newtons) and A is the surface of the bond area (in meters squared). TSS values reported represent an average of six to eight samples.

Table II Effect of Kaolin Content on the Reactivity of Epoxy Resin

Kaolin (phr)	Gel Time (min)	Cure Time (min)	Gel Temperature (°C)	Exotherm Peak (°C)
0	13.0	19.0	93.5	112.5
5	11.0	16.0	90.0	105.0
10	10.5	15.5	87.5	104.0
15	10.5	15.5	88.5	104.0
20	10.5	15.0	90.0	101.0
30	10.5	17.0	88.0	97.0

SEM Analysis. Surfaces of a broken sample under Izod impact conditions were examined with a scanning electron microscope (Philips XL 20, France). Fractured surfaces of different kaolin contents were coated with a thin palladium layer.

RESULTS AND DISCUSSION

Neat epoxy was modified with kaolin as a rigid filler. The changes in the epoxy structure, reactivity, and properties were recorded with infrared (IR) spectroscopy, DSC, mechanical testing, and fractography. The adhesive properties were evaluated with tensile shear testing.

Reactivity

The effect of the kaolin content on the reactivity of the epoxy resin is summarized in Table II.

Figure 1 illustrates the exothermic curves for both the neat and 10-phr-kaolin-modified resin. The temperature during curing was monitored as a function of time. A maximum in this temperature (exotherm peak) was observed for both the neat and modified resins at 112.5°C after 19 min and at 104°C after 15.5 min, respectively. Such an increase might be attributed to the energy released as the epoxy groups reacted. Furthermore, the gel temperature and gel time were indicated when the compound became just rubbery. From the cure curve, the gel time, gel temperature, exotherm peak, and cure time were obtained.

As shown in Table II, when kaolin was added, the gel time and temperature, the exothermic peak (maximum temperature rise), and the cure time all decreased. The gel time decreased from 13 to 10.5 min before leveling off, the gel temperature decreased from 93.5 to 87.5°C, the maximum temperature decreased from 112.5 to 97°C,

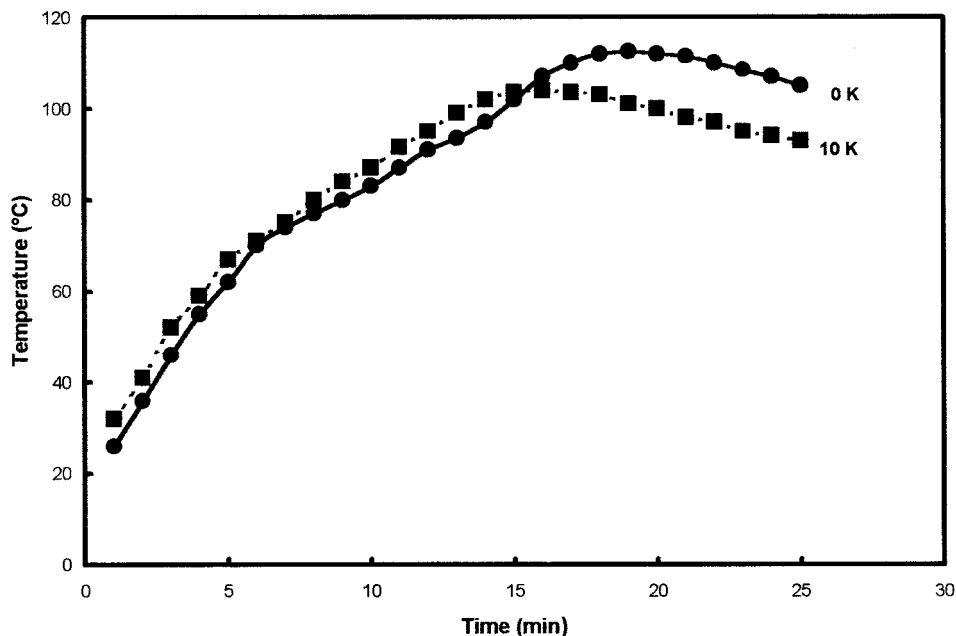


Figure 1 Exothermic curves of both neat epoxy (0 K) and 10-phr kaolin (10 K) of modified epoxy resin.

and the cure time decreased from 19 to 15 min. This behavior could be attributed to restricted molecular mobility of the reactive species induced by the presence and reactivity of kaolin, which thus led to a reduced exothermic peak and increased viscosity. Furthermore, this might also have been caused by the fact that kaolin is an inorganic filler with a higher thermal conductivity [$4.7 \times 10^{-3} \text{ cal s}^{-1} \text{ cm}^{-2} (\text{°C/cm})$] than neat epoxy [$0.5 \times 10^{-3} \text{ cal s}^{-1} \text{ cm}^{-2} (\text{°C/cm})$], thus causing a greater heat dissipation and resulting in a decreased exotherm peak.

IR Spectroscopy

A series of IR spectra were obtained to evaluate the occurrence of any chemical reaction between the epoxy resin and kaolin. They are presented in Figures 2(a, b) and 3(a, b). Figure 2(a, b) represents the IR spectra of both pure epoxy resin without hardener (curve a) and that of epoxy with the hardener, referred to as neat epoxy (curve b).

The epoxy absorbed at approximately 876 and 914 cm^{-1} . Similar results were reported elsewhere¹ as shown in Figure 4 (a typical epoxy resin IR spectrum).

These spectra reveal the presence of an absorption peak at about 3500 cm^{-1} , which belonged to the OH group stretching vibrations of the pure epoxy resin (spectra a), whereas for neat epoxy, the increase in the intensity of this peak [as illustrated in Fig. 2(b)] was related to the reaction of the amine primary groups with epoxy groups and the creation of hydrogen bonding between epoxy hydroxyl, ether, and amine groups and the product obtained.

The drastic reduction observed in the epoxy group intensity peak appearing at about 914 cm^{-1} was an indication of the reaction of epoxy groups with amine groups. The epoxy peak appearing at 876 cm^{-1} was still present, indicating that the reaction was not complete. This is illustrated as follows:

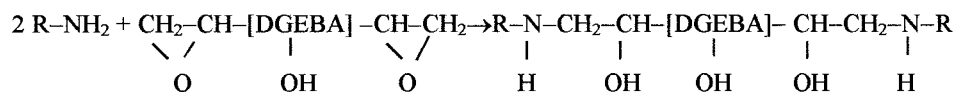


Figure 3(a, b) illustrates a magnification of the IR transmission spectra of neat epoxy and, after modification with different kaolin contents (5, 10, 15, 20,

and 30 phr), at specific intensity peaks [Fig. 3(a), epoxy; Fig. 3(b), hydroxyl]. When kaolin was added, the epoxy peak appearing at about 876 cm^{-1} disap-

