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# Aminimide-cured epoxy resins as surface modifiers for mica flakes in particle-reinforced thermoplastics

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The tensile behaviour of mica-flake-dispersed thermoplastic composites was examined. The mica flakes (phlogopite, muscovite and cerisite) were treated with a combination of epoxy prepolymer and various aminimide curing agents, and then incorporated into polypropylene or acrylonitrile–butadiene–styrene copolymer matrix. It was found that improvement of the filler–matrix interface with the present treatments is comparable to expensive silane coupling treatments. The tensile strength of the composites increased by approximately 20%. In contrast, surface treatment by conventional epoxy resins gave poor results in all respects. The overall behaviour is discussed in terms of the nature of the interface between filler and matrix in the polymer composite materials.

## 1. Introduction

One of the advantages of reinforced thermoplastics as compared with reinforced thermosetting polymers is that they may be processed by high-speed injection moulding. Particle-reinforced plastics have a number of advantages over fibre-reinforced plastics such as ease of processing, low cost of filler, low mould shrinkage and versatility of the shape of products, while the reinforcing effect of particulate fillers on tensile strength is limited. There have been several attempts aimed at the reinforcing effect of flake fillers in polymer composites [1, 2]. The reinforcing mechanism, however, is a subject of controversy.

The performance of polymer composites depends largely on the property of the interface between matrix and filler. Consequently, the surface modification of fillers is a key technology for composite materials. For example, there are a number of processes such as silane coating treatment, direct suspension polymerization [3], polymer encapsulation technique [4, 5], and so forth.

In this study, we report a novel surface treatment method applicable to inorganic fillers (mica flakes) using a specially formulated epoxy resin as a surface modifier.

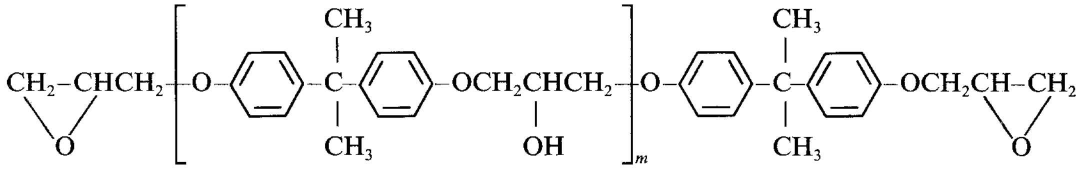
## 2. Experimental details

### 2.1. Materials

The three principal forms of mica flake used as fillers for the composites were phlogopite, muscovite (Repco Ltd., Tokyo) and cerisite (Sanshin Mica). Chemical compositions obtained by X-ray microanalysis, average particle sizes and specific surface areas of these mica flakes are listed in Table I.

Polypropylene (PP) (MA4, Mitsubishi Yuka) and acrylonitrile–butadiene–styrene (ABS) copolymer (QF, Denka) were commercially available and were used for the thermoplastic matrices.

The epoxy prepolymer (Epikote 828, Yuka Shell Epoxy) was derived from the reaction of bisphenol-A and epichlorohydrin and was largely composed of the diglycidyl ether of bisphenol-A. Analysis by gel permeation chromatography (GPC) (Toyo Soda HLC-802; column, GMH6 × 2 + G4000H8 + G2500H8; eluent, chloroform) indicated that Epikote 828 was composed of $m = 0$ (86%; molecular weight 340) and $m = 1$ (14%; molecular weight 620) components in the structure shown below:



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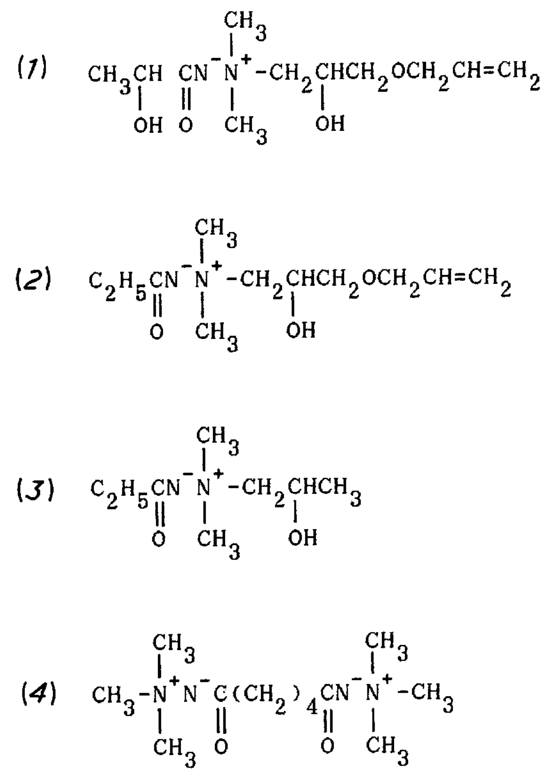
(1) $CH_3CH(OH)C(O)N^-N^+(CH_3)_2-CH_2CH(OH)CH_2OCH_2CH=CH_2$

