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Reduction of residual stress in montmorillonite/epoxy compounds

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An epoxy resin was cured while in intimate contact with small amounts of epoxyphilic montmorillonites. It was determined that cured epoxy exists within the montmorillonite interlayer by the observation of very high interlayer spacings, even greater than 8 nm. Generally, epoxy compounds containing montmorillonites that had been swollen in the curing agent prior to curing exhibited larger interlayer spacings, especially among the non-dispersed montmorillonite layers. The maximum observed residual stress was reduced by greater than 50% in the epoxyphilic montmorillonite/epoxy compounds over that of the pure epoxy. The epoxyphilic montmorillonite/epoxy compounds generally exhibited higher values of glass transition temperature, flexural modulus, and ultimate flexural strength than the pure epoxy. The tyramine–montmorillonite compounds typically had the highest values overall.

1. Introduction

A major advantage of epoxy materials has always been the relatively low cure shrinkage, of the order of 4%–8% [1–3]. However, this small amount of shrinkage may still produce residual stresses high enough to cause cracking and debonding in structural adhesives [4–6]. Regardless of the curing agent, shrinkage below the glass transition temperature, T_g, of epoxy resins increases linearly with a decrease in temperature, so that the operating temperature below T_g becomes very important [1, 6]. Shimbo *et al.* [1] have shown an approximately linear relationship between the shrinkage and the residual stress in the glassy region, except near the T_g.

The magnitude of these internal residual stresses depends on the glass transition temperature, thermal expansion coefficient and the elastic moduli of the epoxy, as well as the curing conditions and the degree of dimensional constraint [1, 4, 7]. The total strain in the resin comes from the shrinkage due to the chemical reaction, the thermal expansion or contraction with changes in temperature, and mechanical strain [4].

The addition of fillers reduces the slope of the residual stress temperature relationship below T_g [6]. Although different fillers behave differently in any one resin, they generally improve the resistance to cracking during thermal cycling. Large loadings of mineral fillers having small expansion coefficients have been used to decrease the shrinkage and internal stresses of epoxy in the glassy region [1]. While increasing the modulus and compressive strength, the addition of fillers to epoxy resins has the general tendency to decrease ultimate elongation, tensile strength and flexural strength [8]. However, at lower concentrations below 5% by weight, it has been shown in injection-moulded polypropylene that the flexural modulus and yield stress, as well as the ultimate tensile strength, remain essentially unchanged [9].

One can imagine that if an expandable smectite clay mineral such as montmorillonite [10] is added to the epoxy resin mixture and expands upon absorption of epoxy, the additional free volume developed within the clay interlayer might reduce the shrinkage and residual stress of the bulk epoxy resin sample.

In order to promote the absorption of epoxy material into the interlayer of the montmorillonite and improve the particle–matrix interactions, the montmorillonite must be modified to an organophilic or, more precisely, "epoxyphilic" nature. This can be done by replacing the naturally occurring inorganic cations with organic cations containing functional groups which react with either the epoxide group or the functional groups of the curing agent [11].

This paper discusses the effect on the residual stress and other physical properties of adding small amounts of modified montmorillonite to an epoxy resin.

2. Experimental procedure

2.1. Materials

The montmorillonite (MMT) used in this study was provided by ECC America Inc. under the trade name Mineral Colloid BP, and subsequently modified by cation exchange reactions to render epoxyphilic [11]. The as-received MMT, originally consisting mainly of sodium cations in the interlayer, has an average particle size of 75 μm in the dry state, and dimensions of

