Preparation and Mechanical Properties of Thick Interlayer Composites

DENNIS G. PEIFFER* and LAWRENCE E. NIELSEN,

Monsanto Company, St. Louis, Missouri 63166

Synopsis

A technique is described for producing a thick interlayer composite material composed of an epoxy resin as the matrix and an acrylic-coated fiberglass filler. Through the use of electrostatic forces, the fibers are encapsulated with a controlled, uniform layer(s) of the rubbery acrylic polymer. This coating is then crosslinked. These fibers are subsequently placed into the epoxy matrix, whereby the interfacial properties of the composite become modified. Rapid diffusion of the resin and curing agent results in an interpenetrating network being formed at the glass–epoxy interface. The placement of a uniform latex coating on the fiberglass surface results in improvements in the mechanical properties of the composite. Increases in damping, impact strength, and tensile properties are described.

INTRODUCTION

Modification of the glass–matrix interface in reinforced polymeric materials has resulted in improvement of the mechanical properties of fiberglass composites. The properties of composite materials are varied by tailoring the properties of the interfacial region[1-7] located between the matrix resin and the reinforcing material. Kardos et al.[3] have shown that significant increases in modulus and strength of graphite reinforced polycarbonate materials can be enhanced by a high-temperature annealing scheme. The annealing process allows a partially crystalline layer to be formed adjacent to the fiber surface. This permits a pathway for the effective transfer of stresses in all parts of the composite from fiber to fiber across the resin–glass interface under loading conditions. Speri and Jenkins[4] in their investigation of the effect of fiber–matrix adhesion on the properties of ABS, concluded that the composite's impact strength varied inversely to the fiber–matrix adhesion and that the tensile strength decreased as the adhesion between the two phases decreased. Parallel to these experimental results, Broutman and Das Aggarwal[5] theoretically showed that the toughness of a composite material can be maximized by controlling the interface modulus.

An important factor that generally has not been studied extensively in regard to the properties of composite materials is the thickness of the interface. Chemisorbed polymerized silane coupling agents form a 5–10 monolayer equivalent thick coating on a fiberglass surface,[6] whereas incorporation of a resin interlayer can result in thicknesses of up to several mils. These various coatings can be applied to the glass surface by several methods, the most important being dipping[3] and spraying.[8] The thickness of the coatings that result from these

* To whom correspondence should be sent. Present address: Exxon Corp., 1600 E. Linden Ave., Bldg. 8, Rm 208A, Linden, N.J. 07036.

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methods is dependent on such variables as solution concentration, solution viscosity, and solvent evaporation rate. As noted by Kardos et al.,[2] the thickness of the interlayer has a pronounced effect on composite properties.

It is the purpose of this work to study the feasibility of placing a uniform polymeric coating of a predetermined thickness on the surface of fiberglass and, if that is possible, to determine its effect on the mechanical properties of a composite. The method that was chosen for the preparation of the polymer coating(s) is a procedure originally developed by Iler.[9,10] Alternate layers of positively and negatively charged colloidal particles can be deposited from sols onto a smooth glass surface utilizing a simple dipping procedure.[10]

Iler's method[10] is based on the fact that the surface of glass is anionic and that oppositely charge particles (ions, polar molecules, latices) will be attracted to this surface. After a monolayer is formed, further deposition is inhibited by electrostatic repulsion. By this means a monolayer of a controlled, uniform thickness can be built up. Multiple layers can be formed by placing between each latex deposit, a layer of oppositely charged particles. This method was so successful, in fact, it was used to study the size of particles less than 35 nm thick.[10]

One disadvantage that is noted[10] is that the films could be easily removed by simply rubbing a piece of absorbent tissue over the surface. This as we shall see can be overcome by depositing a rubbery latex monolayer(s) onto a glass substrate, drying into a film, and subsequently, crosslinking.

