The Use of Mica Flakes for Reducing Internal Stress in Cured Epoxy Resin

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SYNOPSIS

Mica, in the form of flakes of different sizes and size distributions, was mixed with a difunctional epoxy resin to the extent of 10 to 50 parts by weight of the resin. To this resin–filler mixture, a stoichiometric amount of a tetrafunctional curing agent was added. First, a thin aluminium strip was coated with the mica–resin–amine mixture and was subjected to two curing cycles. Second, sheets were cast from the mixture by subjecting them to the same two cure cycles. The internal stresses that developed in the coated samples, and their relaxation with time, were studied. The dynamic torsional spectra of rectangular bars cut from the sheet were also mapped. The debonding and microcracking, resulting from internal stress, have been shown to result in a significant reduction in internal stress in the mica-filled samples, particularly in samples containing large mica flakes in which delamination of the mica layers in the flake has also been shown to occur. However, despite this phenomenon, the filled samples were found to have adequate mechanical and electrical properties. © 1994 John Wiley & Sons, Inc.

INTRODUCTION

It is known that when neat epoxy resin is cured, it can develop internal stresses as it shrinks during cooling from the glass transition temperature (T_g) to room temperature. In a recent study on a diglycidyl ether of bisphenol-A-based epoxy resin, cured with an aromatic curing agent, *viz.* metaphenylene diamine, it was found[1] that an internal stress of about 6 to 8 MPa was induced when an aluminium strip, coated with a thin layer of the epoxy–amine mixture, was allowed to cool to room temperature after curing. Studies of a similar nature, using other epoxy resin systems, have also shown that an internal stress of around the same magnitude is generated on curing and cooling.[2,3] The internal stress, σ_i, at room temperature, for example, may be considered to arise in the case of the coated strip from constraint to shrinkage and can therefore be estimated from the expression $\int_{T_r}^{T_g} E_r (\beta_r - \beta_{al})\, dT$, where T_r stands for room temperature, E_r is the glassy elastic modulus of the resin, and β_r and β_{al} are, respectively, the coefficients of linear thermal expansion of the resin and aluminium. Reduction of internal stress is important for mechanical stability. The above expression suggests that this may be achieved by lowering the linear thermal expansion coefficient of the resin, the elastic modulus of the resin, or the T_g of the resin. For example, dispersion of rubber particles in epoxy resin lowers the elastic modulus and consequently low thermal stress is developed.[4]

In the present investigation, the internal stress, generated in epoxy resin filled with 10 to 50 parts by weight of mica flakes of small size, or with 10 to 30 parts by weight of mica flakes of large size, has been measured and found to be significantly lower than in the neat resin. The presence of mica results in the enhancement of the modulus of the filled resin with a small change in T_g. The coefficient of linear thermal expansion shows a significant reduction. In the filled samples, the debonding of the mica–epoxy interface, delamination of the mica flakes, and matrix cracking have also been observed. The dynamic torsional spectra of filled bulk samples were also obtained and the α' relaxation peak was found to be

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sensitive to internal stress. The possible mechanisms of reduction and relaxation of internal stress in filled samples have been identified and discussed in this article.

EXPERIMENTAL DETAILS

Materials Used

The epoxy resin used in this investigation was Araldite GY-250 (equivalent to Epon 828 of Shell Co.), manufactured by Hindustan Ciba Geigy Ltd., India. It is a liquid at room temperature with a number average molecular weight of 380 and epoxy equivalent of 190. The curing agent used was metaphenylene diamine (mPDA), which is a solid at room temperature, with a melting point of 75°C. In all samples, the stoichiometric amount of curing agent, that is, 14.5 parts per hundred parts of the resin by weight, was used.

The fillers used were the Muscovite type of mica flakes, which were of Indian origin. The size and size distribution were determined from the sieve size and actual size measurements and were as follows:

1. 6 to 32 μm, as shown in Figure 1(a). The majority of particles are similar to an irregular-shaped powder, in contrast to the other two size categories, which are distinctly flaky,
2. 106 to 212 μm (thickness ~ 8 to 12 μm), as shown in Figure 1(b),
3. 212 to 355 μm (thickness ~ 10 to 20 μm), as shown in Figure 1(c).

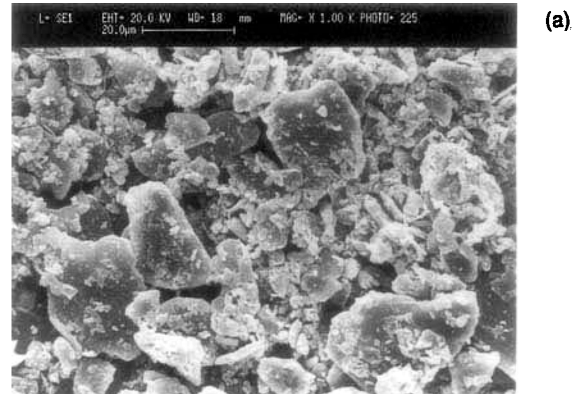
These mica flakes were all waste products without any coupling agent and were used in the as-received condition after drying in an air oven at 110°C for 2 h.

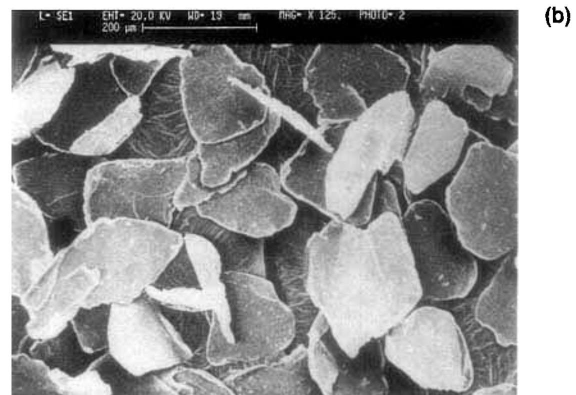
Sample Preparation

Casting of Sheet from Neat Resin

Sheets, 2.5 mm thick, were cast from the neat resin containing a stoichiometric amount of curing agent, *viz.* with 14.5 parts of mPDA per hundred parts of the resin (phr) by weight, using two polished metal plates and Teflon spacers. The resin and the cross-linking agent were heated in separate containers in an oven set at 75°C until the mPDA melted completely. They were then mixed by stirring and the stirred mixture was vacuum degassed for about 7 min before being poured into steel molds.