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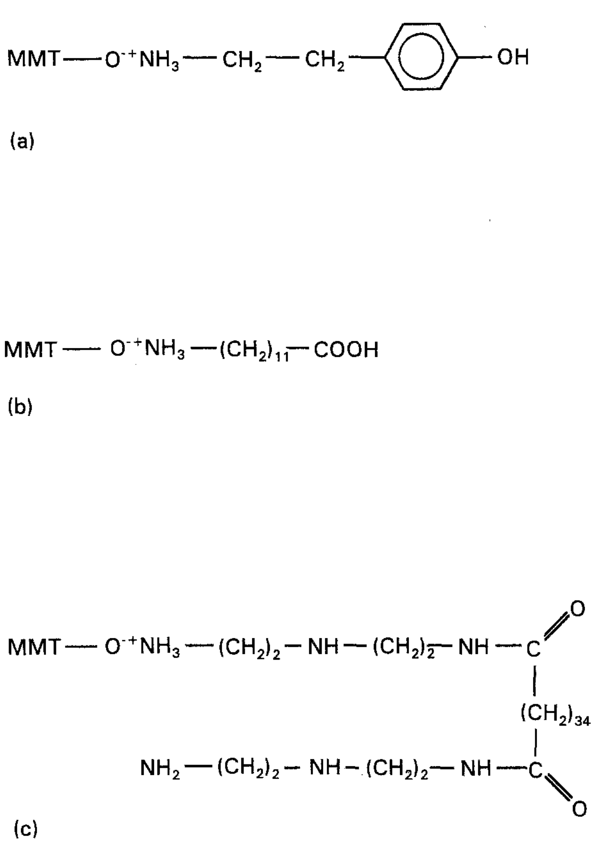

Figure 1 Chemical structures of modified montmorillonites used in this study. (a) TYR-MMT, (b) ALA-MMT, (c) V40-MMT.

about 0.1 μm in length and width when dispersed in water. It has a cation exchange capacity of 90 meq/100 g.

The epoxide resin, EPON 828, a diglycidylether of *bis*-phenol A was provided by Shell Chemical Company. The curing agent, EPON "R" V-40 (Henkel Corporation's Versamid 140) was also provided by Shell Chemical Co. It is a condensation product of polyamines, such as diethylene triamine, with dimer acids or fatty acids. Many isomers of dimer fatty acids and many possible condensation reactions are used in the manufacture of Versamid resins [12].

Three modified MMTs were used in this study. They include montmorillonites with organic cations derived from (a) tyramine hydrochloride (TYR-MMT), (b) aminolauric acid (ALA-MMT) and (c) the polyamide curing agent "R" V-40 (V40-MMT) (Fig. 1).

2.2. Methods

The epoxy materials were prepared by first swelling various concentrations of the modified MMT for a specified period of time and temperature in either the curing agent or epoxide resin. They were mixed daily using a vortex mixer to promote absorption of organic material by the larger MMT particle agglomerates that have a tendency to settle. After swelling for the specified time, the appropriate amount of the other epoxy component (either epoxide resin or curing agent) was then added. The ratio of curing agent to epoxide resin was 80 parts per hundred resin (p.h.r.) (i.e. 55% epoxide resin and 44% curing agent for pure epoxy) corresponding approximately to a 1:1 ratio of active amine hydrogens to epoxide groups. Because the modified MMTs contain amine hydrogen within their structures, this will slightly modify the actual ratio between active hydrogen and epoxide groups. The mixture was then mixed by hand for 2–3 min and poured into an aluminium mould cavity (10 mm × 50 mm × 100 mm) sprayed with a non-silicone mould release agent, Mold Wiz.

Residual stress measurements were calculated from the birefringence of the cast moulded epoxy samples as observed in a polarizing microscope with a 550 nm sensitive plate placed between the sample and the analyser at 45° to the crossed polarizing elements as described in ASTM C-978 [13]. In order to determine the proper sign of the residual stress, the sample was first placed 0° to the polarizer, then rotated + 45° (blue position) and then rotated − 90° (orange position) observing the colours at both positions. The birefringence was calculated by dividing the equivalent retardation, as determined according to the ASTM standard, by the specimen thickness. The stress-optical coefficient was determined on the pure epoxy using a polariscope as described in ASTM D-4093 [14]. A sample was machined from a block to produce a specimen with a neck section having the dimensions 6.32 mm × 5.75 mm with parallel sides. The specimen was placed between cross polarizers in a polariscope set up in transmission. An increasing tensile force was slowly applied to the specimen. At the appearance of each successive fringe (zero retardation), the force was recorded. The force values were then converted to stress by dividing by the cross-sectional area of the specimen neck. The stress-optical coefficient was determined by the slope of the stress versus fringe-order line. The residual stress of the epoxy materials was then calculated by dividing the birefringence by the stress-optical coefficient. The stress-optical coefficients of the epoxy matrix in the MMT/epoxy composites (which contain 2%–5% MMT) were assumed to be the same as the pure epoxy.