(2) $C_2H_5C(O)N^-N^+(CH_3)_2-CH_2CH(OH)CH_2OCH_2CH=CH_2$

(3) $C_2H_5C(O)N^-N^+(CH_3)_2-CH_2CH(OH)CH_3$

(4) $(CH_3)_3N^+N^-C(O)(CH_2)_4C(O)N^-N^+(CH_3)_3$

*Figure 1* Structures of aminimide compounds.

The structures of the aminimide compounds (*1* to *4*) used in this study as latent curing agents for epoxide are shown in Fig. 1. These aminimide compounds were synthesized as reported previously [6–8]. Triethylenetetramine (Tokyo Kasei) (*5*) and boron trifluoride monoethylamine complex (Hashimoto Kasei) (*6*) used as reference curing agents for epoxide were the purest reagents commercially available and were used without further purification. We also used a silane coupler, (γ-aminopropyl) triethoxysilane (Shinetsu Kagaku) (*7*) as a surface modifier for mica flake.

TABLE I Compositions and dimensions of mica flakes

| Component (wt %)* | Phlogopite | Muscovite | Cerisite |
|---|---|---|---|
| $SiO_2$ | 41 | 46 | 49 |
| $Al_2O_3$ | 16 | 37 | 34 |
| MgO | 21 | 0.4 | 0.4 |
| $K_2O$ | 10 | 8.8 | 9.7 |
| $Na_2O$ | 0.5 | 0.6 | 0.5 |
| F | 2.2 | 0.2 | – |
| $Fe_2O_3$ | 1.2 | 1.0 | 1.1 |
| FeO | 7.8 | 1.3 | – |
| CaO | – | 0.2 | 0.01 |
| $TiO_2$ | 0.4 | – | 0.4 |
| $B_2O_3$ | – | – | – |
| $H_2O$ | 1.0 | 5.0 | 5.0 |
| Average particle size (μm) | 35 | 40 | 18 |
| Specific surface area ($m^2\,g^{-1}$) | 4.05 | 4.10 | 0.62 |

*Obtained by X-ray microanalysis.

## 2.2. Methods

Fig. 2 shows the sample preparation and the testing methods for mica-reinforced thermoplastics.

### *2.2.1. Surface treatment of mica flakes*

The mica flakes (phlogopite, muscovite and cerisite) were coated with Epikote 828 and aminimides (*1* to *4*) or conventional curing agents (*5* and *6*). Epikote 828 (0.9 g) and a curing agent (0.1 g) (*1* to *6*) were dissolved in 100 ml of ethanol. The mica flakes were immersed in the ethanol solution with continuous stirring and then dried to give surface-modified mica flakes encapsulated by epoxy prepolymer with the curing agent.