Two curing cycles were used, *viz.* (a) standard cure (SC) samples were prepared by curing at 75°C for 2 h, followed by 125°C for 2 h, and (b) postcure (PC) samples were prepared by postcuring the SC





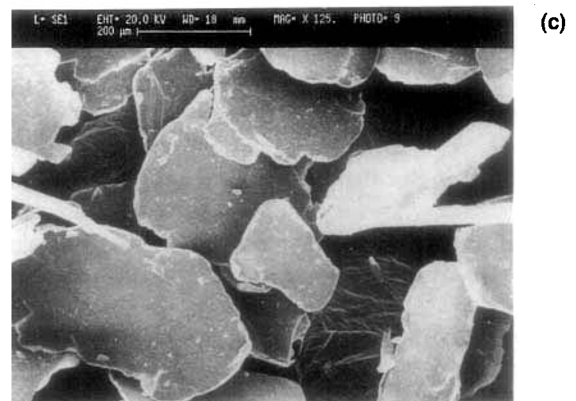


Figure 1 Scanning Electron Micrographs of mica flakes (a) 6–32 μm, (b) 106–212 μm, and (c) 212–355 μm.

samples at 175°C for 6 h in nitrogen environment. The oven was switched off after the completion of each of the two curing cycles and the sample was taken out after allowing it to cool overnight in the oven. Since cooling is achieved by switching off the oven heaters and allowing the oven to come to ambient condition, the initial cooling rate is faster than the later cooling rate, as was actually observed by monitoring the temperature during cooling. It was observed that it took just over 3 h for the temperature to decrease from 175°C to room temperature. The effect of the kinetic nature of the glass transition temperature on internal stress in epoxy system has been discussed in an earlier paper.[1] The generation of internal stress is related predominantly to the rate of cooling of the sample, from the T_g downwards; the higher the rate of cooling, the further the sample would be from its equilibrium state and the greater the internal stress. Experiments, under a controlled cooling rate, were reported in the earlier article[1] to show that internal stresses can be minimized by allowing molecular relaxation, which reduces frozen-in conformational energy.

Casting of Sheet from Filled Resin

Sheets of mica-filled epoxy resin, 2.5 mm thick, were cast using the same mold that was used for casting neat resin sheets. An appropriate amount of mica, dried at 110°C, was mixed with the hot resin at about 90°C by stirring. The mixture was degassed by applying a vacuum. The temperature of the degassed mixture was allowed to decrease to 75°C when the stoichiometric amount of molten mPDA at 75°C was added to it, while stirring to ensure good mixing. The mixture was again degassed for 7 min. The degassed mixture was poured into the heated steel mold, which was then placed in the oven, where it was subjected to the standard and postcure cycles described earlier. To prevent the settling down of the mica filler in the initial phase of the cure cycle, the position of the base plate of the steel mold was appropriately changed a few times during the first half hour of curing. It was ensured that the cast sheets had uniform distribution of the filler.

The following mica flake-filled epoxy samples were prepared:

1. Flakes, 6–32 μm in size: samples were prepared, containing 10, 20, 30, 40, and 50 parts by weight (pbw) of mica, in 100 parts of the resin–amine mixture,
2. Flakes, 106–212 μm in size: samples were prepared containing 10, 20, and 30 pbw of flakes,
3. Flakes, 212–355 μm in size: samples were prepared containing 10 and 20 pbw of flakes.

In cases (2) and (3), a still higher mica flake content resulted in too high a viscosity, which made degassing and processing difficult and, therefore, these preparations were not used.

Scanning electron micrographs of mica-filled resin samples, presented later, show that in these samples the platelets had a predominantly planar orientation.

Aluminium Strips Coated with Resin and Resin-Filled Mixture

Aluminium strips, 90 mm long, 15 mm wide, and 0.2 mm thick, were used as the base plate. The neat resin and mica-resin mixtures, both with a stoichiometric amount of curing agent, were coated over one side of the strip. The strip was placed between two parallel plates with spacers to yield a coating thickness of about 0.1 mm in the case of neat resin and up to 0.4 mm in the case of the resin-filler mixture. The strips were then cured in an air oven in both standard-cure and postcure conditions.

Measurements and Characterization

Density

The density of the cured neat resin sample was determined in a carbon tetrachloride-n-heptane density gradient column. For the filled samples containing small sized mica flakes, a method based on Archimedes' principle was used. Small pieces of the composite were cut and were weighed in air, and in double-distilled water, using a microbalance. From the loss of weight in water, and knowing the density of double distilled water, the volume of the composite pieces was obtained, from which the density was estimated. In each case, the average of five measurements was taken as the density of the sample.

Thermal Expansion

Mercury dilatometers were used for measuring the volume expansion of neat resin samples and filled epoxy resin samples, containing the smallest sized mica flakes. The specific volume–temperature curves were plotted by combining the data thus obtained with the density data and the volume thermal expansion coefficient was taken as $(1/V)\ (dV/dT)$, where V is the specific volume and dV/dT is the slope of the specific volume–temperature curve. The linear coefficients of thermal expansion were taken to be one third of the corresponding volume expan-

sion coefficients. The assumption underlying these estimates is that the thermal expansion is isotropic in nature. Since the resin, which forms from about 80 to 96% percent of the volume of the composite, is isotropic, anisotropy can arise from the thermal expansion of mica. The coefficient of linear thermal expansion of mica, parallel to the plane of the flake, is around $10^{-7}\,°C^{-1}$, while in the perpendicular direction, it is twice this value. Since the coefficient of linear thermal expansion of cured epoxy resin is at least 300 times greater than that for mica, the direct contribution of mica to thermal expansion of the composite would be insignificant. However, the expansion of the resin is constrained, due to the presence of mica, and as a result, the composite expansion would be less than that of the resin. It may also be noted that most of the mica particles are small [Fig. 1(a)] and have the shape of irregular powder rather than that of a flake. All of these factors justify the assumption of isotropic volume expansion of the composite.