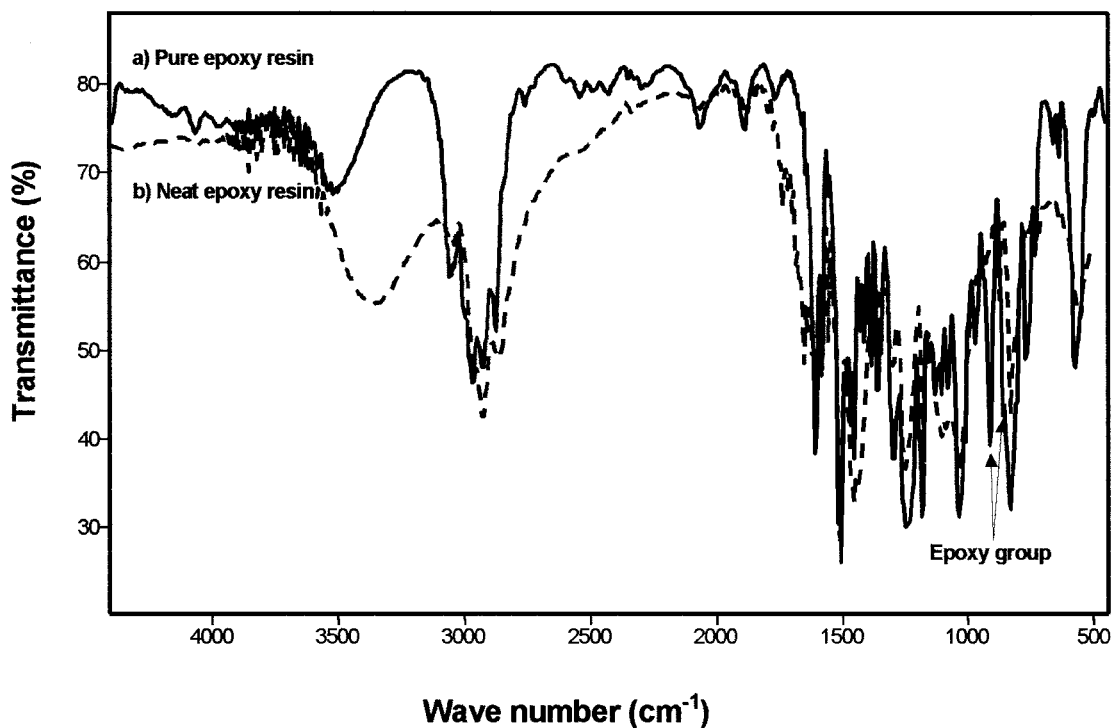
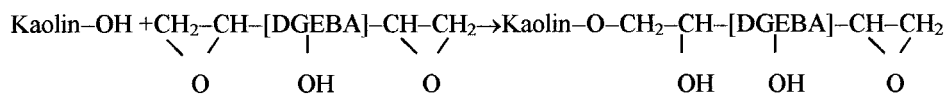


Figure 2 IR spectra of both (a) pure epoxy resin (no hardener) and (b) neat epoxy resin (with hardener).

peared gradually. This means that the hydroxyl groups on the surface of kaolin were suspected to

react as acids (proton donors) with the epoxy resin according to the following reaction scheme:⁴¹



The reappearance of the epoxy intensity peak at 914 cm^{-1} was attributed to groups belonging to kaolin. This was confirmed by the fact that natural kaolin absorbs at this specific wavelength range (914 cm^{-1}), as shown in Figure 5.

Figure 3(b) illustrates peaks appearing at about 3620 cm^{-1} when kaolin is added; such peaks belong to the kaolin OH group. It has been reported in the literature³⁹ (and based on the chemical composition of kaolin; see Table III), that H_2O cannot be removed even at postcure temperatures as high as 120°C . A comparison between the IR spectra of natural and calcined kaolin (at $\sim 500^\circ\text{C}$) was performed and is presented in Figure 5. When calcined, the kaolin OH peak appearing precisely at 3620 cm^{-1} was greatly reduced. This peak did not totally disappear because the calcination was not completed. This goes along with results reported in the literature.⁴¹ In

general, the hydroxyl group absorbed in the range of $3300\text{--}3700 \text{ cm}^{-1}$, as shown in Figure 4(b).

Figure 4 shows the effect of kaolin content on the transmittance percentage. Logically, an order was expected to be obtained. Unfortunately, because of the preparation difficulties (thickness uniformity and dispersion homogeneity), this order was missing. This might have been caused by the following factors: First, the dispersion of kaolin in the resin matrix was not perfectly uniform and might have affected the transmittance capabilities. The other potential reason is the eventual poor dispersion of the compound (kaolin and resin) within the KBr powder prior to IR observation.

The previously discussed results, concerning the decrease in the epoxy intensity peaks, were further confirmed by a quantitative measurement of the degree of cure. We achieved this by monitoring the ratio of the absorbance of epoxy group

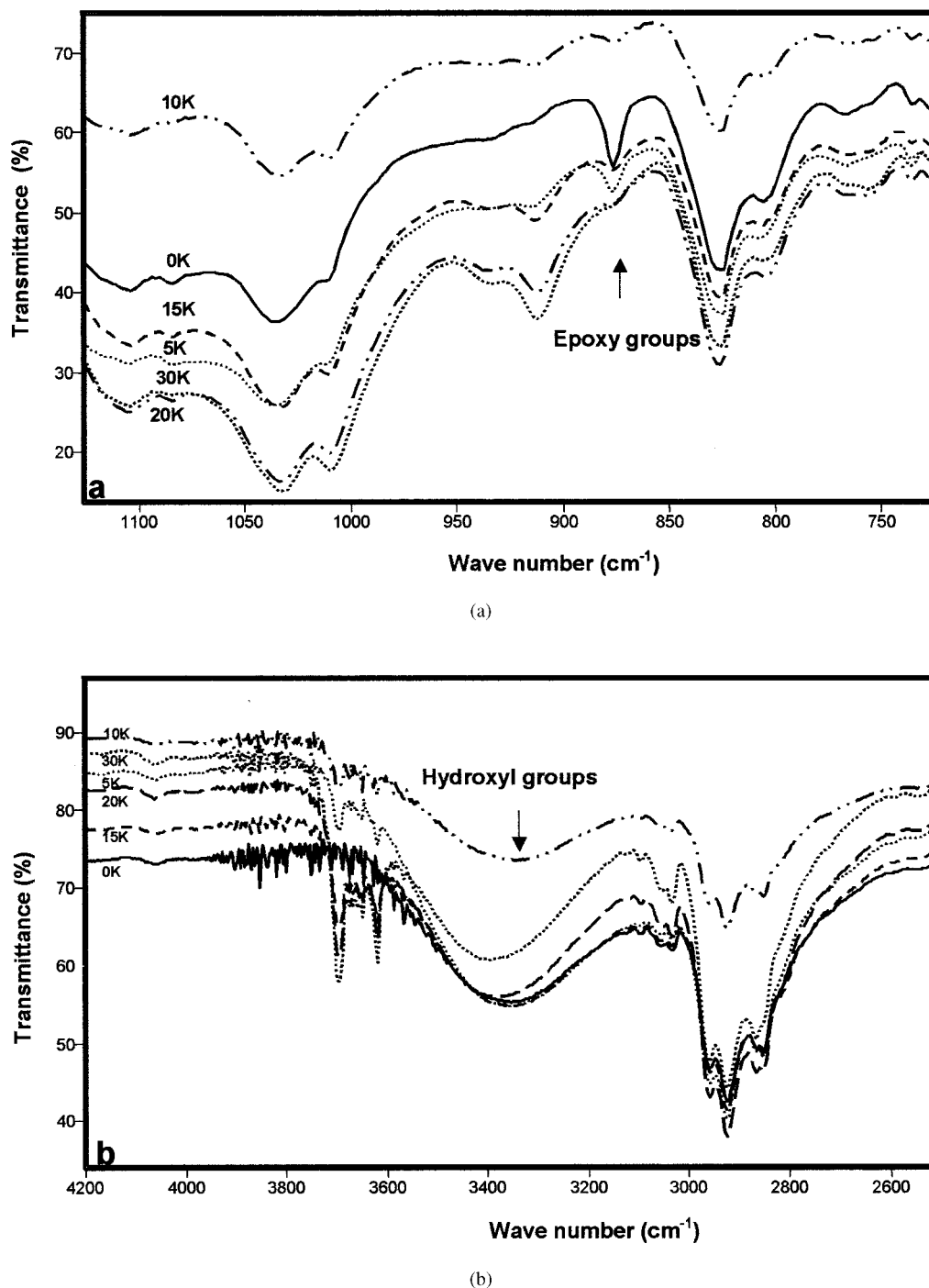


Figure 3 Magnification of the IR spectra of (a) epoxy groups and (b) hydroxyl groups in the epoxy/kaolin/hardener reaction mixture.