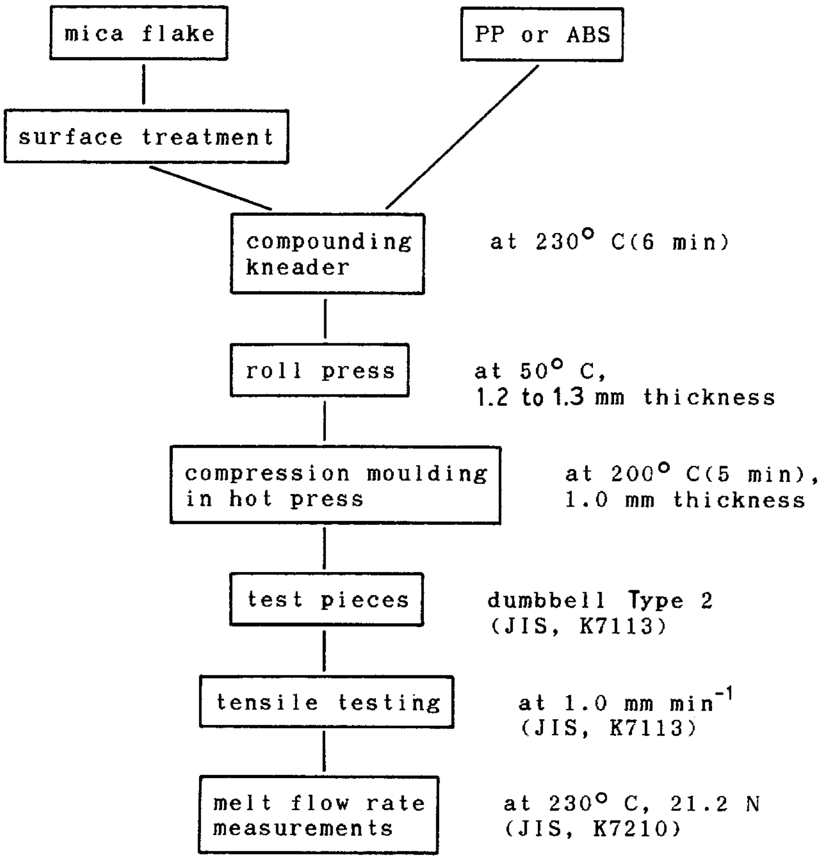

*Figure 2* Preparation of mica-reinforced thermoplastic composites and their testing methods.

The amounts of surface modifier (Epikote 828 + curing agent) added to mica flakes were varied from 0.25 to 2.25%. In the case of polypropylene – phlogopite mica composites the mica flake was coated with a silane coupling agent, ($\gamma$-aminopropyl) triethoxysilane (*7*) as a reference. It was applied by immersing the mica flake (100 g) in 1% solution of ethanol (*7*, 1.0 g in 100 ml of ethanol) and then dried so as to give surface-coated mica modified with the silane-based coupling agent.

These surface-modified mica flakes were subject to subsequent heating at 110° C (3 h) or 110° C (3 h) + 180° C (0.5 h). A coating layer adhering tightly to the mica surface was thus obtained.

### 2.2.2. Preparation of composite specimens

After the heat treatment, these differently modified fillers were kneaded with PP or ABS matrix in a compounding kneader (Brabender Plastograph, Haake) at 230° C for 6 min. The volume fraction ($V_f$) of mica was fixed at 0.15. The composite specimens were prepared by preliminary setting through a rolling press at 50° C followed by compression moulding in a hot-press apparatus at 200° C for 5 min.

### 2.2.3. Tensile measurements

The composite specimens for tensile measurements were shaped to meet the requirements of tension test specimen Type 2 (Japanese Industrial Standards (JIS) K7113: thickness, 1 mm; gauge length, 40 mm; width of narrow section, 10 mm). The measurements were made using an Instron tester according to the JIS K7113 procedure at room temperature with a cross-head speed of 1 mm min$^{-1}$. Tensile strength and ultimate elongation were determined from the stress – strain curves. In all cases, ten to eleven specimens per sample were tested and the measured values were averaged.

### 2.2.4. Melt flow rate measurements

The melt flow rate (MFR, measured in g per 10 min) measurements were conducted using a Melt Indexer (Toyo Seiki) according to the JIS K7210 procedure, at 230° C with a loading of 21.2 N for 10 min, in the case of PP composites.

## 3. Results and discussion

### 3.1. Effect of surface treatment on tensile strength and melt flow rate

Fig. 3 shows the effects of surface treatment on tensile strength and MFR for PP – phlogopite mica composites ($V_f$ = 0.15). This is a typical example of the composites when the epoxy-coated fillers are used. A similar trend of improving tensile strength as well as MFR was observed in other composite systems with varying epoxy formulations.

The tensile strength and the MFR increased with the amount of resin retained on the surface up to 1% and then levelled off. The tensile strength increased by 17% with 1% resin retention. The reinforcing effect of the surface treatment with the aminimide-cured epoxy resin (Epikote 828 + *1*) is comparable to that with ($\gamma$-aminopropyl) triethoxysilane, which has been popularly used as a surface modifier to mica flakes. The value of MFR increased twice as much as that of the untreated composite. This increase in MFR suggests an improved dispersion of the mica flakes, resulting in an increase in tensile strength.