Internal Stress

The resin and filled resin-coated aluminium strip bent, due to the difference in contraction coefficients between the different materials. The deflection at the central portion of the beam was measured with the help of a spherometer, and this allowed the internal stress to be estimated,[1] using an expression that is credited to Nakamura et al.[3] In each case, at least four coated strips were studied. It was observed that the curvature of the coated metal assembly decreased with the passage of time. It was further observed that initially the decrease was rapid, but after two days, the rate of change was much less. The first measurement of curvature was, therefore, made after an overnight cooldown of the assembly in the oven, which was switched off after the curing sequence was complete. The assembly was taken out next morning (12 h after reaching room temperature) and the curvature was measured. The subsequent measurements were made at 24 h intervals.

Scanning Electron Microscopy

The scanning electron micrographs of cast samples after etching, and of the coated aluminium strips, were obtained on a Cambridge Stereoscan 360 scanning electron microscope (SEM) of Cambridge Instruments, UK. The samples were mounted on aluminium stubs and were sputter-coated with gold or silver for observation in the SEM.

Dynamic Torsional Measurements

Dynamic torsional measurements were made on rectangular strips, cut from the cast sheets, using a free oscillating inverted torsion pendulum.[5] Damping curves were obtained in the temperature range of −100 to 180°C, from which the loss factor, tan δ, was estimated and the storage torsional modulus G' was calculated, using standard procedures laid down in ASTM D-2236.

Tensile Stress–Strain Behaviour

The tensile tests were conducted at room temperature on an Instron tensile tester model 1112, using a load cell of 500 kg capacity. The tests were made on rectangular strips, of a gauge length 7.5 cm, at a constant crosshead speed of 1 cm/min. In each case, at least ten samples were tested and the average of ten readings were taken. The tensile modulus was obtained from the initial slope. The tensile strength was taken as the stress at break and the elongation at break was taken as the strain when the sample broke.

Dielectric Measurements

The dielectric measurements were made on neat resin and filled resin, containing 10 to 40 parts by weight of mica flakes, 6–32 μm in size, using a Hewlett Packard Model 4192 LF impedance analyzer. The sample was cut from thin cast films, 0.3 mm thick, and the sample was coated on both sides with aluminium over a circular area of 0.636 cm^2 on a vacuum-coating unit. The dielectric constant was measured between room temperature and 180°C at frequencies of 1 kHz to 1 MHz.

RESULTS AND DISCUSSION

Filled Samples Containing Mica Flakes, 6–32 μm in Size

Internal Stress as Estimated from the Bending of the Coated Metal Strip

Internal stress is generated as the unfilled or filled resin coating on the metal plate approaches room temperature during the cooling part of the curing cycle and the internal stress was estimated from the curvature acquired by the plate. For the sake of clarity, only the data on neat resin and on three filled resin samples have been shown in Figure 2.

It is noteworthy that, compared to the neat resin

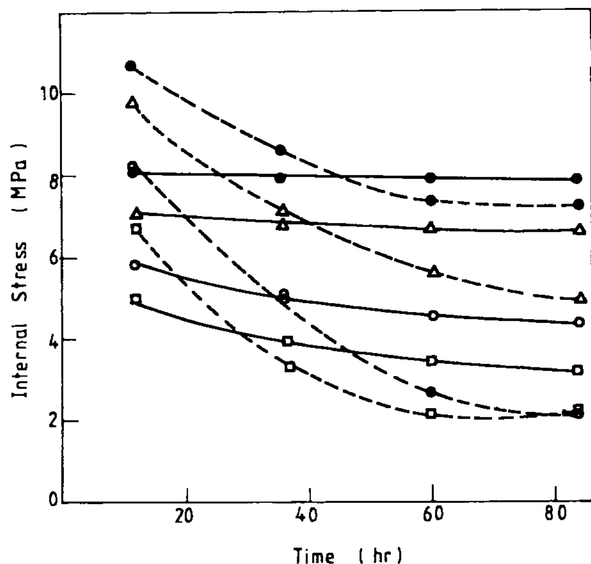


Figure 2 Internal stress data for standard-cure (——) and postcure (---) unfilled (●) and filled epoxy samples containing mica, 6–32 μm size. (△) 10, (○) 30, (□) 50 pbw.

sample, the internal stress is significantly lower in the filled samples and that, with increasing mica content, the internal stress decreases. In addition, upon postcuring, the internal stress generated is considerably higher as compared to that generated in the corresponding standard-cure sample. However, the postcure samples also show rapid relaxation of stress with time. Both these features, shown by the filled samples, are broadly similar to the neat resin case.[1]

In the previous publication on internal stress in neat resin,[1] it was shown that the internal stress in the coated plate arises predominantly due to the difference in thermal contraction coefficients between the resin and the metal; as the coated metal plate cools from T_g to room temperature, the internal stress develops, due to the constraints to lateral shrinkage of the thin adhesive layer. The postcure neat resin sample has a higher T_g and a higher thermal expansion coefficient, as compared to the corresponding standard-cure sample,[6] and this results in a higher internal stress in the former sample. The higher rate of stress relaxation in the postcure neat samples was attributed[1] to the relatively higher amount of free volume trapped in these samples and, consequently, at room temperature the samples were farther from their equilibrium state as compared to their corresponding, standard-cure counterparts. It should also be pointed out that the bent aluminium strip applies an opposite moment, which results in tensile forces in the resin layer, and accelerates the process of stress relaxation.[1]

One important and obvious reason for the reduction of internal stress in the mica-filled samples is the expected reduction of the thermal contraction coefficient of the filled sample, as compared to that of the neat resin. This aspect was studied in some detail to gain an understanding of the problem.