EXPERIMENTAL

Iler's method[10] for the placement of colloidal particles onto a glass surface is relatively simple. Starting with a clean glass surface, the first step is to deposit a layer of a positively charged material on it. This is accomplished by dipping the glass into a 0.5% aqueous solution of an appropriate surface charge-reversing agent (described later). The glass is subsequently removed, rinsed under distilled water, and air dried. This glass is then dipped into a 5% latex solution, the pH of which was adjusted to 2. Again the glass is rinsed under a stream of distilled water and air dried. The temperature at which the entire coating process takes place is 25°C. Distilled water was used in all solutions. After air drying, the acrylic-coated fibers were heated in an air circulating oven for 20 min at 155°C.

Several substances that reverse surface charge were tested (example: hexadecyltrimethylammonium chloride) but most failed to give a uniform latex coating, presumably because these substances are quite soluble in water. Their coatings cannot survive the vigorous rinsing step. A colloidal alumina* was found to be a very effective surface charge-reversing agent, allowing a uniform latex coating to be placed upon the glass surface.

A cross-sectional view of the deposition of the latex particles (L) onto a glass surface (G) and then film formation upon drying is shown in Figure 1. The anionic charge on the uncoated glass surface was reversed using colloidal alumina (Baymal). The colloidal alumina (B) consists of fibrils of AlOOH having a diameter of approximately 5 nm.[9] Deposited upon the alumina is the monolayer latex coating, which upon drying produces a polymer film with a thickness that

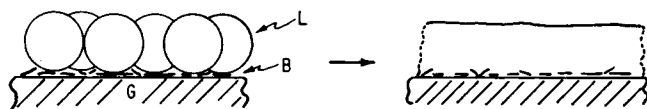* "Baymal" E. I. duPont de Nemours & Co. trademark for colloidal alumina.

Fig. 1. Schematic cross section showing the formation of a monolayer latex film; G is the glass substrate; B is the colloidal alumina layer; L is the latex layer.

approximates the diameter of the latex particles (100 nm). Multiple layers (i.e., thicker latex coatings) of latex can be formed by alternating the layers with the oppositely charged species.

The chopped strand fibers (Owens Corning 832DC, epoxy compatible) were $\frac{1}{4}$ in. in length, each strand being composed of filaments about 6 nm in diameter. The sizing that was on these fibers was eliminated by burning in a high-temperature oven at 600°C for 30 min so as to expose the anionic glass surface. No attempt was made to study their surface chemistry. These fibers were subsequently placed in the appropriate coating solutions as previously described.

The latex solution consisted of a self-crosslinkable acrylic polymer (Rohm and Haas Rhoplex HA-8). The T_g of the acrylic material is -14°C.

A measured amount of the coated fibers was placed into a mold. An epoxy resin consisting of a matrix resin (Epon[†] 815) and the curing agent triethylenetetramine (TETA) in the ratio of seven parts resin to one part curing agent was poured over the random arrangement of fibers in the mold cavity. The mold was then placed into a vacuum oven at 60°C in which degassing of the material took place for 20 min. A cure cycle of 24 hr at 25°C and then at 60°C for 24 hr was used. The tensile specimens were cast from a 4×4 in.^{2} Teflon mold. The thickness of this mold was 0.125 in. The samples for tensile testing were machined using a carbide burr. The dimensions of these specimens were $\frac{1}{2} \times \frac{5}{2}$ in.^{2} conforming to ASTM (D-638-647). Tensile properties were measured on an Instron Testing Machine at a crosshead speed of 0.1 in./min.

The notched Izod measurements followed the procedure of ASTM-D256.

In order to eliminate the need for burning off the silane coating from fiberglass, a cationic-sized fiberglass sample was obtained. The sample was kindly supplied by Owens Corning (designated as 2219-194-4). An initial latex monolayer can be placed directly onto the glass surface without first placing a colloidal alumina (Baymal) surface coating on. However, the procedure for placing a multilayer latex coating on the surface follows the recipe previously described.

A slightly different composite preparation was followed for the cationic 2219-194-4 fiberglass. The mixture of matrix resin and coated fiberglass were degassed in a stainless-steel mold at 60°C. The mold cover and appropriate spacer were then put into place. This was then compressed in a heated Carver press (100°C) for 4 hr. The epoxy–fiberglass composite was cooled in the mold, then taken out and machined to the ASTM specifications.