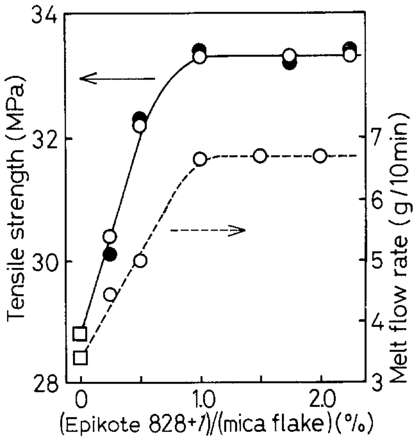

*Figure 3* Effect of surface treatment on tensile strength and melt flow rate for polypropylene–phlogopite mica composites ($V_f$ = 0.15). (□) Without surface treatment; (○) Epikote 828 (0.9 g) + *1* (0.1 g), 110° C (3 h); (●) Epikote 828 (0.9 g) + *1* (0.1 g), 110° C (3 h) + 180° C (0.5 h).

In general, mica flakes are highly irregular in both diameter and thickness. Moreover, the alignment, stacking and distribution of flakes are supposedly random. The presence of resin-rich regions, voids, flake imperfections, failure of filler–matrix adhesion, and other inhomogeneous sites will lower the strength of a composite. The surface modifiers can penetrate into the narrow cracks on mica flakes so as to increase the intrinsic flake strength. The increase in MFR suggests an improved dispersion of mica flakes in the matrix resin. Furthermore, the surface treatments reinforce the adhesion between fillers and matrix polymers. The overall reinforcing effect seen in tensile measurements (Fig. 3) is attributed to the combined effect of the various factors described above.

We have already applied this specific type of epoxy resin (aminimide-cured epoxy resin) as a binder of a solid lubricant, and succeeded in preparing a composite material having a low friction coefficient and low rate of abrasion [9]. These excellent properties were attributed to the toughness and good adhesivity of this specific epoxy resin binding the lubricant particles tightly. Control experiments with conventional epoxy resins gave poor results in all respects. The tough and strong epoxy resin can claim wide applicability to composite materials in general.

### 3.2. Tensile properties of various mica-dispersed thermoplastics

The reinforcing effects of the epoxy–aminimide (*1* to *4*) systems were examined in various mica-flake-dispersed thermoplastics (Tables II to V). Tables II to IV are for the composites of PP with phlogopite, muscovite and cerisite mica, respectively. Table V is for the combination of ABS with phlogopite mica.

For both matrix polymers (PP in Tables II to IV, ABS in Table V), an excellent reinforcing effect as judged by the tensile strength was demonstrated when

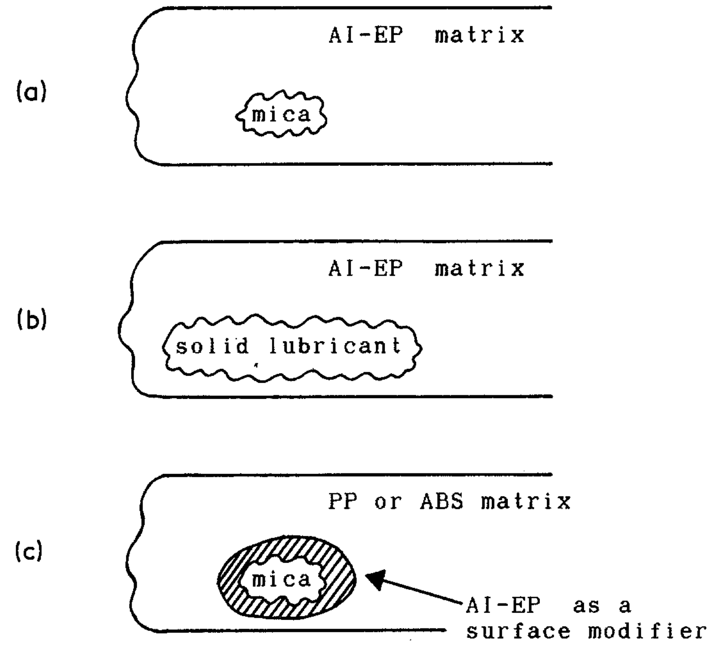

*Figure 4* The structural concept of composite systems containing aminimide-cured epoxy resins: (a) mica-dispersed aminimide-cured epoxy resin composite [11, 12]; (b) solid lubricant/aminimide-cured epoxy resin composite [9]; (c) surface-modified mica-reinforced thermoplastics in the present study. AI-EP = aminimide-cured epoxy resin.

the fillers were treated with the combination of epoxy resin with aminimide compound (*1* to *4*).

While the effects of the present surface treatment are comparable to the best known method with silane coupling agents, the merits of the present methods are as follows: (a) the present epoxy resin is stable for several months at room temperature after formulation so that the handling is very easy; (b) the epoxy resin is stable against moisture while silane couplers are not; and (c) the reagent costs about 1/5 to 1/10 of silane coupling agents. Superior reinforcing effects are reported for mica-dispersed thermoplastics (polystyrene copolymer and polyester resin) using specific polymer encapsulation techniques [1]. However, from the standpoints of cost, performance and ease of handling, the present surface treatment will be superior to the conventional method with silane coupling agents and other specific methods [1–5].