X-ray diffraction studies were conducted on specimens cut from the cast moulded samples. The bottom surface of the specimen, being very flat, was exposed to the X-ray radiation. A Phillips XRG 3100 X-ray generator equipped with a nickel-filtered CuK_α (1.5418 nm) X-ray source, connected to a Phillips APD 3520 type PW 1710 diffractometer controller, was used. The scanning speed was 0.005° $2\theta\,s^{-1}$. Intensity values were corrected using a sine function to account for errors resulting from geometrical considerations at low angles.

Small-angle X-ray scattering (SAXS) was performed on a Rigaku Denki 2201 goniometer equipped with a Rigaku Denki Rotaflex RU-200 X-ray generator (CuK_α/nickel filtered). Lorenzian corrections of SAXS curves were done by multiplying the intensity (counts per second) by S^2 where $S = 2\sin\theta/\lambda$ ($\lambda = 1.54178$ nm).

Glass transition temperatures were obtained on 5–10 mg samples cut from the cast moulded piece on a Perkin–Elmer DSC-7. The samples were scanned at a rate of 10 °C min^{-1} from 30–100 °C, held for 60 min to ensure completion of the epoxy reaction, and scanned again. The T_g values reported are from the second scan.

Dynamic mechanical characterization was conducted using a Perkin–Elmer DMA with a three-point bend fixture attached. The specimens (1 mm × 2.5 mm × 20 mm) were cut from the centre of the cast moulded samples using a diamond saw at low speed. The specimens were conditioned at 100 °C for 7 h. A temperature sweep at 5 °C min^{-1} from 25–120 °C at a frequency of 1 Hz was used to determine the tan δ for the epoxy materials in addition to the dynamic modulus.

Static three-point bend tests were performed on specimens (1 mm × 2.5 mm × 20 mm) cut from the centre of the cast moulded specimens using a diamond saw and conditioned at 100 °C for 7 h, identically as in the dynamic mechanical test. A Scott Tester with a mini load cell attachment was used [15]. Previous studies have proven the validity of this test procedure [15, 16]. The deflection rate was approximately 40 mm min^{-1}. The modulus, stress and strain were calculated as described in ASTM D-790 [17].

A Jeol 840-A scanning electron microscope was used to observe the particle–matrix adhesion and particle sizes in the cured epoxy/MMT composites on the fracture surface from the static three-point bend test.

3. Results and discussion

All the test results in this paper, unless otherwise noted, were determined on the same moulded specimen for each sample material in order to avoid batch-to-batch differences. Concentrations of MMT above 10%–20% resulted in uncured epoxy samples due to very low mobility. Therefore, only concentrations below these values will be reported.

3.1. General observations

A wide variety of swelling conditions and MMT concentration levels were tested with three different modified MMTs to determine which samples should be further studied in depth. The criteria used to choose samples for further study included the degree of absorption of epoxy material between the layers of the MMT as measured by X-ray diffraction, and the extent of cross-linking as measured by the glass transition temperature.

3.1.1. General absorption behaviour

A detailed study on the swelling behaviour of ALA-MMT is reported elsewhere [18]. However, the effect of the swelling conditions on the final MMT interlayer spacing will be reviewed here.

A wide-angle X-ray diffractometer (WAXD) was used to determine the absorption of epoxy by observing changes in the 001 spacing (*d*-spacing) of the MMT layers. This technique is limited to a maximum spacing measurement of 8.6 nm. The effect of the epoxy component, either the epoxide resin or the polyamide curing agent, in which the MMT is swollen is shown in Fig. 2 for a fully cured epoxy sample containing 5% ALA-MMT swollen for 5 days at 80 °C. As indicated by the broad peak near 3 nm, cured epoxy exists between the MMT layers when swollen in the curing agent (a), but apparently not to any great extent when swollen in the epoxide (b). The intensity of the 1.7 nm peak in the epoxide swollen sample, which corresponds to the spacing of ALA-MMT alone, is much more intense than the 1.25 nm peak. This 1.25 nm peak corresponds to the spacing observed in pure Na-MMT indicating a collapse of the ALA-MMT layers, probably due to desorption of aminolauric acid during the cure process [18]. Similar results for cured samples of TYR-MMT and V40-MMT are observed. As swelling time is increased, the intensity and sharpness of the peak near 3 nm is enhanced. Similarly, increasing the swelling temperature increases the intensity and definition of this peak.