A Toyo Rheovibron DDV-III-C was used to measure the dynamic mechanical properties of the composites. The damping characteristics (tanδ) were obtained from -80°C to about 140°C at a frequency of 11 Hz.

Electron micrographs of fracture surfaces were obtained from a Cambridge scanning electron microscope. All samples observed under the scanning electron microscope were coated with a 150 Å gold film utilizing a Polaron specimen coating unit (Model No. E5100 series II sputter coater).

[†] "Epon," Shell Chemical Corporation trademark for epoxy resins.

Coating Uniformity and Continuity

Electron micrographs (shown in Fig. 2) were obtained on 3-mil-diam "E" glass (supplied by DeBell and Richardson) in order to confirm that a uniform, continuous acrylic film could be placed on a glass surface utilizing Iler's method.[10] Figure 2(a) shows the surface of the virgin glass that was thoroughly washed in distilled water. The surface is composed of many irregular shaped protrusions of various sizes. A wide distribution of sizes is apparent. These protrusions remained on the glass surface even when washed in a hot acidic bath. In Figure 2(b) is shown the results of Iler's coating procedure[10] using colloidal alumina and acrylic latex. The many smaller sized bulges have been essentially buried under the acrylic film. The smaller number of larger bulges are covered by the latex but still can be seen to protrude from the surface.

Micrographs obtained at a lower magnification substantiates that the coating is quite uniform over the entire fiber surface. Up to the present time, it was difficult to get a uniform polymeric coating with a predetermined thickness on a solid surface without forming agglomerates. (See, for example, Ref. 11.)

Estimation of the coating thickness can be determined by burning off the coating in a high-temperature oven at 600°C for 60 min. The weight loss as measured by a Sartorius balance (accurate to 0.0001 g) is assumed to be due primarily to the coating. Calculation of the average coating thickness can easily be completed after this measurement. The results indicate the original silane coatings are about 275 Å thick, while each latex layer is about 1000 Å thick.

Matrix-Interlayer Interaction

Before placing the latex-coated fiberglass strands into a polymeric matrix, it is of interest to ascertain whether the polymer matrix "interacts" with it. The type of interaction that would be of concern here is to determine if the two components of the epoxy resin swell the crosslinked acrylic coating. Shown in Figure 3 are the results of placing several thin (~1 mil) acrylic films into each of the components of epoxy matrix. The average weight increase was measured

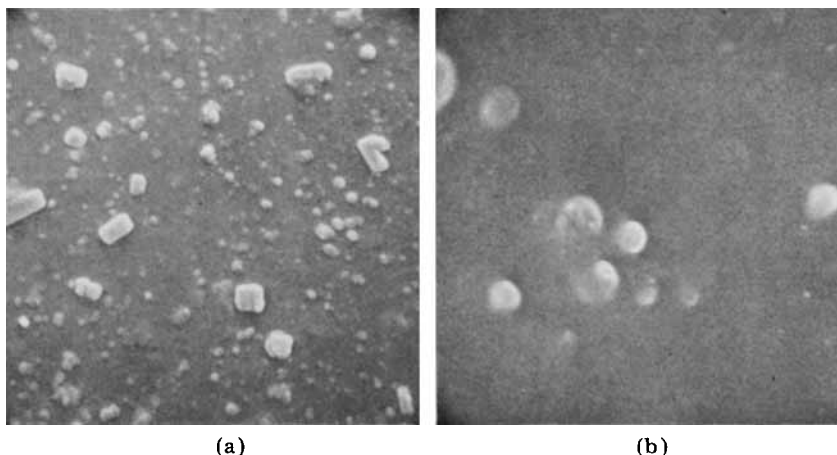(a)   (b)