($\sim 876\text{ cm}^{-1}$) to that of an aromatic carbon–hydrogen deformation band at 828 cm^{-1} (unreacted group). This ratio was plotted against the kaolin content and is presented in Figure 6.

DSC

Figure 7 shows T_g as obtained from DSC thermograms of the epoxy resin versus kaolin content. Ka-

olin caused a steady decrease in T_g by about 10°C until 15 phr was reached before leveling off. This indicated an incomplete cure at the boundary layer between the filler and the resin. In fact, this further confirmed the IR analysis results that revealed that kaolin addition reduced the reacted parts of epoxy resin while acting chemically and physically to separate the crosslinking points and

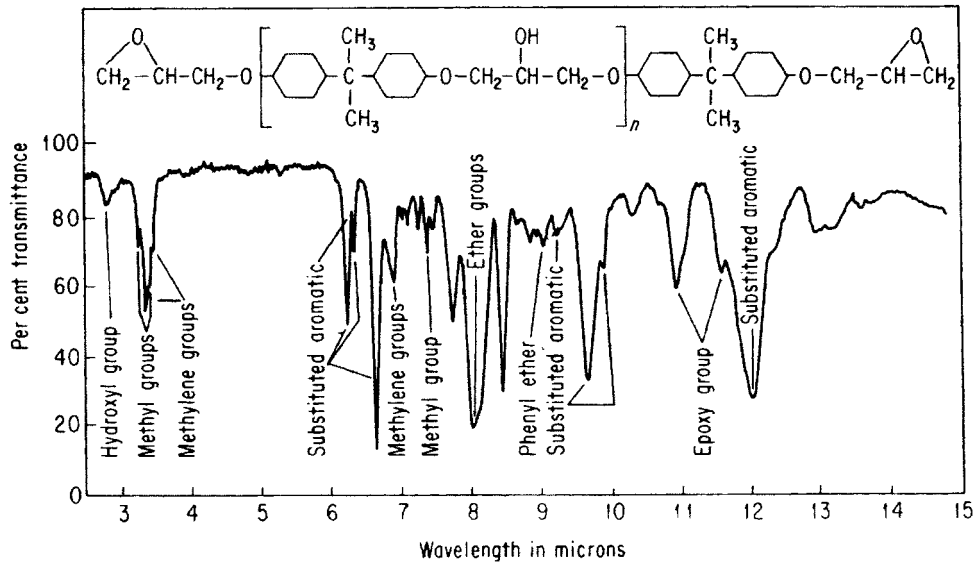


Figure 4 IR spectra of a typical epoxy resin (DGEBA).

decreasing thus either the crosslink density or the matrix T_g . Similar results have been reported elsewhere.⁴²

Mechanical Properties

Tensile Properties

The effect of kaolin content on the tensile properties of the epoxy resin is illustrated in Table IV.

Figure 8 represents the stress-strain curve of both neat resin and the 10-phr-kaolin-modified epoxy resin. An increase in stress at break was observed, accompanied by a decrease in elongation at break. The specimens broke in a brittle manner with no apparent yielding. It is well known that fillers affect tensile properties according to packing characteristics, size, and interfacial bonding.⁴¹

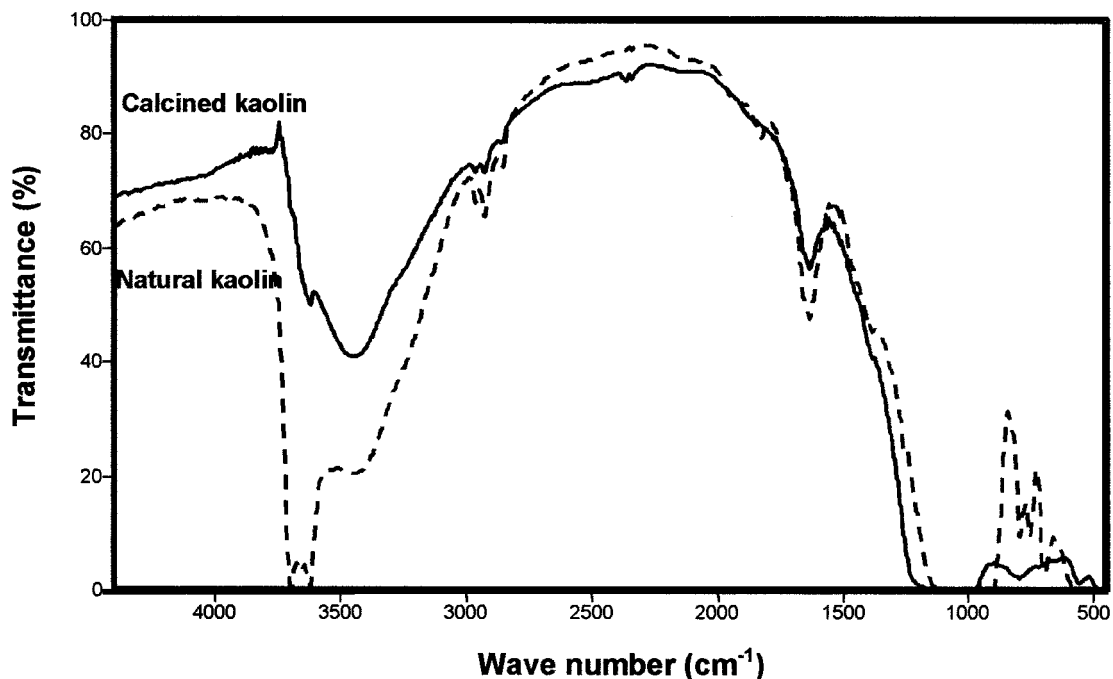


Figure 5 IR spectra of both natural and calcined kaolin.

Table III Kaolin Characteristics

Constituents	Composition (%)
Silicon oxide (SiO ₂)	45.8
Aluminium oxide (Al ₂ O ₃)	33.64
Iron oxide (Fe ₂ O ₃)	1.03
(FeO)	0.27
Calcium oxide (CaO)	1.27
Magnesium oxide (MgO)	< 0.05
Titanium oxide (TiO ₂)	0.11
Phosphor oxide (P ₂ O ₅)	0.15
Sulphur oxide (SO ₃)	0.15
Sodium oxide (Na ₂ O)	0.39
Potassium oxide (K ₂ O)	2.40
Loss on ignition	10.09

As shown in Table IV, the U_B , which was the area under the stress–strain curve, attained a maximum at approximately 10-phr kaolin content, a value at which the toughening reached its maximum. The stress at break, as with the U_B , peaked around a 10-phr kaolin content. The explanation for such a phenomenon may relate to the fact that the matrix was restricted in its ability to stretch between packed particles or around large particles when a critical kaolin content was reached. In our case, the content was 10 phr. Beyond this value, some agglomeration may have taken place and acted as a stress concentrator, causing a decrease in tensile properties associated with dewetting or debonding of the particles from the matrix.