Thermal Contraction Characteristics of the Filled Cast Sheet

The specific volume–temperature plots were obtained for postcure samples that were cut from the cast sheets with the help of a dilatometer and which are shown in Figure 3; the data for the neat resin is also included, since it provides the reference point. The volumetric thermal expansion coefficients in the glassy state were obtained from the slopes of these plots and the coefficient of linear thermal expansion, β, for the sample was taken as one third of the volumetric expansion coefficient. As shown in Figure 4, β decreases with increasing filler content, as expected. Also shown in Figure 4 is the predicted value of β, obtained from the rule of mixtures, according

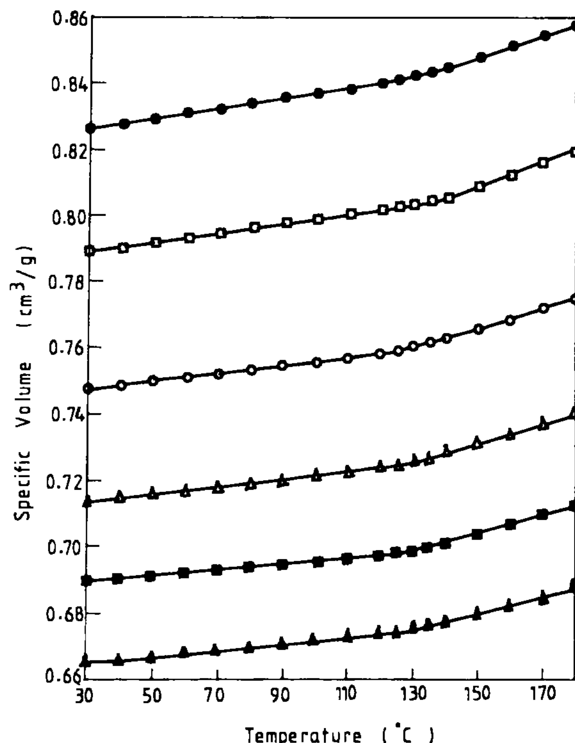


Figure 3 Specific volume–temperature plots for unfilled (●) and filled epoxy samples containing mica flakes. (□) 10, (○) 20, (△) 30, (■) 40, and (▲) 50 pbw.

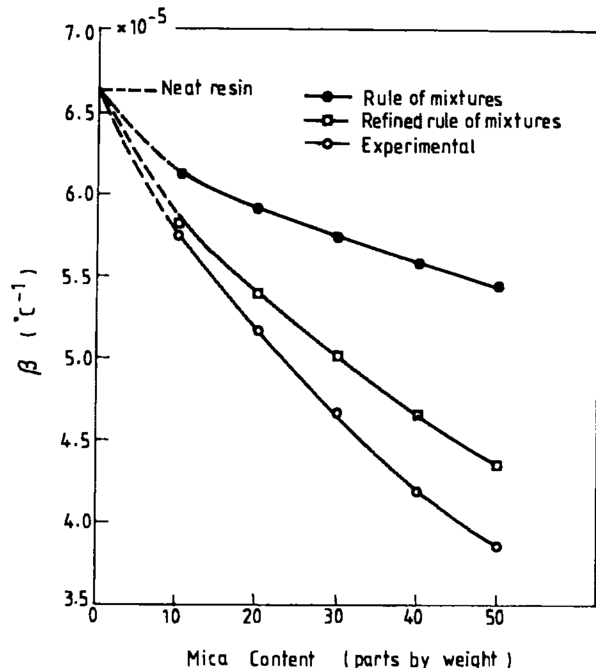


Figure 4 Measured and predicted coefficient of linear thermal expansion (below T_g) of epoxy resin, filled with mica flakes, 6–32 μm in size.

to which the coefficient of the linear thermal expansion of the composite, β_{comp}, is given as

$$\beta_{\text{comp}} = \beta_f V_f + \beta_r V_r \tag{1}$$

where β_f and β_r are the coefficients of the linear thermal expansion of the filler and the resin, respectively, and V_f and V_r are their volume fractions. The experimental values are seen to be considerably less than the predicted values. Wang and Kwei[7] have refined the rule of mixtures by taking into account the effect due to the difference in resin and filler stiffnesses and Poisson ratios; the prediction of their refined rule is closer to the experimental curve, as shown in Figure 4. It is noteworthy that the three curves converge to the experimental value of β for the postcure neat resin at $V_f = 0$. The lower internal stress in the filled samples and the progressive decrease of internal stress with increasing filler content could thus arise at least partly from the reduced thermal expansion of the composite.

Debonding of the Interface and Microcracking of the Matrix

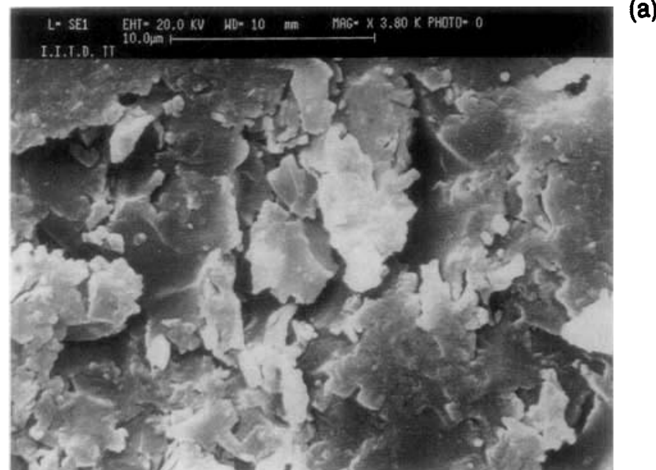
The data presented in Figure 2 shows upon close examination, that in the postcure composite samples, loaded with a high amount of the filler, the internal stress appears to have relaxed with the passage of time to its equilibrium value, while the stress continues to relax in the sample with low filler loading.

It is known[8,9] that during the cooling of the sample after high temperature curing, thermal stresses are set up as the polymer shrinks and that these thermal stresses cause cracks around the filler particles. The high modulus filler does not distort and, consequently, the brittle matrix cracks. This aspect was therefore investigated with the help of SEM.