Fig. 2. Scanning electron micrographs of the surface of untreated and latex treated fiberglass: (a) no latex coating, (b) one monolayer latex coating, 10,000×.
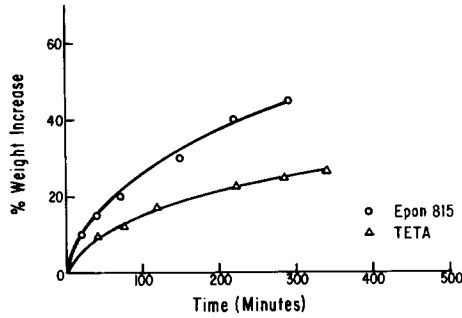
Fig. 3. Absorption (represented as the % weight increase) of Epon 815 and TETA (curing agent) into the crosslinked acrylic film as a function of time.

as a function of time. Both components swell the films considerably with the largest increase found with Epon 815. In each case, a large weight increase (due to swelling) is found at short times, while at longer times the weight increase begins to level off.

Good adhesion between the interlayer and epoxy matrix would be expected because of this diffusion. This is due primarily to the interpenetrating polymer networks (IPN) formed between the crosslinked acrylic system and the cross-linked epoxy system. Enhancement of mechanical properties due to such interpretation has been observed for these systems.[12]

Evaluation of Mechanical Properties

The tensile properties and impact strengths of the various composites (using 832DC fiberglass) are shown in Tables I and II, respectively. In all cases, the modulus (E), elongation ($\Delta L/L_0$), and the breaking stress (σ) are a function of the volume fraction (V/O) of the reinforcing fibers. It should be noted that the word uncoated implies that the original coating was burnt off exposing the glass surface. The designation 832 DC implies the as-received coated fibers, while the latex-coated fibers are fibers with the original coating burnt off and replaced with a mono-latex acrylic coating.

Embedding uncoated fibers into the epoxy matrix has a deleterious effect on the tensile properties as compared to the unreinforced matrix, only the modulus

TABLE I
Effect of Innerlayer on Composite Properties

Composite	V/O	E (psi $\times 10^5$)	$(\Delta L/L_0)_{Break} \times 10^2$	σ_{Break} (ksi)
Matrix	—	3.2	1.0	10.
Uncoated fibers	10	3.84	0.48	5.9
Uncoated fibers	20	5.16	0.47	9.2
Uncoated fibers	30	7.0	0.43	12.6
832 DC fibers	10	3.52	2.0	13.0
832 DC fibers	20	4.16	1.95	14.3
832 DC fibers	25	4.48	1.87	15.1
Latex coated fibers	10	3.2	1.7	8.1
Latex coated fibers	20	4.16	1.82	8.7

TABLE II
Izod Impact Measurements

Sample	Ft lb/in.
Unreinforced	1.00
10% (uncoated)	0.80
20% (uncoated)	1.00
10% (832DC)	3.4
25% (832DC)	5.6
10% (latex coated)	2.4
20% (latex coated)	4.0

is found to increase significantly. The coated fibers, however, produce composites with improved properties. The addition of an interlayer to the surface of fillers has increased stress–strain levels. The improved elongation arises from alteration of the matrix resin in the interfacial region. This parallels the observations of Kenyon and Duffy[13] in which they found that the ultimate elongation of glass-bead-filled epoxy composites can be increased by altering the matrix resin in the vicinity of the interface. The toughness of such systems also can be increased by coating the beads with a thin layer of flexible epoxy prior to casting of the composite.[3]

Table II shows the effectiveness of the coated fibers in dissipating the energy of an impact. Increases in impact strength are observed in composites containing coated fibers. For example, the 25% 832 DC material has an impact strength of 1.4 ft lb while the 20% latex coated fiber material has a value of 1.0 ft lb. The 20% uncoated fiber composite impact strength is 0.25 ft lb. Plueddeman,[14] for example, applied a thin rubbery layer at the interface of a glass resin composite and found marked improvement in toughness and strength. A laminate with a rubbery coating deposited from a 1% toluene solution on a silane-treated glass had an impact resistance 2.5 times greater than that obtained with only silane treated glass, and with only an 11% reduction in strength.