The effect of MMT concentration is shown in Fig. 3. As concentration is increased, absorption is decreased under the same swelling conditions. MMT layer dispersion becomes less efficient with increasing concentration because less epoxy material is available per volume of MMT and therefore absorption is less efficient.

A limited number of experiments was performed using small-angle X-ray scattering. The appearance of peaks near 8.5, 10 and 17 nm are evident for V40-MMT swollen in the curing agent for 1 day at 55 °C (Fig. 4). This proves that many MMT layers are dispersed throughout the matrix.

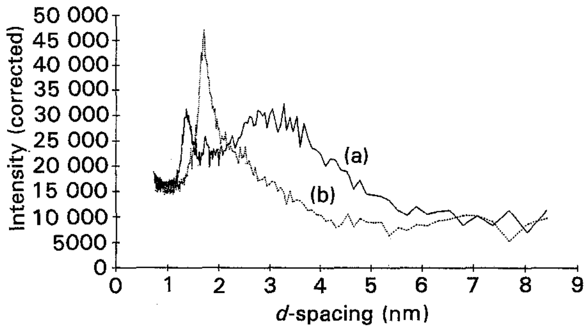

Figure 2 X-ray diffractometer scans of fully cured epoxy samples containing 5% ALA-MMT swollen for 5 days at 80°C in (a) V-40 curing agent, or (b) epoxide resin.

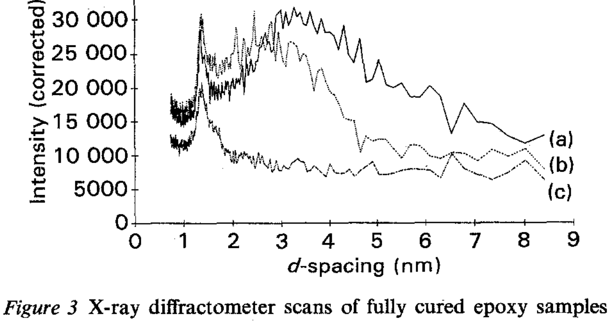

Figure 3 X-ray diffractometer scans of fully cured epoxy samples containing (a) 5% V40-MMT, (b) 10% V40-MMT, or (c) 20% V40-MMT swollen in the curing agent for 5 days at 80 °C.

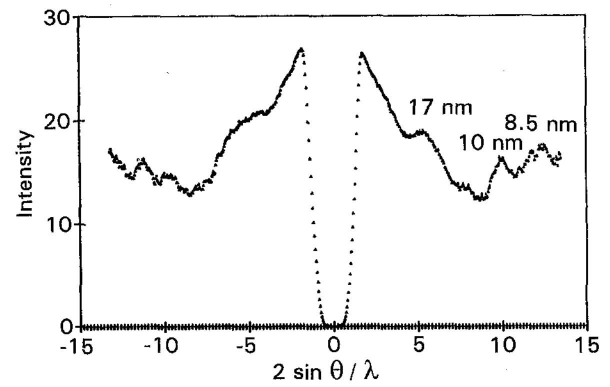

Figure 4 Small-angle X-ray scattering scan for a fully cured epoxy sample containing 5% V40-MMT swollen in the curing agent for 1 day at 55 °C.