The same arguments hold true for the strain at break; this property decreased with the kaolin content increasing from 3.52 to about 1.35%. The evolution of E as a function of kaolin content is also shown in Table IV. In agreement with many studies,^{2,4–8} E increased when the rigid filler content increased. The modulus increased linearly from 1.85 to about 2.7 GPa with the kaolin content, following the rule of mixture. This might have been caused by the fact that the modulus of kaolin is 10 times higher (20 GPa) than that of the matrix. The addition of these rigid particles might have stiffened the matrix, inducing the observed increase in modulus; in addition, the platelet shape of kaolin might have also contributed to such an increase.⁴¹ It was assumed that the space between the kaolin particles was filled with the matrix, thus minimizing the presence of voids and bubbles and leading, consequently, to an increase in modulus. The shape, the nature of the interface, and the degree of adhesion are generally not very important factors in determining the elastic modulus but are essential in determining both the strength and stress–strain behavior of composites.⁴³

Izod IS

Figure 9 shows the Izod IS of the notched and unnotched specimens as a function of kaolin content. The Izod IS of both notched and unnotched specimens exhibited a bell-shaped curve with a maximum at a 10-phr kaolin content.

Notched samples showed lower values than the unnotched ones. The main reason behind this be-

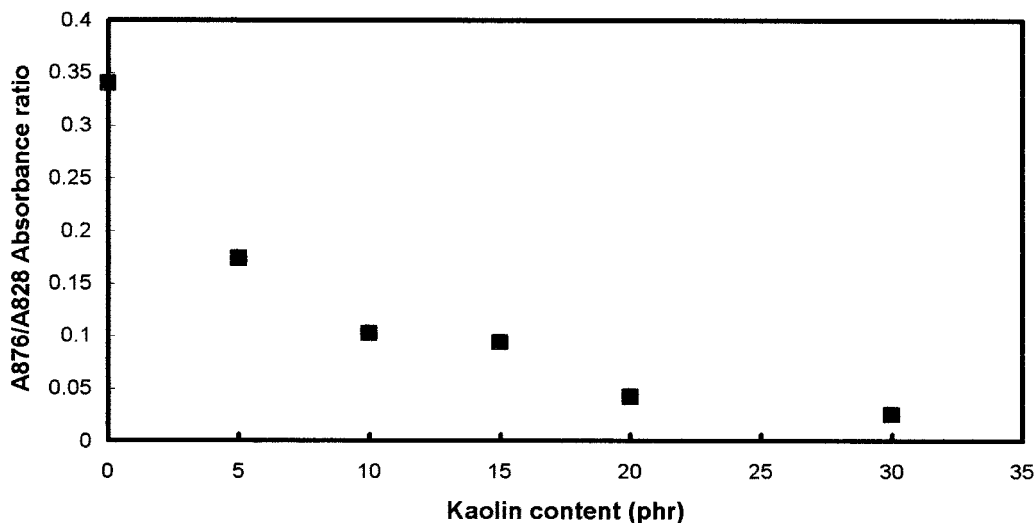


Figure 6 Effect of kaolin content on the absorbance at 876 and 828 cm^{-1} of epoxy resin.

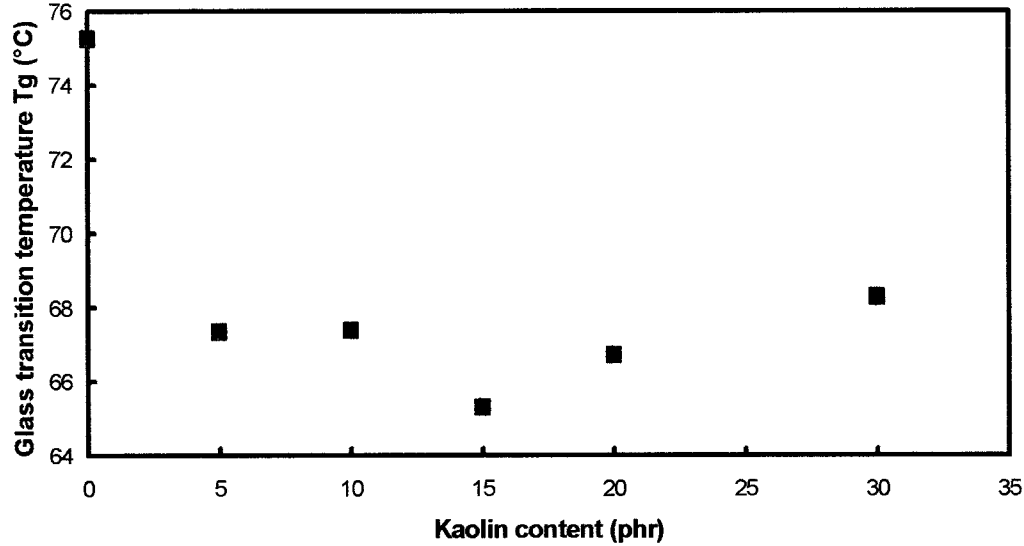


Figure 7 Effect of kaolin content on T_g of epoxy resin.

havior was that notches act as stress concentrators, which lead to a decrease in the IS. Furthermore, the sensitivity of a material to notches is also affected by the fact that fracture is a process that involves both crack initiation and propagation. In notched specimens, an apparent crack is already initiated, so the amount of energy absorbed is dependent primarily on the energy to propagate the crack. However, in unnotched specimens, the energy to initiate the crack is added onto that required for its propagation.

For notched and unnotched specimens, the IS reached maximum values of 1.53 and 8.32 kJ/m², respectively, at 10 phr before decreasing with increased kaolin content. This corresponded to a twofold increase in IS caused by the addition of just 10-phr kaolin compared to the unfilled resin. This further showed the beneficial effect of using kaolin. The formation of air bubbles and voids was practically unavoidable. The voids not only reduced the stress-bearing area but acted as stress raisers, thus initiating cracks. Therefore,

the observed initial steep rise may have been induced by increased kaolin to the resin bond and the filling of the voids in the resin matrix.⁵

At maximum IS values corresponding to the maximum filler packing fraction, the space between particles was supposed to be filled with matrix, and no voids or air bubbles were present. The final decrease was probably caused by the excess of kaolin and insufficient resin content to cover up the voids inherent to the matrix, as already reported by Srivastava and Shembekar⁵. The filler particles were always separated by at least the film of matrix necessary to coat the particles, and residual stresses would increase as the film thickness decreased.⁵ Another factor to consider is the platelet shape of kaolin, which might have affected such behavior. In fact, as long as the critical filler content is not reached, the surface area of contact between the filler and the matrix increases, reaching a maximum (in this study at 10 phr) that corresponds to a saturation of the interface, indicating strong adhesion between