One should note that the addition of uncoated fibers to the epoxy matrix does not increase the impact strength, in fact, may even decrease it. One reason for this is probably due to the weakening of the fibers by the high-temperature removal of the 832 DC coating.

The need for burning off a nonionic-sized fiberglass sample can be eliminated by using a cationic-sized glass specimen such as the 2219-194-4 material. Presented in Table III are the impact strengths of several composites that have varying interlayer thickness (placed over the original cationic size). One should note that the impact values are a function of the coating thickness. Up to two latex layers an increase in impact strength is observed, while with greater than two layers a decrease is found. In all cases studied, the latex-coated fiberglass composites have greater impact resistance than an uncoated fiberglass material.

These points are clearly brought out in Figure 4 in which are shown the impact strengths of these composites as a function of interlayer thickness (see also Table III). The impact values intersect the ordinate at the impact strength of the unsized (and uncoated) fiberglass composite.

It is of interest to compare these impact values with that obtained from the cationic-sized fiberglass (2219-194-4) composite. As stated previously, the

TABLE III
Composite Impact Strength as a Function of Interlayer Thickness

Number of latex layers[a]	Notched Izod impact strength[c] (ft lbs)
0[b]	0.30
1	1.08
2	1.84
3	1.55
4	1.32

[a] A single layer of latex is approximately 1000 Å thick.
[b] Zero layers of latex implies that the fiberglass used in the composite was uncoated or unsized.
[c] The composite contained 30 V/O fiberglass.

thickness of this coating is about 275 Å. The impact strength is found to be 1.62 ft lb. Therefore, it seems that the silane coating has little effect on the impact strength whenever it is coated over by the rubbery interlayer. In other words, the impact properties of the rubbery interlayer composite is essentially controlled by the thickness of the latex interlayer.

Furthermore, Buchnall and Smith[15] have observed in their studies on rubber-toughened plastic materials that the T_g of the elastomeric phase has a significant effect on impact properties. The rubbery phase must have a low enough T_g so as to remain elastomeric at the testing temperature and at the specific loading rate. For an increase in the impact to occur, the elastomeric phase must be able to relax even under the very high loading rates found in an impact test. Increases in the impact resistance of a thick interlayer composite (as compared to those in Table III) would be expected if the T_g of the rubbery interlayer was lower.

Damping Characteristics

The interaction between macromolecules in the solid state can be conveniently studied utilizing dynamic mechanical methods. These measurements are quite sensitive to changes in the environment that are experienced by polymer chains.[16,17] An example of this effect is the shifts in the glass transition temperature T_g of two compatible polymers that are blended together. These
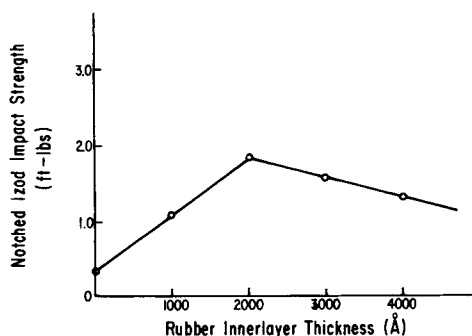

Fig. 4. Notched Izod impact strength of a 30 V/O fiberglass composite possessing varying interlayer thickness.

changes in T_g, as compared to the unblended polymers, indicates a certain degree of mixing (interaction) has taken place.

Presented in Figure 5 is the loss tangent (tanδ) as a function of temperature of two composite materials containing fiberglass coated with a rubbery interlayer of definite thickness. For comparison the results obtained from the composite containing no interlayer (zero latex layer) is included. In all cases the T_g of the epoxy matrix (at about 105°C) does not shift as the thickness of the interlayer is increased. It should be noted that by increasing the interlayer thickness, one increases the amount of rubber in the composite. The low temperature relaxation that occurs between −40 and −50°C is unaffected by the presence of rubber.