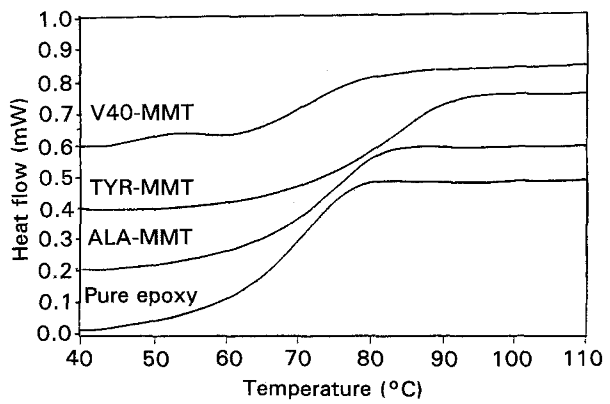

Figure 5 Typical DSC scans for pure epoxy and epoxy containing low compositions of V40-MMT, TYR-MMT and ALA-MMT.

3.1.2. Extent of cure

In many cases, the T_g of the composites was higher than that of the pure epoxy. This is due to two factors: reinforcement of the epoxy molecules by the MMT layers, and the character of the organic cation intercalated into the MMT interlayer. Fig. 5 shows typical DSC curves for the pure epoxy and clay/epoxy compounds. Shorter segments between cross-links and more rigid segments between cross-links would raise the T_g of epoxy, e.g. ethylenediamine cross-linked epoxy has a higher T_g than TETA cross-linked epoxy which, in turn, has a higher T_g than Versamid 140 cross-linked epoxy [19]. The increase in T_gs observed in the MMT-epoxy compounds implies that some reactions with the epoxyphilic montmorillonite interlayer surfaces may have occurred. The observation that the T_g of MMT-epoxy composites resulting from swelling of the modified-MMT in the polyamide curing agent is higher than that from the swelling in the epoxide resin, also corroborates with the notion that the epoxy reaction has a greater tendency to occur in the interlayer when the modified MMT is swollen in the curing agent prior to the addition of the epoxide resin.

The modification chemistry plays an important role in the glass transition behaviour of the epoxy materials. The TYR-MMT epoxy compounds generally have slightly higher T_gs than the ALA-MMT and V40-MMT epoxy compounds when prepared under the same conditions. With the 5% TYR-MMT epoxy compounds, higher T_gs are observed when swollen in the curing agent rather than in the epoxide (Fig. 6). Because TYR-MMT results in more absorbed epoxy when swollen in the curing agent, the individual layers may act as reinforcement which restricts the movement of the epoxy, thereby raising the T_g slightly. A rise in heat distortion temperature, which is related to T_g, has been reported for clay/epoxy composites in which the individual layers were dispersed throughout the epoxy [20].

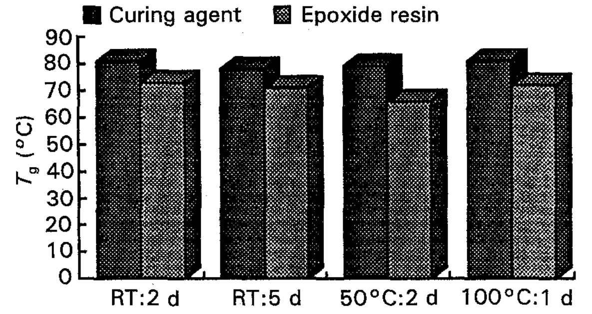

Figure 6 The effect of swelling conditions on the glass transition temperature of epoxy composites containing 5% TYR-MMT.

It can be concluded from these initial studies that swelling the MMT in the curing agent results in better absorption of epoxy and that increasing the duration and temperature of swelling improves the amount of absorption that has occurred after curing is complete. However, swelling the MMT in curing agent for 10 days or longer at 80 °C or higher, often adversely affects the curing reaction which results in longer post-cure requirements and, in extreme cases, much lower final T_gs. This is probably due to thermal degradation of the curing agent. These effects are not as apparent when MMT is swollen in the epoxide resin.

3.2. Further evaluations

The samples chosen for further study include T_gs equal to or higher than pure epoxy after several days of post-curing at room temperature. These samples include those that show evidence of poor absorption, as well as those showing good absorption to determine the effect, if any, on the physical properties. The swelling conditions for the epoxy composites chosen for further study are listed in Table I. The interlayer spacings and relative intensities of these montmorillonite/epoxy compounds are shown in Table II.