The surfaces of the postcure cast sheet composite samples, containing 10 and 50 parts by weight of mica powder, were etched with concentrated nitric acid for 5 min to reveal the inner structure. The etched surfaces were then examined on a scanning electron microscope. As shown in typical micrographs presented in Figures 5(a) and (b), the sample with low mica content showed distinct microcracks, which were numerous, while the sample with high mica content had fewer microcracks. The microcracks appeared to arise from debonding of the interface between the filler and the resin or from matrix cracking. Since these microcracks would be expected to increase the specific volume of the resin in the composite, it was of obvious interest to reduce the composite specific volume data of Figure 3 to the specific volume of the resin alone. It is noteworthy that the normalized data, presented in Figure 6, shows that the resin in samples containing 10 and 20 pbw of mica has a higher specific volume than the neat resin. It would thus appear that the stress relaxation characteristics of the composite sample, containing a low amount of filler, could be related to such microcracks as these, providing a mechanism of relaxation of internal stress.

It is recognized that shrinkage stresses during cure, and thermal stresses due to differences between the thermal expansion coefficients of the matrix and the filler, may have major effects on the internal stresses within a composite material, which are often sufficient to produce microcracking even in the absence of external loads. It has been pointed out[10] that the residual stress distribution is difficult to map. Hull has shown[11] that in the fiber-reinforced matrix there will be a distribution of tensile and compressive microstresses present in the matrix, with tensile stresses being more likely at low volume fractions, and it is possible that these stresses may generate interface cracking. In flakes, the possibility of a tensile stress near the periphery of the flake is low. However, between two neighboring flakes and away from the edges (where the stresses would be

(a)



(b)

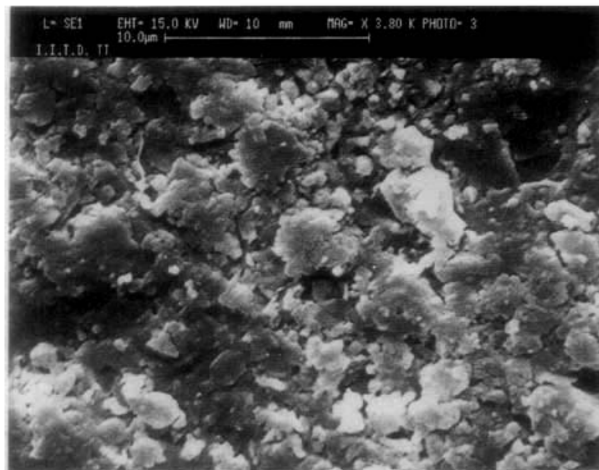


Figure 5 Scanning electron micrographs of epoxy resin sheets, filled with mica flakes, 6–32 μm in size, after etching: (a) containing 20 parts by weight of flakes and (b) containing 50 parts by weight of flakes.

expected to be mainly compressive), a tensile stress is likely to develop to maintain overall equilibrium. Low[12] has shown that residual stress plays a significant role in the failure process of filled epoxy systems. These residual stresses arise from the thermal expansion mismatch between the epoxy and the dispersed phase. He showed that compressive radial and tensile tangential stresses are generated at the interface when the filler has a lower thermal expansion mismatch between the epoxy and the dispersed phase. The presence of such stresses tends to enhance interface debonding and encourage catastrophic unstable fracture, resulting in a flat fracture surface.

Analysis of the Data Obtained from the Bending of Coated Metal Strips

The internal stress that arises in the coated metal strips was estimated using the following approximate approach. Assuming that the adhesion of the thin coating on the base aluminium strip is good, as was

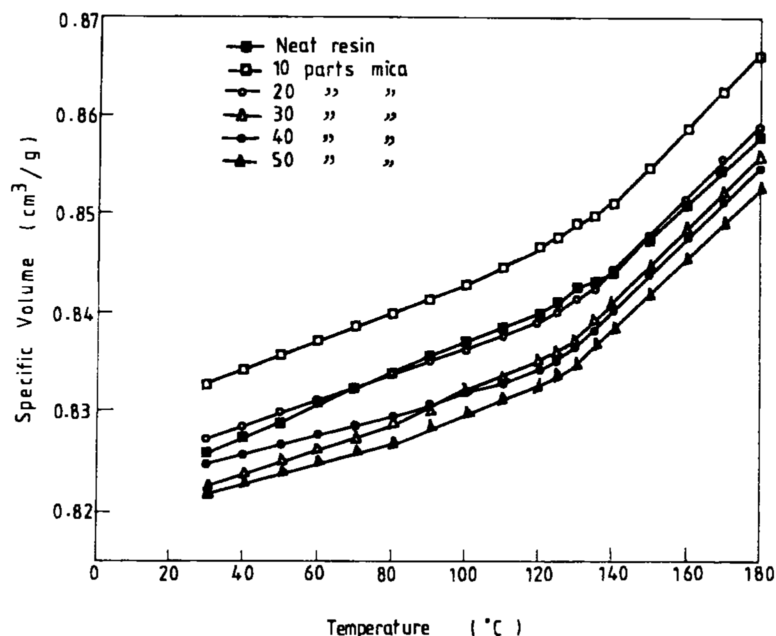


Figure 6 Specific volume–temperature plots of Figure 3, normalized for the resin alone.

the case for the neat resin,[1] the internal stress, σ_i, that would be expected to develop, due to the constraint to shrinkage of the composite layer as it cools from T_g to room temperature (T_r), would be given by[2,4]

$$\sigma_i = \int_{T_r}^{T_g} E_{\text{comp}}(\beta_{\text{comp}} - \beta_{\text{al}})\, dT \tag{2}$$

where E_{comp} is the elastic modulus of the composite layer and β_{comp} and β_{al} are the linear expansion coefficients of the composite layer and aluminium strip, respectively.