The magnitude of both transitions are approximately identical within experimental error. These observations indicate that the acrylic rubber and the epoxy resin have phase separated even though a significant amount of both the epoxy resin and curing agent diffused into the crosslinked rubber (see Fig. 3). In essence the IPN at the glass interface is composed of two separate phases interlocked together.

A broad damping range is observed between T_g and −10°C. The magnitude of this damping is a function of the interlayer thickness; that is, the thicker the interlayer the higher is the tanδ value. The increase in damping is not a linear function of the interlayer thickness. This is probably due to the fact that a finite amount of time is needed for the epoxy resin and curing agent to diffuse through the rubber before a significant amount of crosslinking occurs. The thicker the interlayer, the longer the time it takes for the diffusing species to reach the glass surface. Therefore, a concentration gradient of the crosslinked epoxy matrix is expected through the rubbery interlayer. This, in turn, would produce a gradient in the crosslink density. The higher crosslink density being at the outer surface of the interlayer. A more uniform structure would be expected in the
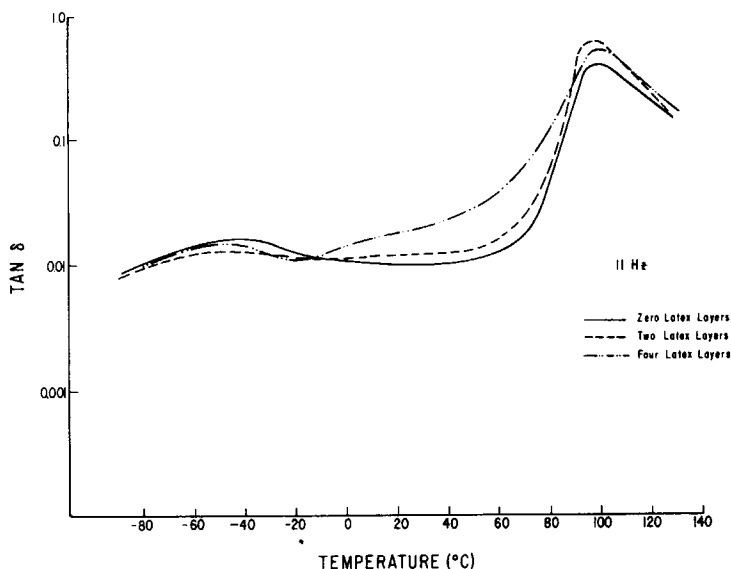

Fig. 5. Damping properties vs temperature of several composite materials containing rubbery interlayers of varying thickness.

interlayers that are thin (e.g., two latex layers). The magnitude and broadness of the damping range can be attributed to this gradient phenomena.

Scanning Electron Microscopy

The fracture surfaces that resulted from the Izod impact measurements were examined utilizing the scanning electron microscope. Significant differences were revealed in the fracture behavior of the uncoated fiberglass composite (Fig. 6) and those composites containing a coupling agent (832 DC), (Fig. 7) or a rubbery acrylic interlayer (Fig. 8). In Figure 6 a magnified view of several individual fibers shows that failure occurred at the glass/resin interface with patches of epoxy resin adhering to the glass surface. This is fracture behavior typical for a brittle matrix composite material.[19] The low impact strength of this composite
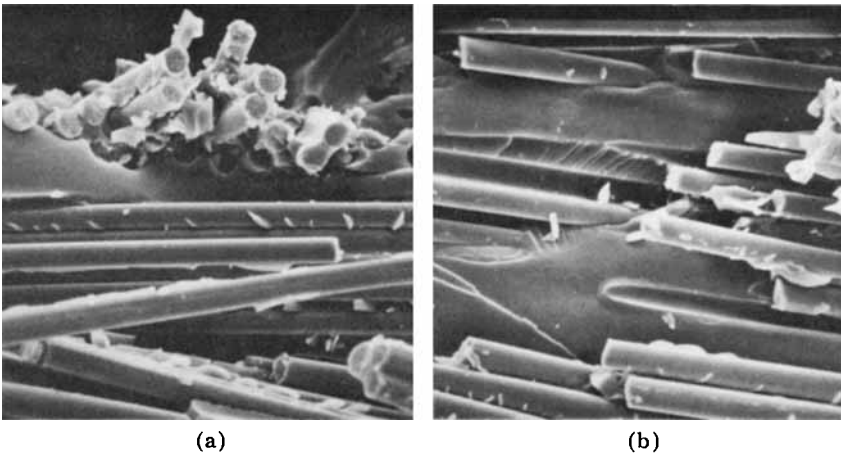