3.2.1. Residual stress

Table III lists the maximum birefringence values for each sample and the corresponding maximum residual stress calculated from the measured stress optical coefficient of $450 \times 10^{-13}\,m^2\,N^{-1}$. The addition of modified MMT to epoxy under the specified swelling and curing conditions reduces the residual stress by approximately 60% as measured by this technique.

The residual stress profile in the unfilled epoxy is much more clearly defined than in the filled epoxy

TABLE I *d*-spacings and relative intensity of montmorillonite/epoxy composites; S = strong, M = medium, Sh = shoulder, Br = broad, D = diffuse

Sample code	MMT type	Swelling agent	Swelling temp. (°C)	Swelling time (d)
A	Pure epoxy			
B	2% TYR	Epoxide Resin	22 (RT)	3
C	2% TYR	Curing Agent	50	3
D	2% TYR	Curing Agent	22 (RT)	3
E	5% TYR	Curing Agent	22 (RT)	2
F	2% V40	Curing Agent	50	4
G	5% ALA	Curing Agent	22 (RT)	6
H	2% ALA	Epoxide Resin	80	5

TABLE II Swelling conditions of montmorillonite/epoxy composites

Sample	*d*-spacing (nm)	Relative Intensity
B 2% TYR-MMT	1.47	Strong
C 2% TYR-MMT	1.35	Medium
	2	Shoulder
D 2% TYR-MMT	1.39	Strong
	2.2–4.2	Strong
E 5% TYR-MMT	1.32	Strong
F 2% V40-MMT	1.34	Medium
	1.9	Shoulder
G 5% ALA-MMT	1.38	Strong
	3.6	Strong, broad
H 2% ALA-MMT	1.74	Strong
	2 +	Shoulder, diffuse

TABLE III Maximum birefringence and the corresponding residual stress of epoxy and montmorillonite/epoxy composites

Sample	Max. birefringence $(\times 10^5)$	Max. residual stress (MPa)
A Pure epoxy	13.1	2.9
B 2% TYR-MMT	5.0	1.1
C 2% TYR-MMT	5.0	1.1
D 2% TYR-MMT	4.3	1.0
E 5% TYR-MMT	5.1	1.1
F 2% V40-MMT	5.2	1.2
G 5% ALA-MMT	4.3	1.0
H 2% ALA-MMT	4.4	1.0

samples. The MMT particles, no doubt, block the transmission of light. In addition, stress fields surrounding some particles are evident for thinly sliced specimens. The reduction in maximum residual stress, however, is still clear.

The development of residual stress in these systems results from two distinct phenomena. As the epoxy resin cross-links, its T_g rises from approximately -30 °C through the curing temperature, where the epoxy becomes glassy as main-chain motion ceases, up to its final T_g near 70 °C. The residual stress increases in the glassy state as the amount of shrinkage increases with the continued cross-linking reaction. As the cured epoxy is cooled to room temperature, residual stresses are increased due to thermal contraction.

As the cross-linking reaction occurs, especially in the case when epoxyphilic MMTs are swollen in the curing agent, the growing epoxy chains are absorbed into interlayer space. The cross-linking reaction in the interlayer would lock-in free volume in the non-dispersed layers. If the shrinkage due to the cross-linking reaction is accompanied exactly by the creation of free volume as the MMT expands, then no residual stresses will be developed. As the composite contracts thermally, some additional stresses may develop around the MMT particles due to the different thermal expansion coefficients of the MMT and epoxy.

3.2.2. Dynamic mechanical behaviour

Dynamic mechanical behaviour can elucidate the mechanical properties of the epoxy molecules with minimum effects from the voids or large agglomerates, because the molecules themselves are being tested rather than the bulk continuum. Typical DMA temperature sweep scans for TYR-MMT, ALA-MMT and V40-MMT epoxy compounds, as well as pure epoxy, are shown in Fig. 7. The room-temperature dynamic modulus of the compounds is found to be greater or unchanged from pure epoxy (Fig. 8). With the exception of the V40-MMT sample (F), the temperature of the onset of the tan δ, which correlates well with the T_g as measured by DSC, for the composite materials is equal to or greater than that of the pure epoxy.