Table IV Effect of Kaolin Content on the Tensile Properties of Epoxy Resin

Kaolin (phr)	E (GPa)	Stress at break σ_B (MPa)	Strain at break ϵ_B (%)	U_B (J)
0	1.85 ± 0.08	34.37 ± 0.81	3.52 ± 0.18	0.85 ± 0.09
5	2.08 ± 0.23	36.94 ± 1.01	3.46 ± 0.15	0.89 ± 0.12
10	2.21 ± 0.18	39.96 ± 0.58	3.34 ± 0.35	0.89 ± 0.12
15	2.40 ± 0.20	38.72 ± 1.74	2.69 ± 0.39	0.64 ± 0.11
20	2.42 ± 0.47	25.50 ± 3.48	1.35 ± 0.12	0.24 ± 0.05
30	2.70 ± 0.20	31.64 ± 2.91	1.60 ± 0.12	0.34 ± 0.05

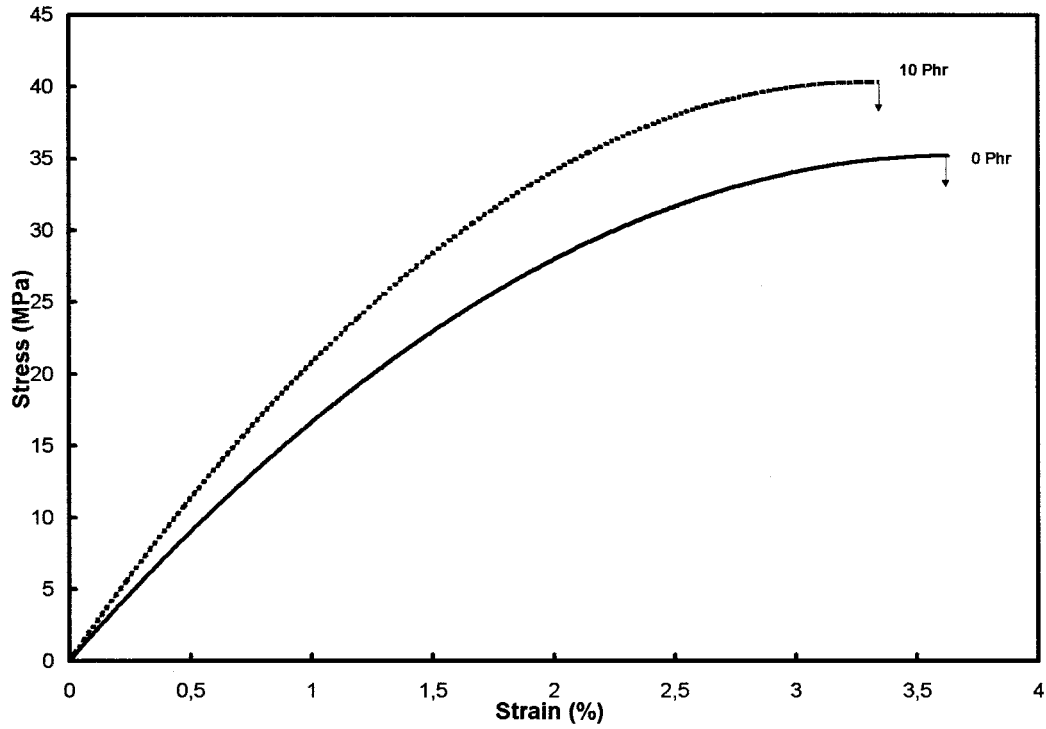


Figure 8 Stress–strain curves of neat epoxy (0 phr) and 10-phr kaolin-modified epoxy.

the filler and the matrix. The IR spectra revealed the occurrence of a chemical reaction between kaolin and the epoxy resin, which led to good interfa-

cial adhesion and resulted in improved IS. The following decrease was probably caused by filler agglomeration, which led to stress concentration.

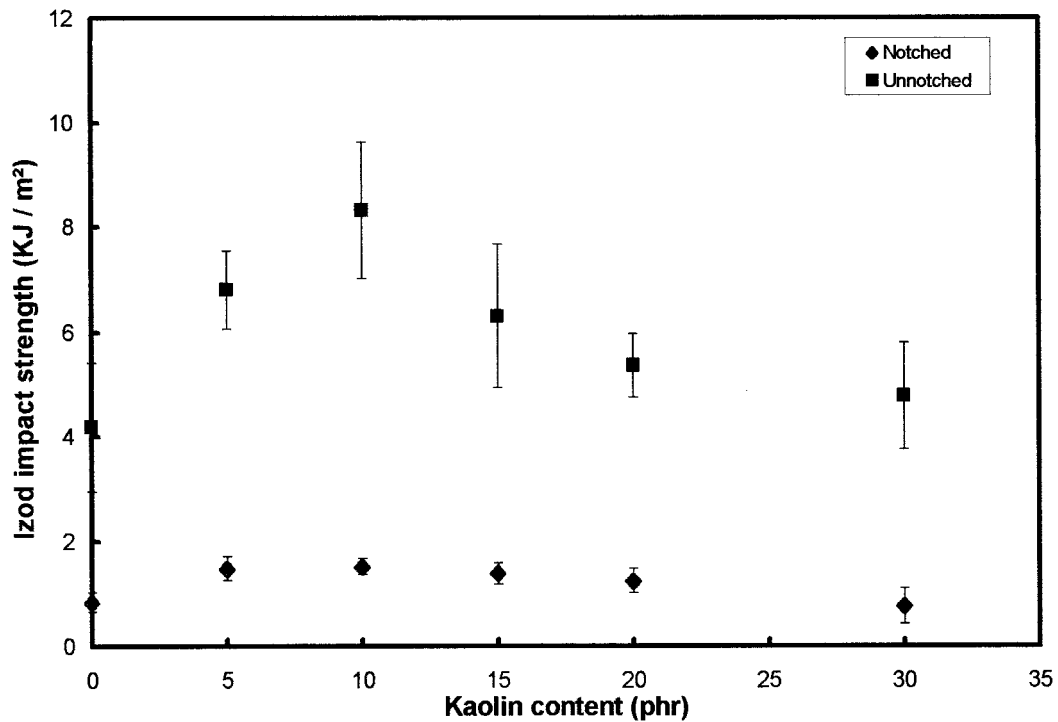


Figure 9 Effect of kaolin content on the Izod IS of epoxy resin.