(a)   (b)

Fig. 6. Scanning electron micrographs showing two views of the fracture surface of an uncoated fiberglass-epoxy matrix composite, 500×.
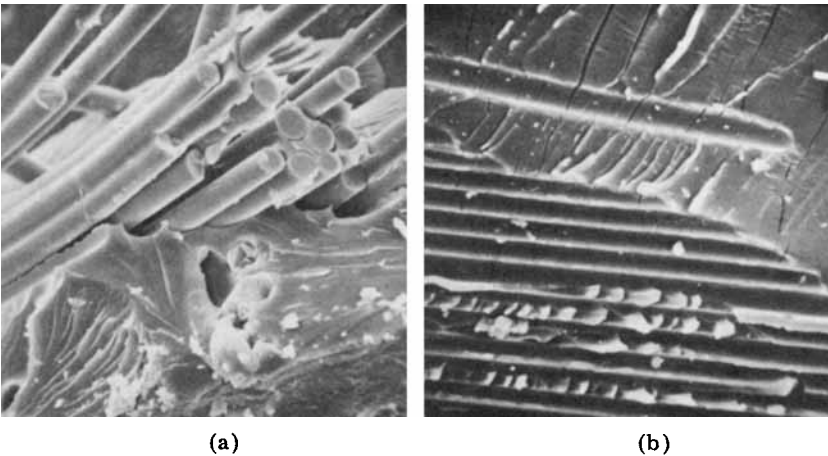

(a)   (b)

Fig. 7. Scanning electron micrographs showing two views of the fracture surface of the 832 DC coated fiberglass-epoxy matrix composite, 500×.
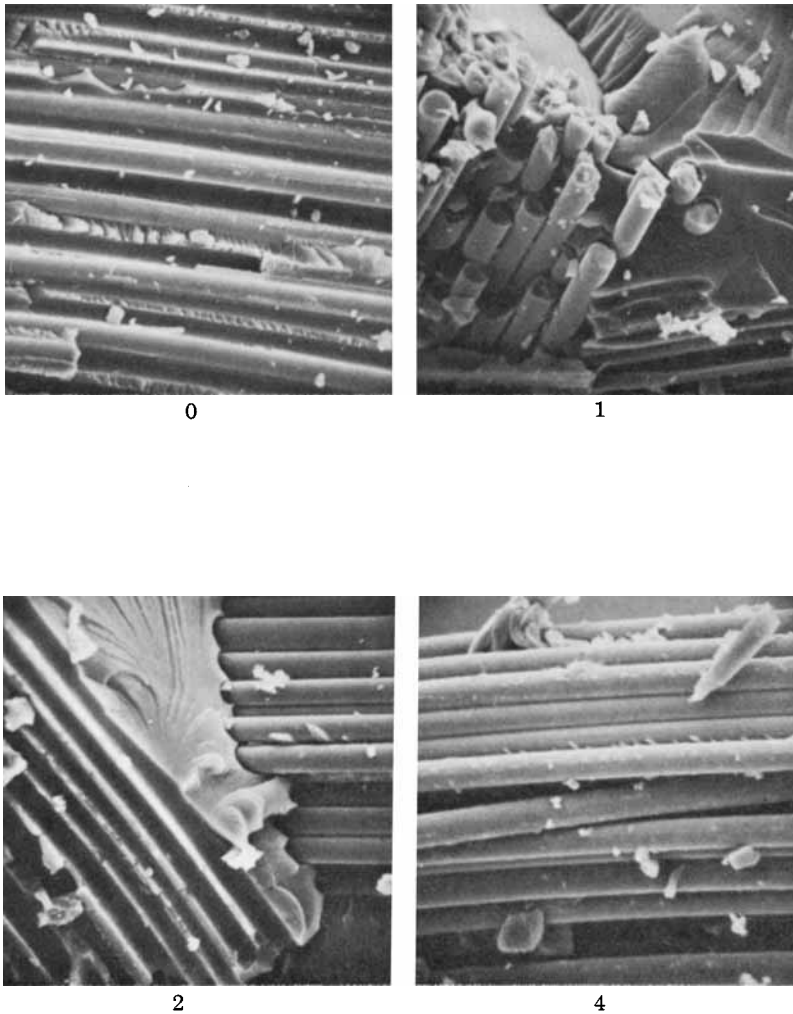
Fig. 8. Fracture surfaces of epoxy composites containing fiberglass coated with rubbery interlayers of varying thickness. The number under each electron micrograph designates the number of latex layers that comprise the interlayer, V/O fiberglass is 0.3 500×.