Table I Internal Stress in Epoxy Resin Filled with Mica Flakes (6–32 μm in Size)

	Internal Stress (MPa)		
	Calculated	Measured	
Postcured Sample	Eq. (2)	12 h	84 h
Neat resin	18.12	10.8	7.2
Mica-filled samples			
10 Parts by weight (pbw)	16.40	9.9	4.8
20 pbw	16.60	9.0	3.0
30 pbw	16.31	8.3	2.7
40 pbw	14.37	7.4	1.7
50 pbw	11.59	6.7	2.1

The estimated values of internal stress are shown in Table I; also included in Table I are the measured values of internal stress. It is noteworthy that, in the cases of all the samples studied, the value of internal stress, estimated from eq. (2), is much higher than the measured stress. Piggott made a similar observation[13] for the steel–epoxy system and attributed it to the viscoelastic behavior of epoxy resin. On the other hand, in composite laminates, such as carbon–epoxy laminates, cracking has been extensively observed due to residual thermal stresses and this also results in stress relaxation. It must be emphasized that in the present study, the first measurement of internal stress was made about 12 h after the oven had reached room temperature. A considerable amount of stress relaxation would already have occurred during this period. Considering this, the general trend predicted by eq. (2) appears to be satisfactory. The calculated values of internal stress for the various filled samples, which depend on the modulus, thermal expansion coefficient, and T_g of the composite layer, are not significantly different. This is apparently because the increase in modulus with increasing mica content is offset by the decrease in thermal expansion coefficient and also because the T_g of the filled samples is only slightly lower (Table II), as compared to the T_g of the neat resin. The lowering of T_g has been attributed[14] to the reduction in crosslink density, due to the presence of mica in the filled samples.

Table II Glass Transition Temperature of Epoxy Resin Filled with Mica Flakes (6–32 μm in Size)

Postcured Sample	Glass Transition Temp. (°C) From the Peak Position of Tan δ Peak in Torsion	Glass Transition Temp. (°C) Dilatometric
Neat resin	158	136
Mica-filled sample		
10 parts by weight (pbw)	153	133
20 pbw	147	130
30 pbw	150	130
40 pbw	148	127
50 pbw	146	126

Filled Samples Containing Mica Flakes, 106–212 μm in Size

The internal stress, as obtained from the bending of aluminium strips coated with epoxy resin, filled with 10, 20, and 30 parts by weight of mica flakes, 106–212 μm in size, and subjected to standard and postcure cycles, is shown as a function of time in Figure 7. There is significant stress relaxation, particularly in the postcure samples. The edge of the coated plate was observed on a scanning electron microscope. As shown in Figure 8, there is debonding of the aluminium–epoxy–mica interface, which will cause stress relaxation. This is in addition to the viscoelastic effects of the resin.

The edge of the cast epoxy sheet, containing 106–212 μm mica flakes, was etched and was observed under SEM. As shown in Figure 9, the thermal stresses induce the debonding of the mica–epoxy interface and flake delamination and matrix cracking also occur. These act as additional stress relaxation mechanisms.

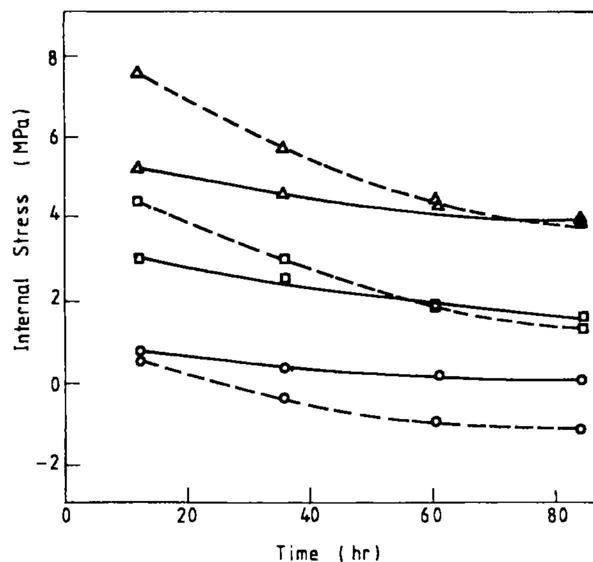


Figure 7 Internal stress data for standard cure (——) and postcure (- - -)-filled epoxy samples, containing mica flakes, 106–212 μm in size. (△) 10, (□) 20, and (○) 30 pbw.

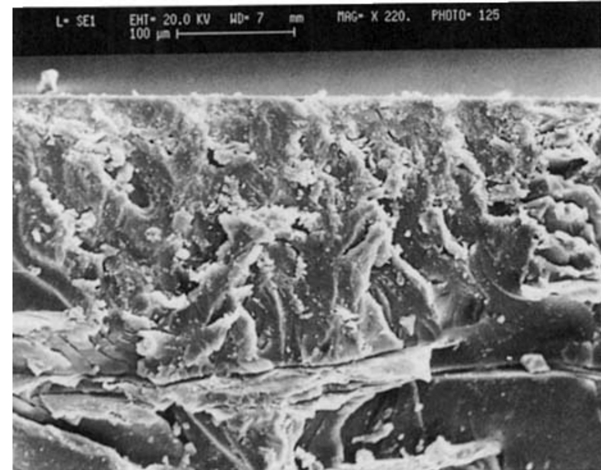


Figure 8 Scanning electron micrograph of aluminium strip, coated with epoxy resin, filled with mica flakes, 106–212 μm in size and seen along the edge; debonding of the interface has occurred.

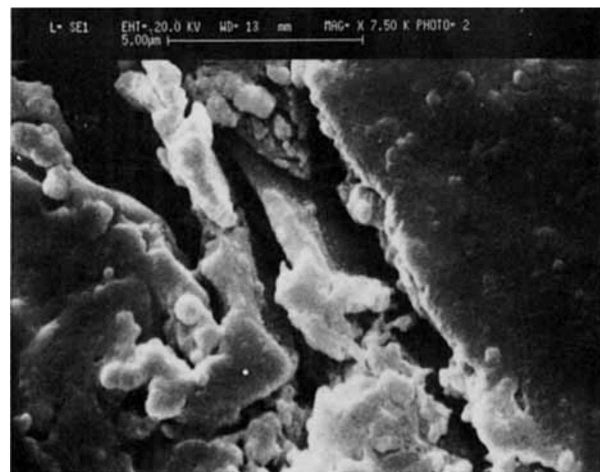


Figure 9 Scanning electron micrograph of cast epoxy sheet, filled with mica flakes, 106–212 μm in size, after etching; debonding of the interface and flake delamination have occurred.

