

# Nanoscale highly filled epoxy nanocomposite

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## Abstract

A new technique has been developed to prepare a highly filled epoxy-montmorillonite (MMT) nanocomposite using an organically modified MMT. Composites with clay content up to 70 wt.% exhibit unusual transparency, which is related to the spatial distribution of the mineral nanodomains. Dispersion of the layered silicate within the crosslinked epoxy matrix was verified using X-ray diffraction pattern, revealing layer spacings of 30 and 70 Å. Examination of these materials by scanning electron microscopy and transmission electron microscopy showed that intercalates have wholly layered morphology at all scales, oriented parallel to the surface of the specimen and have good wetting to the silicate surface by the epoxy matrix. Silicate lamellae intercalated with epoxy resin assembled into a cluster of about 50–120 nm thickness. These clusters assembled into superclusters with an average thickness of 300 nm. Studies by the Vickers hardness test of an epoxy-MMT nanocomposite containing 60 wt.% MMT indicated that the diamond pyramid hardness was 10–29 kg/mm<sup>2</sup>. © 2002 Elsevier Science Ltd. All rights reserved.

**Keywords:** Epoxy; Montmorillonite; Nanocomposite; Intercalation

## 1. Introduction

Nanocomposites are a relatively new class of materials, which exhibit ultrafine phase dimensions, typically in the range 1–100 nm [1]. Experimental work on these materials has generally shown that virtually all types and classes of nanocomposites lead to new and improved properties when compared to their micro- and macro-composite counterparts [1].

Polymer nanocomposites, especially polymer-layered silicate nanocomposites, represent a radical alternative to conventionally (macroscopically) filled polymers. Because of their nanometer-size dispersion, the nanocomposites exhibit markedly improved properties when compared with the pure polymers or conventional composites. These include increased modulus and strength [2], decreased permeability [3,4], decreased shrinkage

[5,6], increased heat resistance and decreased flammability [7,8].

Montmorillonite (MMT) belongs to the general family of 2:1 layered silicates. Their crystal structure consists of layers made of two silica tetrahedra fused to an edge-shared octahedral sheet of either aluminum or magnesium hydroxide. Isomorphic substitution within the layers generates negative charges that are normally counterbalanced by cations residing in the interlayer space. In pristine layered silicates the interlayer cations are usually hydrated Na<sup>+</sup> or K<sup>+</sup> ions. Ions exchange reactions with cationic surfactants including primary, secondary, tertiary and quaternary ammonium ions rendering the normally hydrophilic silicate surface organophilic. The organic cations lower the surface energy of the silicate surface and make intercalation of many engineering polymers possible due to improving the wetting characteristics with the polymer matrix.

The reactions of chemically modified smectite clays and organic molecules typically afford intercalation compounds (with well-defined compositions and basal

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spacing) [9] and clay-polymer hybrid composites. The latter composites are engineering polymers encapsulated between smectite clay particles. Toyota researchers discovered several clay-polymer nanocomposites, including systems based on the dispersion of alkylammonium exchanged forms in semicrystalline nylon 6 [10] and polyimide [3,11]. It has been reported in the patent literature [12] that dispersed MMT particles improved several mechanical properties of amine cured epoxy resin. However, it was necessary to use *N,N*-dimethylformamide as a swelling solvent to achieve clay delamination in the polymer matrix. Wang and Pinnaivaia have reported delamination of MMT in an epoxy resin by heating an onium ion exchanged form of MMT with epoxy resin to temperatures of 200–300 °C [13]. The product of the high temperature curing reaction is an intractable powder rather than a continuous solid epoxy matrix.

It has been demonstrated that the feasibility of dispersing molecular silicate layers within a macromolecular matrix, results in significant improvements in physical properties with only modest particulate contents (<20 wt.%). Thus, it seems that a great need still exists for the development of a nanocomposite with a high content of the clay. Therefore, the present paper is directed to prepare an epoxy-MMT nanocomposite in an attempt to improve the physical properties. The delamination of the resulting matrix at lower temperatures than previously reported [13] can be processed. Also, the structure and the morphological hierarchy of its nanostructure are studied. In addition, the physical transparency of the resulting composites at high content of the clay is examined.