Although positive effects of surface treatments on the tensile properties for all composites are observed, the effects are better for the surface treatment with the aminimide (*1* to *4*)-cured epoxy resins than for the reference treatments with conventional epoxy resin. The characteristics of this particular surface modification will be discussed in the following section.

### 3.3. Interpretation of the excellent capability of the present epoxy resin as a surface modifier for mica flakes

The requirements for a surface modifier to be effective in composite materials are as follows.

(i) Good adhesion between filler surface and the modifier.

(ii) Improved wettability of the modified surface with the matrix polymer.

(iii) Shock-absorbing and stress-releasing properties of the interface between filler and matrix.

(iv) High mechanical strength of the interfacial layer.

A series of the present epoxy resins is expected to meet all these requirements. Our previous studies indicate that (a) these specific epoxy resins are excellent adhesives [6]; (b) they are tough and strong, exhibiting elongations as high as 15% at breakage [10]; (c) a considerable reinforcing effect of mica flakes without any surface treatment is observed when the resin is used as a matrix for mica-dispersed epoxy resin composites [11, 12]; and (d) when the epoxy resin is used as binder for a powdery solid lubricant, it

TABLE II Tensile properties of polypropylene – phlogopite mica composites ($V_f = 0.15$)*

| Surface treatment | Heating condition† | Tensile strength (MPa) | Increase in tensile strength (%) | Ultimate elongation (%) |
|---|---|---|---|---|
| Without surface treatment | – | 28.8 | – | 1.3 |
| Epikote 828 + *2* | a | 33.7 | 17.0 | 2.4 |
| | b | 34.1 | 18.4 | 2.2 |
| Epikote 828 + *3* | a | 33.3 | 15.6 | 1.6 |
| | b | 33.8 | 17.4 | 1.3 |
| Epikote 828 + *4* | a | 33.1 | 14.9 | 1.6 |
| | b | 33.3 | 15.6 | 1.3 |
| ($\gamma$-Aminopropyl) triethoxysilane | a | 34.3 | 19.1 | 1.4 |
| Epikote 828 + triethylenetetramine | a | 30.1 | 4.5 | 1.4 |

*Phlogopite mica flake (100 g) was surface-treated by Epikote 828 (0.9 g) with aminimides (*2* to *4*, 0.1 g), Epikote 828 (0.9 g) with triethylenetetramine (0.1 g), or ($\gamma$-aminopropyl) triethoxysilane (1.0 g).

†a: 110° C (3 h), b: 110° C (3 h) + 180° C (0.5 h).

TABLE III Tensile properties of polypropylene – muscovite mica composites ($V_f$ = 0.15)*

| Surface treatment | Heating condition† | Tensile strength (MPa) | Increase in tensile strength (%) | Ultimate elongation (%) |
|---|---|---|---|---|
| Without surface treatment | – | 31.7 | – | 0.8 |
| Epikote 828 + *2* | a | 36.4 | 14.8 | 1.0 |
| | b | 37.7 | 18.9 | 0.9 |
| Epikote 828 + *3* | a | 33.3 | 5.0 | 0.9 |
| | b | 34.3 | 8.2 | 0.8 |
| Epikote 828 + triethylenetetramine | a | 34.4 | 8.5 | 0.9 |

*Muscovite mica flake (100 g) was surface-treated by Epikote 828 (0.9 g) with aminimides (*4* and *5*, 0.1 g) or Epikote 828 (0.9 g) with triethylenetetramine (0.1 g).

†a: 110° C (3 h), b: 110° C (3 h) + 180° C (0.5 h).

exhibits excellent performance [9]. These characteristics are not common to conventional epoxy resins.

Sketches of our polymer composite systems are shown in Fig. 4. In the case of Fig. 4a, the reinforcing effect is attributed to the properties of the aminimide-cured epoxy resin, such as hardness, toughness and good adhesion. The excellent anti-abrasion and low friction properties of the polymer composite in the case of Fig. 4b are also the result of the "tight and tough bonding effect" between the solid lubricant and the matrix. On the other hand, we should consider the filler – matrix interface (or interphase) from a different point of view in the present case (Fig. 4c).