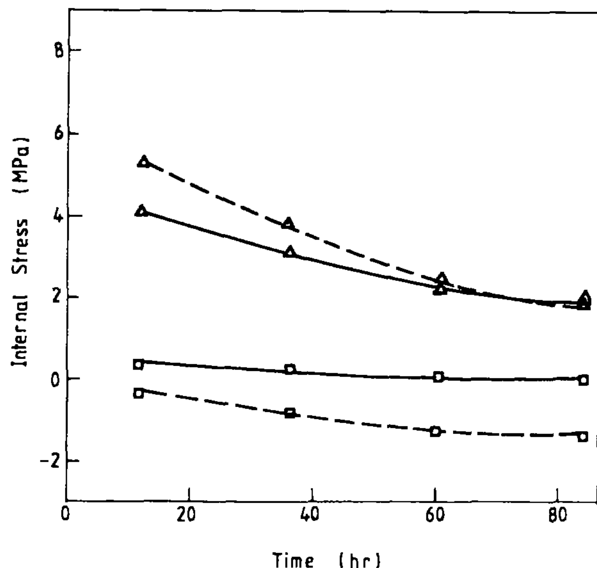


Figure 10 Internal stress data for standard cure (——) and postcure (---)-filled epoxy samples, containing mica flakes, 212–355 μm in size. (△) 10, and (□) 20 pbw.

Filled Samples Containing Mica Flakes, 212–355 μm in Size

The internal stress, as obtained from the bending of aluminium strips coated with epoxy resin, filled with 10 and 20 parts by weight of mica flakes, 212–355 μm in size, and subjected to standard and postcure cycles, is shown as a function of time in Figure 10. It is noteworthy that for the postcure sample containing 20 parts by weight of mica flakes, the internal stress becomes negative as the coated strip acquires a reverse curvature. An edgewise micrograph of the coated plate is shown in Figure 11 (in which the aluminium plate is towards the right end), and clear debonding of the interface can be seen.

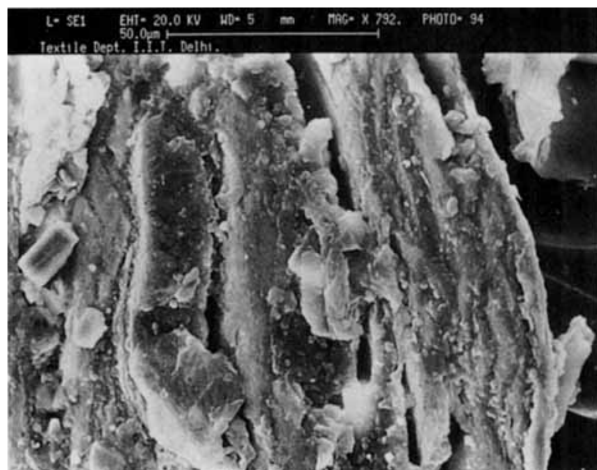


Figure 11 Scanning electron micrograph of aluminium strip, coated with epoxy resin, filled with mica flakes, 212–355 μm in size, seen along the edge; the interface has debonded.

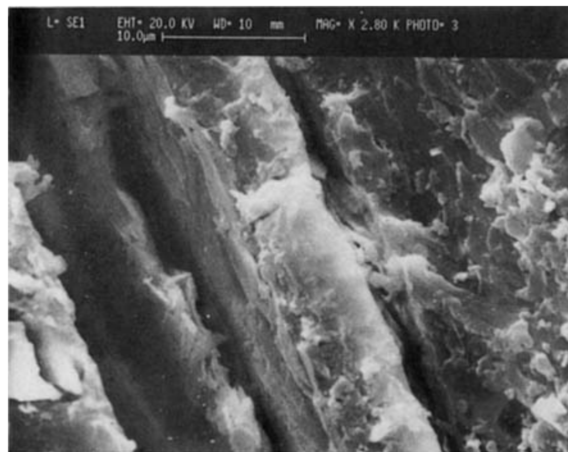


Figure 12 Scanning electron micrograph of cast epoxy sheet, filled with mica flakes, 212–355 μm in size, after etching; the flake–resin interfaces have debonded and flake delamination has occurred.

The etched cast sheet (Fig. 12) shows interfacial debonding on both sides of the flake and flake delamination in the middle.

Dynamic Torsional Spectra

In the earlier study[1] on internal stress in neat resin, it was shown that the α' peak, which spans the 50 to 100°C range in the dynamic torsional spectrum

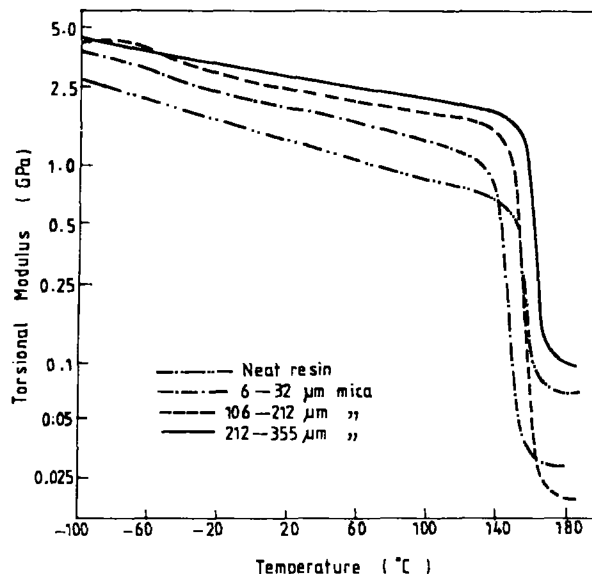


Figure 13 Storage Torsional Modulus of cast sheets of epoxy resin, filled with 20 parts by weight of mica flakes of different sizes.