Fig. 9 shows glass transition temperatures obtained from DSC measurements for the epoxy compounds (B–H). All T_gs are greater than or equal to pure epoxy (A) which corroborates with the tan δ data.

3.2.3. Electron microscopy

Fig. 10 clearly shows the layered structure of the MMT on the micrometre level where bulk epoxy may be absorbed, providing a mechanism for good adhesion between large particles and the epoxy matrix to complement the interactions on the nano-scale. For applied purposes, techniques such as improved mixing, dispersants, and ultrasound must be utilized in order to break down the agglomerates to the elementary particles. This would improve the swelling behaviour (and thus improved shrinkage compensation and reduction of residual stress) and the particle–matrix interaction.

4. Conclusion

Cured epoxy material was shown to exist between the layers of epoxyphilic montmorillonites resulting in significant increases in interlayer spacings. Spacings greater than 8 nm were observed using small-angle X-ray scattering.

The glass transition temperature of the epoxy composites was observed to increase over that of the virgin epoxy, especially when the modified montmorillonites

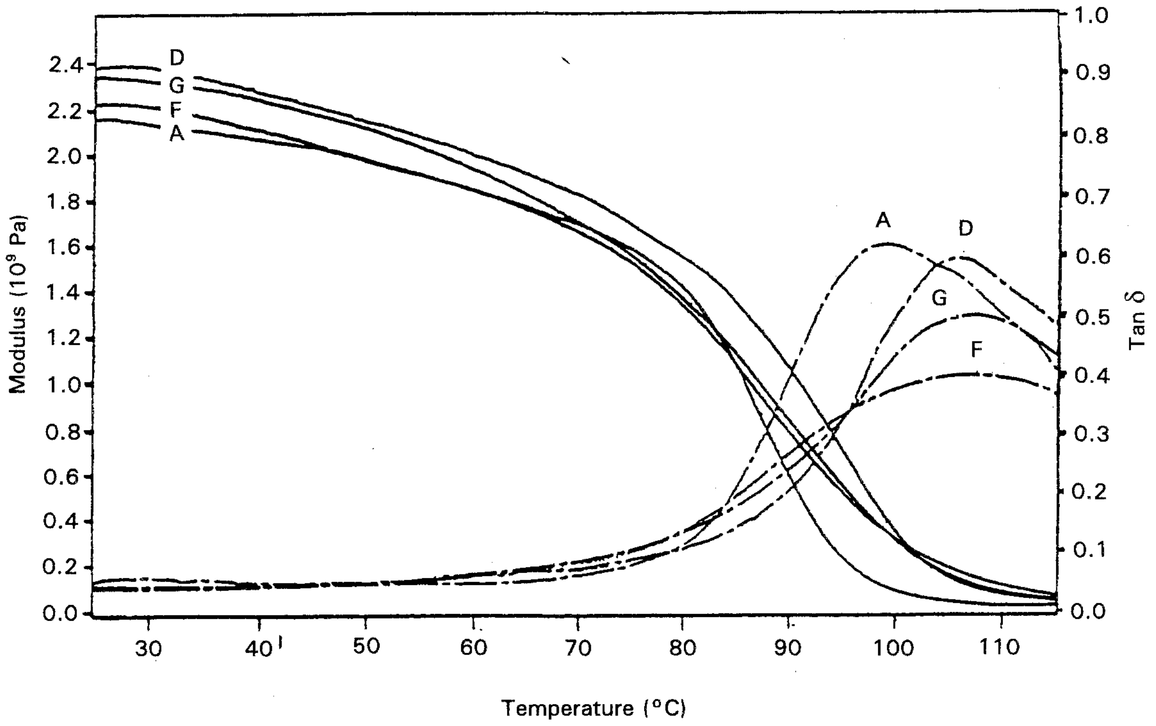

Figure 7 Typical DMA scans at 1 Hz from 25–120 °C for pure epoxy and epoxy/MMT composites. (——) Storage modulus, (- - -) tan δ.