A mica surface is very hydrophilic. The epoxy prepolymer containing a water-soluble curing agent will have a good affinity to the mica surface (Requirement (i)) while the hydrophilic ylide structure ($\geqslant N^+ - N^-(C=O)-$) decomposes during curing so that the mica surface after curing turns to be hydrophobic relative to the intact mica surface. Therefore, the treated surface should have a better affinity to the matrix resins which are generally non-polar (Requirement (ii)).

Requirement (iii), relevant to stress concentration and stress relaxation, is the most interesting problem. The interface is the most highly stressed region in a composite material. It must be effective to lower these stress concentrations either by placing a buffer material of intermediate modulus or a ductile one in the interphase. The intermediate layer would act as a damper to decrease the stress concentration caused by the modulus mismatch. This concept, called the "graded modulus interphase", has been applied by Cheng *et al.* [13] to improve the strength of graphite-reinforced polycarbonate. They partially crystallized polycarbonate around short graphite fibres so that brittle graphite fibres and amorphous polycarbonate were interphased by the crystalline polymer having an intermediate modulus. The concept of reducing stress concentration at the interface between a brittle matrix and glass fibres by applying a "rubber damper" inner layer to the glass was first described by Lavengood and Michno [14].

In the present study, measurements of the tensile properties of mica-dispersed thermoplastics indicated that the inner layer improves mechanical properties through three distinct mechanisms as follows: (a) the interphase layer acts as a spacer and prevents flake–flake contact during processing, which brings about a high stress concentration after curing; (b) the interphase layer seems to heal flaws in the mica flake and increase the intrinsic flake strength [1]; and (c) the interphase layer is much less stiff than the brittle mica flakes and provides a local deformation mechanism to reduce the interfacial stress concentration.

Epoxy resins with conventional curing agents (*5* and *6*) are much inferior to the aminimide-cured resin. This is probably due to the brittle nature of the former resins.

The specific behaviour of aminimide-cured systems seems to be derived from their curing mechanism [7, 8]. At elevated temperature, aminimides decompose to yield tertiary amines and isocyanates, both of which participate in curing reactions. As we have discussed in previous articles [10–12], comparatively slow curing with tertiary amines (polymerization catalysts) at high temperature above $T_g$ would provide a stress-free matrix. Furthermore, the participation

TABLE IV Tensile properties of polypropylene – cerisite mica composites ($V_f$ = 0.15)*

| Surface treatment | Heating condition† | Tensile strength (MPa) | Increase in tensile strength (%) | Ultimate elongation (%) |
|---|---|---|---|---|
| Without surface treatment | – | 24.7 | – | 3.1 |
| Epikote 828 + *1* | a | 28.9 | 17.0 | 3.4 |
| | b | 27.4 | 10.9 | 3.4 |
| Epikote 828 + *2* | a | 28.3 | 14.6 | 5.1 |
| | b | 29.5 | 19.4 | 4.3 |
| Epikote 828 + *3* | a | 27.5 | 11.3 | 2.7 |
| | b | 29.5 | 19.4 | 3.0 |

*Cerisite mica flake (100 g) was surface-treated by Epikote 828 (0.9 g) with aminimides (*1* to *3*, 0.1 g).

†a: 110° C (3 h), b: 110° C (3 h) + 180° C (0.5 h).

TABLE V Tensile properties of ABS – phlogopite mica composites ($V_f = 0.15$)*

| Surface treatment | Heating condition† | Tensile strength (MPa) | Increase in tensile strength (%) | Ultimate elongation (%) |
|---|---|---|---|---|
| Without surface treatment | – | 35.5 | – | 0.6 |
| Epikote 828 + *1* | a | 38.0 | 7.0 | 0.7 |
| Epikote 828 + *2* | a | 40.1 | 13.0 | 0.8 |
| Epikote 828 + *3* | a | 39.9 | 12.4 | 0.8 |
| Epikote 828 + $C_2H_5NH_2 \cdot BF_3$ | a | 36.7 | 3.4 | 0.6 |

*Phlogopite mica flake (100 g) was surface-treated by Epikote 828 (0.9 g) with aminimides (*1* to *3*, 0.1 g) or Epikote 828 (0.9 g) with $C_2H_5NH_2 \cdot BF_3$ (0.1 g).

†a: 110° C (3 h).

of isocyanate either via urethane or via oxazolidone formation would also modify the properties.

In conclusion, the interfacial layer of aminimide-cured epoxy resins is advantageous since it seems to satisfy all requirements (i), (ii), (iii) and (iv) for the filler–matrix interphase described above.

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