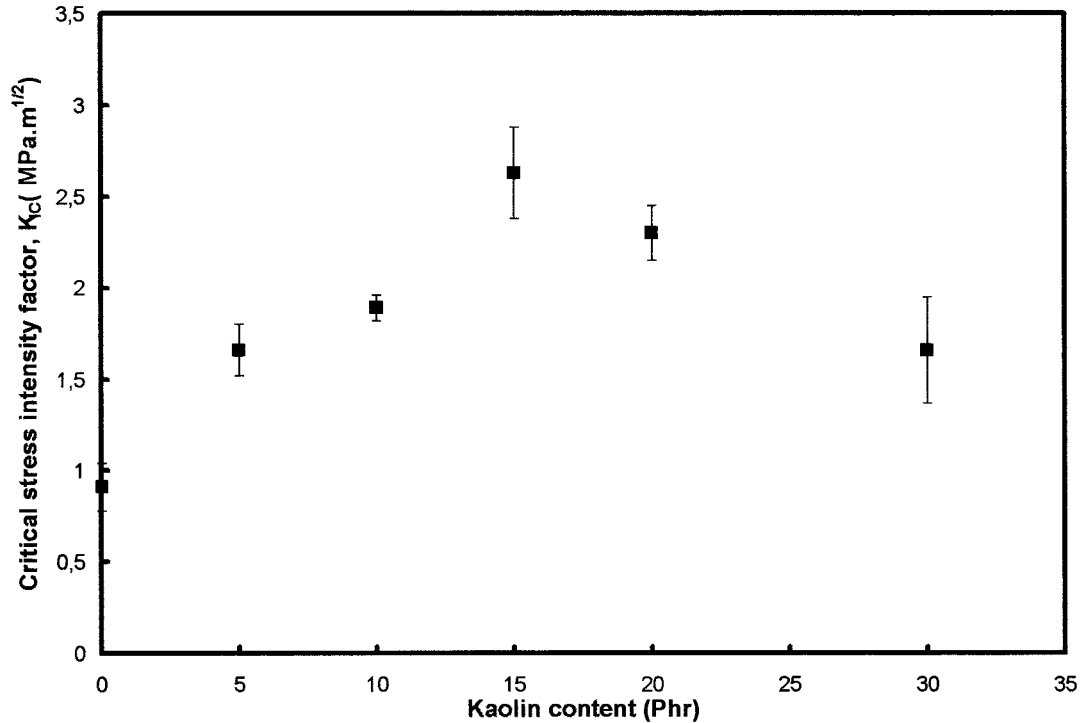


Figure 10 Effect of kaolin content on the K_{IC} of epoxy resin.

Another important finding in this study relates to the drastic difference between notched and unnotched specimens in terms of IS. For the unfilled specimens, the IS reached 4.19 kJ/m², but when notched, a fivefold decrease was observed (0.85 kJ/m²). This ratio remained constant when specimens were filled with 5–30-phr kaolin. Once more, this further confirmed the notch sensitivity of the epoxy resin and the inability of kaolin to affect this behavior, a behavior that might be attributed to the large number of imperfections built already into these materials, including size, particle size distribution, shape, air entrapment, bubbles, and orientation.

K_{IC}

Figure 10 shows the effect of kaolin content on the K_{IC} . A bell-shaped trend was obtained with a maximum at 15 phr. At this level (15 phr of kaolin), a threefold increase in the K_{IC} , from 0.91 to 2.63 MPa m^{1/2}, was observed.

Fellahi et al.³⁷ reported similar results when modifying the same epoxy resin type as a matrix but when using 30 phr of polyurethane with a chain extender as a modifier.

There are a number of possible mechanisms that can explain this phenomenon:

- The toughness may be increased by the rigid filler, diverting the crack and causing a larger surface area of fracture.³
- An increase in toughness may arise from increased plastic deformation of the matrix.³
- The most generally accepted explanation for this behavior was proposed originally by Lange.⁴⁴ He suggested that the augmentation may be caused by the obstacles pinning the crack and causing the crack front to bow out between the particles. In fact, SEM analysis seems to support this mechanism [Fig. 12(d), shown later] in addition to some localized plastic shear yielding caused by the presence of kaolin particles.

The decrease in toughness that occurred at concentrations greater than 15 phr might have been caused by the fact that the contribution from the pinning process became lower than the reduction induced by the loss of toughness in the matrix because of the excess of kaolin.⁵

A trend similar to that for IS was observed, except that the maximum was reached at 10 phr. This difference might be attributed to the fact that the tests were done under different conditions. K_{IC} was realized at a relatively low speed, whereas the impact was done at a high speed. In

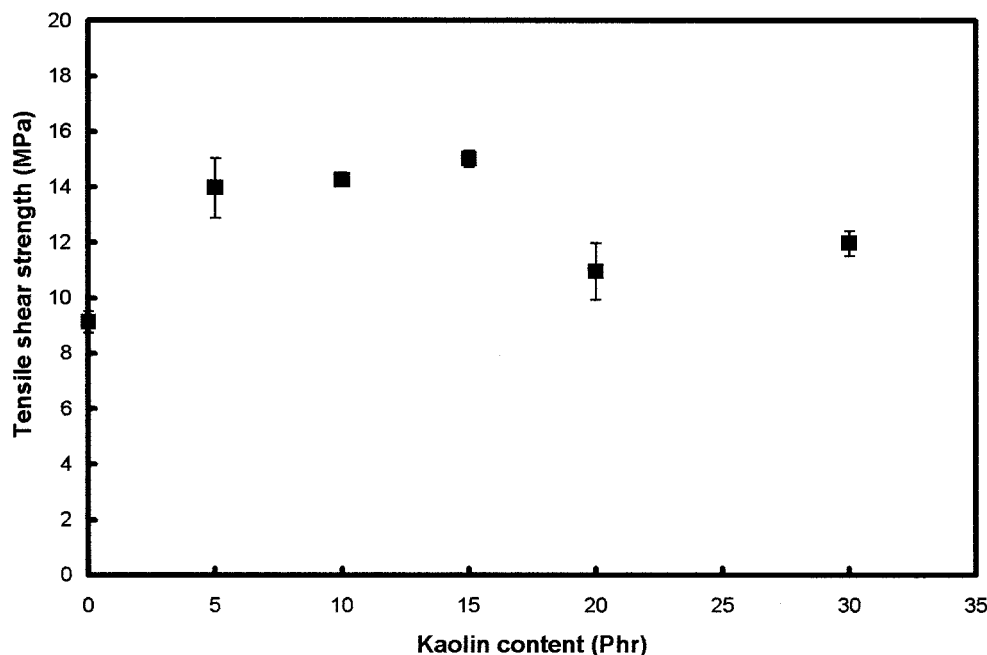


Figure 11 Effect of kaolin content on the TSS of epoxy resin.

other words; when tested at a high speed (impact), the molecules would not have had time to relax or respond to this type of loading, and consequently, only a small amount of filler could be tolerated, whereas a higher filler loading could be tolerated when molecules were tested at a slow speed.⁴⁵

Adhesive Properties (TSS)

Figure 11 shows the TSS of the epoxy resin as a function of the kaolin content at room temperature. The introduction of kaolin led to an increase in the TSS of epoxy resin; in fact, the greatest efficiency (60%) was achieved by the introduction of 15 phr of kaolin. The most probable mechanism is that kaolin, by reducing shrinkage, was particularly effective in increasing the adhesive strength of epoxy resin in addition to the chemical reaction between epoxy and kaolin.¹

This validated the results of tensile, impact, and K_{IC} testing, where the maximum was between 10- and 15-phr kaolin content, depending on the testing conditions. This means that the improvement of the matrix properties led to an enhancement of its adhesive properties. However, beyond 15 phr of kaolin, a decrease in adhesive properties was observed. This might have been caused by a decrease in the degree of cure and an increase in resin viscosity, which led to poor wetting of the substrate and resulted in poor adhesion.

Five parts per hundred resin of kaolin is a sufficient amount to give maximum adhesive properties (14 MPa). When economic considerations are important, 15 phr of kaolin gives the same performance (15 MPa).

It was reported¹ that a general purpose epoxy resin adhesive, containing 14 phr of fine mica, gave a tensile lap shear of 16.3 MPa with an aluminum-to-aluminum bond, whereas a talc-modified epoxy resin yielded the same strength at a much higher loading (60 phr) compared to the unfilled resin with a lap shear strength of 7.1 MPa.

Fractography

Figure 12 shows the micrographs of impact-fractured samples of neat epoxy resin [Fig. 12(a)], 5 and 10 phr of kaolin at 1000 \times [Fig. 12(b, c)], 5 and 10 phr of kaolin at 1000 \times taken at specified positions [Fig. 12(d, e)], and 15 phr of kaolin at 1000 \times [Fig. 12(f)].