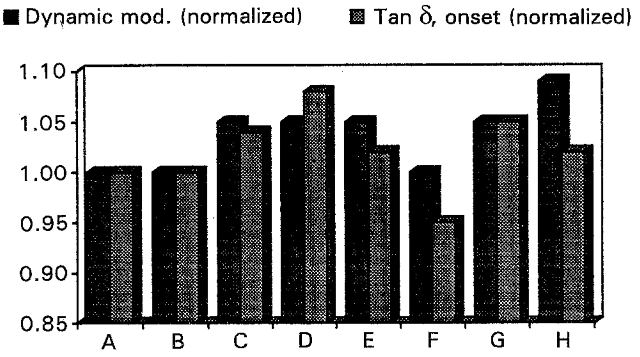

Figure 8 Dynamic modulus and tan δ values, normalized with respect to pure epoxy (A), of montmorillonite/epoxy composites (B–H).

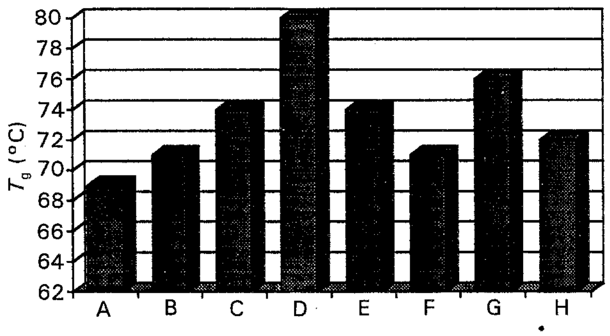

Figure 9 Glass transition temperatures of pure epoxy (A) and montmorillonite/epoxy composites (B-H).

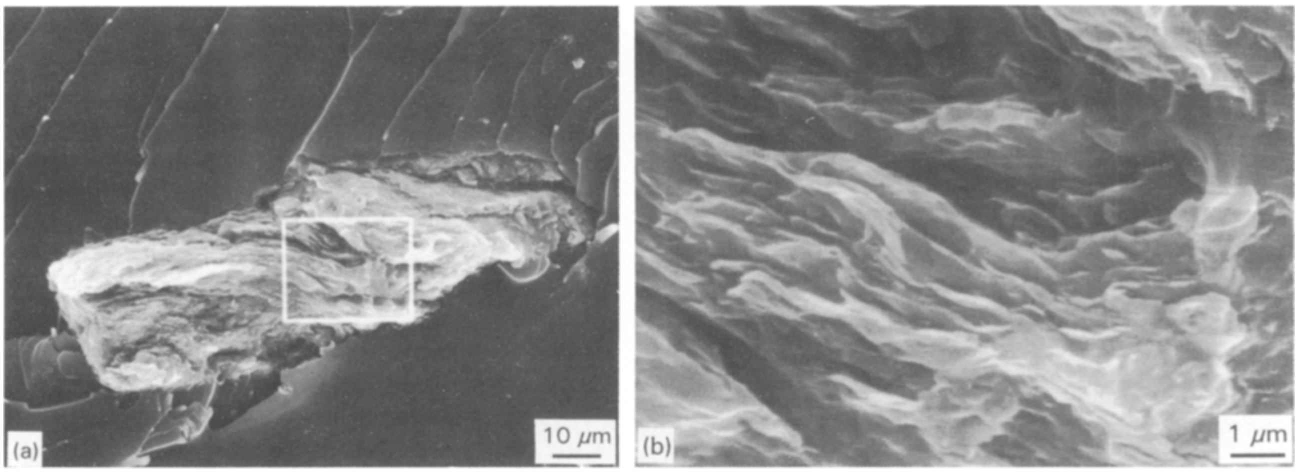

Figure 10 Evidence of the layered structure of montmorillonite at different magnifications.

were swollen in the curing agent prior to curing of the epoxy.

The maximum observed residual stress in cured epoxy, as observed by birefringence measurements, was reduced by more than 50% upon the addition of the epoxyphilic montmorillonites at low concentrations.

The flexural modulus of the montmorillonite/epoxy composites as measured by dynamic mechanical analysis, was shown to remain unchanged or increase slightly over pure epoxy, with the largest increase observed for the tyramine-modified montmorillonite.

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