(see Table III) is reflected in this mode of failure. These results are in sharp contrast to the fracture surfaces of the composites containing coated fiberglass.

In composites containing a coated fiberglass material, the impact strength was found to be improved (see Table II). Electron micrographs (of the fracture surfaces) reveal a sharp contrast to the uncoated fiberglass material. Figure 7 shows the effect of using a silane coating (832 DC). Good adhesion between the fiberglass and the epoxy matrix is observed, leading to the fracturing of the matrix. Such fracturing is an energy absorbing process which leads to an increase in impact strength. As noted in Table II, the impact strength of a 20 V/O uncoated fiberglass/epoxy composite is 0.25 ft lb, while a value of 0.85 ft lb is observed for a 10 V/O silane coated fiberglass composite.

Turning to the fracture surfaces of the materials (see Table III and Fig. 8)

containing the thick interlayer, one notes that fracture occurred at the glass/resin interface in all cases. Only when the interlayer thickness is large does fracture take place within the interlayer region. This is due to the limited amount of epoxy resin diffusion (and therefore, lower crosslink density) near the glass surface as compared to the outer surface of the interlayer.

The thick interlayer(s) produce a diffuse boundary around the filler particles, thus avoiding the sharp discontinuity in mechanical properties between filler and matrix. The introduction of an elastomeric interlayer acts as an energy absorber,[5] stress delocalizer, and crack arrestor[11] allowing for increases in impact strength. These effects, as we have observed, are a function of the interlayer thickness.

Parallel to this study Xanthos and Woodhams[11] have shown that there is an advantage to locating an energy absorbing layer at the fiber–matrix interface rather than randomly in the matrix. Large increases in impact resistance were found when the elastomeric phase was at the interface, while little or no improvement was achieved when isolated from the interface.

SUMMARY

Many methods[20] have been devised for producing polymeric films. These have ranged from simply dipping whereby the rate of withdrawal of the substrate from the coating solution determines film thickness, to chemiphoresis,[21] in which chemical reactions occur between the substrate (e.g., steel) and the bath, resulting in coagulation and deposition of the polymer coating. Utilizing the method devised by Iler[10] for the deposition of colloidal particles on a substrate, controlled films of uniform thickness can be produced. The thickness of the film is controlled by the size of the latex particles. The particles are attracted to the glass surface by electrostatic forces. There is no need for the use of an applied electric current.

Composites having controlled interlayer properties (therefore controlled composite properties) can be produced. The nature of the interlayer can be varied by changing the molecular structure of the latex, its T_g, and thickness. The placement of an elastomeric interlayer on a fiberglass surface results in significant improvement in the mechanical properties of an epoxy composite. Increases in impact strength and damping were observed.

It has not escaped the attention of the authors that this is a means of attaining uniform, ultrathin films or membranes. For example, a film can be "deposited" onto the surface of a suitable substrate as described previously. The film could then be removed by dissolving the substrate in a solvent system whereby the film would be free to be used.

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