As far as the neat epoxy resin is concerned, a typical profile for epoxy resins was evident, exhibiting fine lines that emanated mainly from the crack-initiation region [Fig. 12(a)]. These lines extended approximately along the crack-propagation direction and were associated with the point of arrest of the crack front. The surface was very shiny and very smooth, indicating brittle behavior. Similar results have been reported elsewhere.^{15,37}

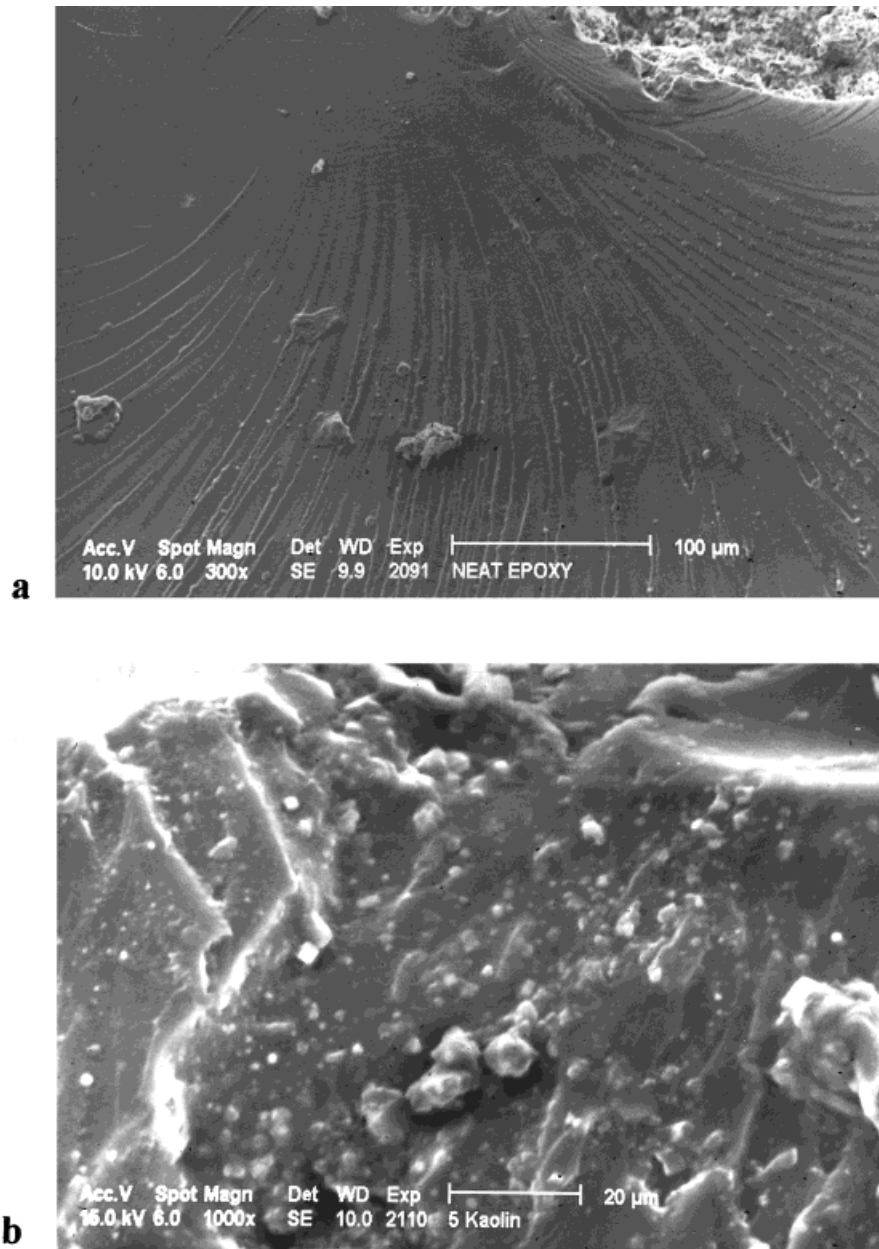


Figure 12 Micrographs of impact-fractured surfaces of (a) neat epoxy resin (300 \times), (b) epoxy/5-phr kaolin (1000 \times), (c) epoxy/10-phr kaolin (1000 \times), (d) epoxy/5-phr kaolin (1000 \times) at a critical position, (e) epoxy/10-phr kaolin (1000 \times) at a critical position, and (f) epoxy/15-phr kaolin (1000 \times).

The fractured surfaces of kaolin-modified epoxy resin are shown on Figure 12(b–f). Figure 12(b, c) shows views of 5- and 10-phr-kaolin modified samples at the same magnification (1000 \times), respectively. Both samples exhibited similar fracture surfaces. It has to be mentioned that at 10 phr of kaolin, a much denser structure was observed; this was attributed to the excess of kaolin. For both concentrations, a homogeneous structure was observed with the presence of kaolin

particles firmly attached to the matrix. This was an indication that good interfacial adhesion was established between the matrix and the filler, which resulted in an increased toughness. The incorporation of kaolin reduced the degree of cure, as shown by the reduction in T_g , and somewhat improved the toughness. Figure 12(d) was taken close to, whereas Figure 12(e) was taken opposite to, the notch area, and both show the presence of some whitening, which is an indication of a plas-