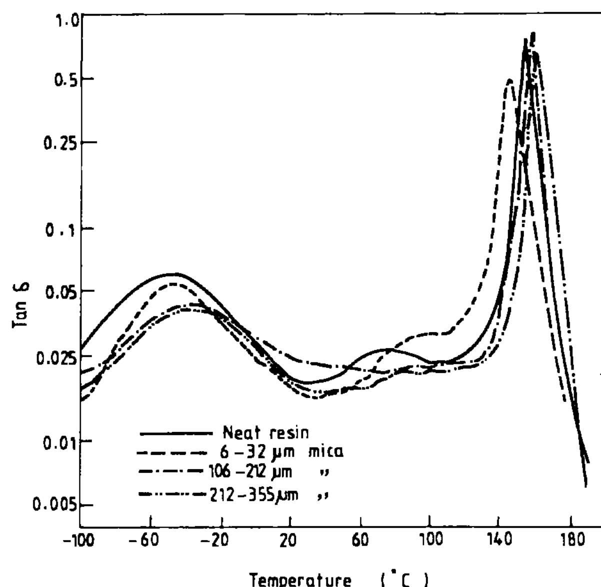


Figure 14 Torsional tan δ of cast sheets of epoxy resin, filled with 20 parts by weight of mica flakes of different sizes.

of the stoichiometric sample, is related to the frozen-in internal stresses. It was further shown that this peak becomes progressively more flat with the increase in aging time, thus suggesting that the internal stresses relaxed upon aging.

The dynamic spectra for some samples are presented in Figures 13 and 14, in which the effects of the filler, *viz.* mica flakes of varying sizes, on the torsional modulus and on the relaxation peaks of epoxy resin, containing 20 parts by weight of mica flakes, are shown. It is noteworthy that, below T_g, the torsional modulus increases with flake size and the α' peak is almost completely flat in the case of the filled sample containing mica flakes that are 212–355 μm in size, thus indicating that a reduction in internal stress is most pronounced in this case. This observation, made on a sample cut from the cast sheet, is supported by the earlier result that is reported for the coated metal strip, which also showed zero internal stress when the coating was of epoxy resin filled with 20 parts by weight of mica flakes of the same size.

Mechanical Properties of Filled Samples

The present studies have shown that, in the mica-filled samples, thermal stresses can induce cracks in the resin and between the resin and the flake and also can result in delamination of the mica flakes. These defects would be expected to have a significant effect on the mechanical properties of the mica-filled samples. Though a detailed study was made of the mechanical properties, only some data on filled samples, obtained from studies on the postcure sheet, are presented in Table III to give some idea of how the fillers affect these properties. It is observed that the effects are not so large as to render the mica-filled epoxy samples unfit for potential applications. The use of coupling agents may further reduce the adverse effect of the filler on the tensile strength of the filled material. Another possibility, which has been reported,[15] is the use of aminimide compounds as latent curing agents, which may result in an increase of strength of mica-reinforced epoxy resin.

Electrical Properties of Filled Samples

The dielectric constant and tan δ of the neat epoxy resin, and of epoxy resin containing 10 to 40 parts by weight of mica flakes, 6 to 32 μm in size, were measured at different temperatures as a function of frequency. The room temperature data, at frequencies of 10 kHz and 1000 KHz, are shown in Table IV. Since Muscovite Mica is stated[16] to have a dielectric constant of 6 to 7.5, the dielectric constant of the filled resin samples will be expected to be higher than that of the neat resin, as is the case (Table IV). However, while the samples, containing

Table III Some Mechanical Properties of Epoxy Resin Filled with 20 Parts by Weight of Mica Flakes

	Mechanical Properties		
Postcured Sample	Initial Modulus (GPa)	Tensile Strength (MPa)	Elongation-to-Break (%)
Neat resin	1.9	74	6.0
Mica flake-filled epoxy resin			
6–32 μm	2.5	50	2.5
106–212 μm	2.6	38	2.0
212–355 μm	2.7	32	1.4

Table IV Some Room Temperature Dielectric Characteristics of Epoxy Resin and Mica Flake-Filled (6–32 μm in Size) Epoxy Resin

Sample	Dielectric Constant		Tan δ	
	10 KHz	1 MHz	10 KHz	1 MHz
Neat resin	4.64	4.11	0.031	0.038
Mica-filled resin				
10 Parts by weight (pbw)	5.12	4.44	0.034	0.039
20 pbw	5.20	4.66	0.031	0.035
30 pbw	4.93	4.43	0.033	0.033
40 pbw	5.07	4.51	0.035	0.037

10 and 20 parts by weight of mica, show the expected increase, the increase in the dielectric constant of samples with higher loading of mica is less than expected. This may be explained as follows. As the data presented in Figure 6 shows, the resin is more densely packed in the samples containing 30 and 40 parts by weight of mica filler, while in samples with low loadings of mica, the resin is relatively loosely packed. Since dense packing will hinder displacement of the dipoles and also hinder the accumulation of charges at the filler–resin interphase, and since the dielectric constant is directly related to these two factors, the rate of increase of dielectric constant is reduced. The tan δ values, on the other hand, are not significantly affected, since the tan δ of Muscovite mica and of epoxy resin are close.

It is also worth pointing out that the dielectric strength of cured epoxy resin, at temperatures of up to 30°C, has been reported to be 75 kV/mm as compared with 1000 kV/mm for Musocovite mica.[16] Thus, the filled samples will be expected to gain in dielectric strength.

The reduction of internal stress in epoxy resin, when filled with mica, is of considerable interest in electrical and electronic devices. The importance of low thermal stress generation in microelectronic device encapsulation has been emphasized.[4]

CONCLUSIONS

The internal stress in mica-filled epoxy samples predominantly originates from the differential expansion (or contraction) between mica flakes and the epoxy matrix. These stresses are set up as the resin shrinks during the curing–cooling cycle and the thermal stresses thus generated can cause cracks in the matrix around and between the mica flakes and also can result in flake delamination. These provide additional stress relaxation mechanisms (in addition to resin viscoelasticity) and can lead to almost zero internal stress in the cast sample. The mechanical and electrical properties of the filled samples are satisfactory.

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