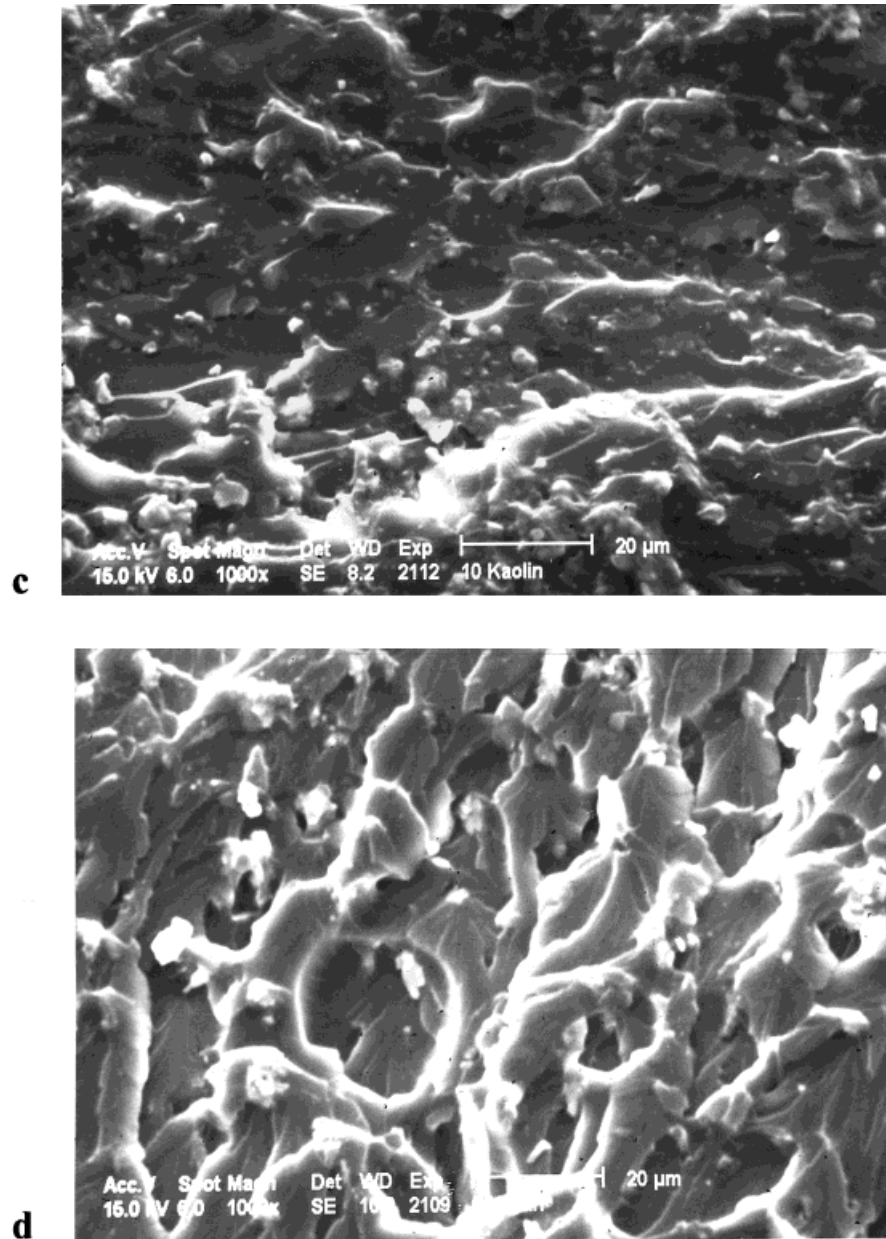


Figure 12 (Continued from the previous page)

tic deformation. At 5 phr [Fig. 12(d)], some crack pinning had taken place, diverting each time the crack propagation, hence, the increase in toughness. This further confirmed the improvement in IS as reported earlier. At 10 phr [Fig. 12(e)], the presence of a greater number of small holes was observed that might have acted as stress concentrators and led to localized plastic shear yielding. This went along with the results of tensile properties, IS, and K_{IC} . Similar results have been reported in the literature.^{3,15}

The fractured surface of 15-phr-kaolin-modified epoxy resin is shown in Figure 12(f). Loose

kaolin particles are clearly seen. Localized smooth-fracture surfaces similar to those of neat epoxy, in addition to the appearance of some holes acting as stress concentrators, might have been responsible for the brittle failure in accordance with the impact results.

The most probable mechanism of deformation occurring was through localized plastic shear yielding induced by the presence of kaolin as the origin of some crack pinning. The presence of kaolin hindered the degree of cure, reducing the matrix brittleness and, consequently, resulting in a tougher matrix.

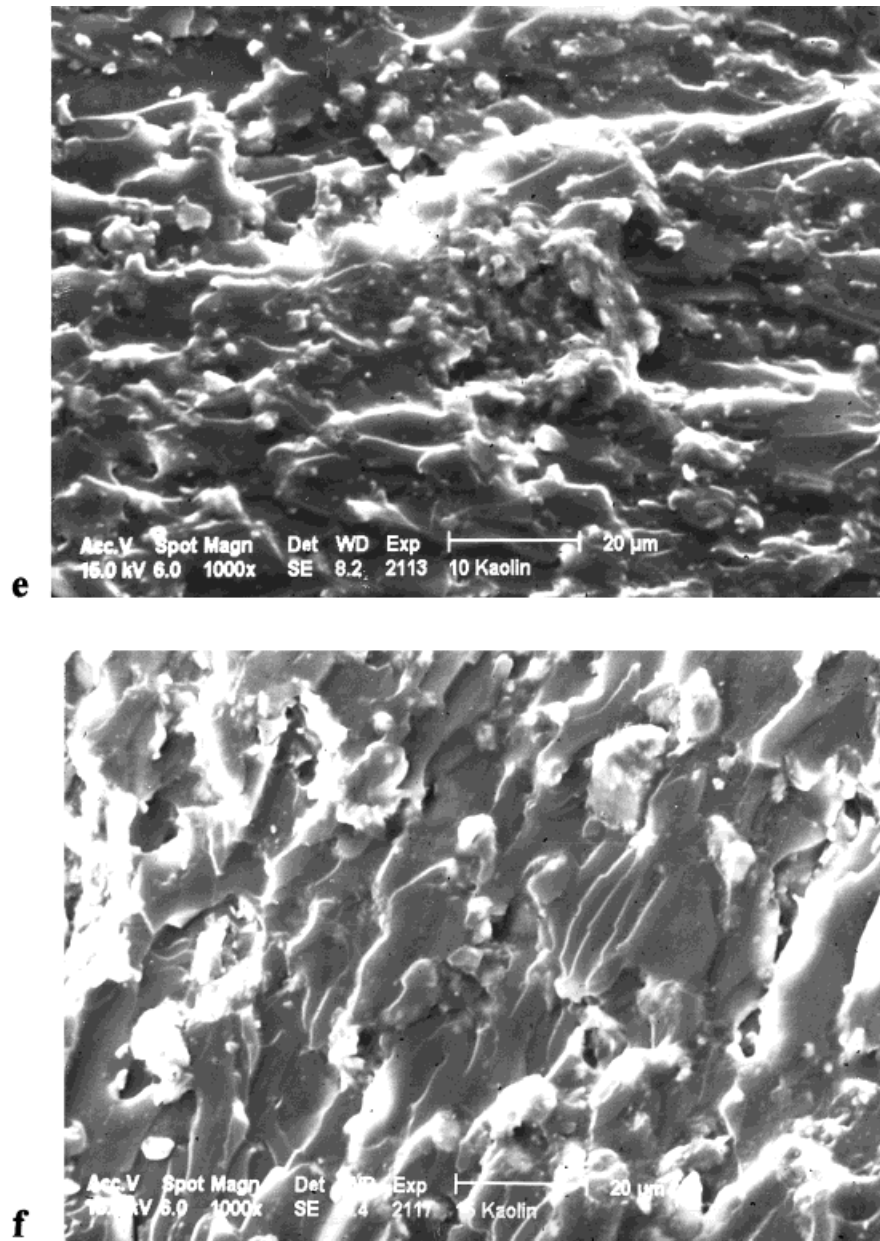


Figure 12 (Continued from the previous page)

CONCLUSIONS

Based on the results obtained and discussed previously, the following conclusions may be drawn: The addition of kaolin to neat epoxy seems to affect the curing parameters, namely, by decreasing the gel and cure times and the cure temperature. The kaolin and the epoxy react chemically, leading to a decrease in the crosslink density and lowering T_g . Most of the tensile properties are found to reach a maximum at approximately 10-phr kaolin content, a value at which the toughen-

ing reaches its maximum and the modulus increases linearly from 1.85 to 2.7 GPa with increasing kaolin content. For both notched and unnotched specimens, a twofold increase in Izod IS is obtained by adding just 10 phr of kaolin (1.53 and 8.32 kJ/m²) compared to the unfilled resin (0.85 and 4.19 kJ/m²). The K_{IC} varies from 0.91 to 2.63 MPa m^{1/2} (a threefold increase) with increased kaolin content. At 15 phr of kaolin, the TSS reaches a maximum value of 15 MPa. SEM analysis reveals that the prevailing toughening mechanism for the epoxy resin under consider-

ation is through localized plastic shear yielding induced by the presence of kaolin particles associated with crack pinning.

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