## 2. Materials

The clay mineral used in this study was organophilic MMT from Southern clay products, Inc. (Gonzales, Texas) under the trade name of claytone (APA). The APA was received as fine particles. The  $d_{001}$  (interlayer or interlamellars) spacing is 18.4 Å. The percentage of organic content (dimethyl benzyl hydrogenated tallow ammonium chloride) was 24%. Trifunctional low viscosity epoxy type (Araldite XVMY 0505) and aromatic hardener (HY 5200) were obtained from Ciba Geigy Inc. The ratio of epoxy/hardener was 3:1 by weight.

## 3. Analytical procedure

Thermogravimetric analysis (TGA) was performed using a Perkin Elmer thermal analyzer system under nitrogen flow at a heating rate of 10.0 °C/min.

The Morphology of the composite was examined by a JOEL JXA-840 scanning electron microscopy (SEM).

A compression molded specimen was deposited on double sided scotch and examined at the fracture surface. The specimen was coated with gold to improve SEM imaging.

Transmission electron microscope (TEM) examination was made for ultra thin films on a Joel JEM-IOOSX instrument at an accelerating voltage of 100 kV. These films were obtained from compression molded plaques after embedding in a low viscosity epoxy resin (spurr).

Wide angle X-ray diffraction (WAXD) measurements were carried out for compressed molded samples using a Phillips autodiffractometer equipped with Ni-filtered Cu-K ( $\lambda = 1.5418 \text{ \AA}$ ) at a scanning rate of 0.008°/s. The diffracted beam of X-rays was also detected photographically. The samples were mounted on paper (non-crystalline material) with glue as adhesive. A strip of X-ray film is held in a circular position around the sample and the surface of the specimen was directed parallel and perpendicular to the ray. After development, the distance on the film from the central spot to a given arc ( $a$ ), together with the radius of the camera ( $x$ ) will determine the diffraction angle ( $\theta$ ) using the equation  $\tan^{-1}(a/x) = 2\theta$ . Hence, the spacing  $d_{001}$  can be calculated from Bragg's equation  $n\lambda = 2d \sin \theta$ .

The Vickers hardness test was measured on a square base diamond pyramid as the indenter. The included angle between opposite faces of the pyramid was 136°. This angle was chosen because it approximates the most desirable ratio of the indentation diameter to ball diameter. A 500 g load was applied at room humidity (50%) to both epoxy and epoxy-MMT (60 wt.% MMT) nanocomposite samples. The diagonals of the indenter were then measured (at 20-magnification) using the optical microscope. The Diamond pyramid hardness number (DPH) was calculated using the following equation [14]:

$$\text{DPH} = 2P \sin(\theta/2)/L^2 = 1.854P/L^2 \quad (1)$$

where  $P$  is the applied load (kg),  $L$  is the average length of diagonals (mm),  $\theta$  is the angle between opposite faces of diamond (136°).

## 4. Experimental

Claytone (APA) was washed with a MeOH/H<sub>2</sub>O (50/50) mixture five times to remove the organic content adsorbed on the surface. After washing, the organic content was found to be 18%. In an electric mixer 10 g of prewashed APA and 250 ml of acetone was stirred for 15 min at room temperature, when a suspension was obtained. To the stirred suspension a mixture of epoxy, hardener and acetone, in the ratio (3:1:20) respectively, was added followed by continuous stirring for 30 min. The content of MMT in this composite was calculated

(55 wt.%). Different composites were also prepared at different MMT contents of 60, 65 and 70 wt.%. The product of each composite was spread on a sheet of aluminum covered with Teflon to form thin films and dried in a vacuum oven at room temperature for 20 h. The thin films were collected in a cylindrical mould which was previously sprayed with a non silicon mould release agent, then compressed at 15,000 psi for 2 h at 110 °C, followed by 2 h at 150 °C and finally for 2 h at 180 °C. The pressure was removed and the mould was allowed to cool at 10 °C/min to room temperature. The produced samples were transparent with 1.7-mm thickness. Interestingly, the optimized clarity of the resulting composite materials was obtained using epoxy (RE-2038) and hardener (HD-3475) from Hysol products Inc., and by decreasing the curing cycle temperature to 100 °C.

## 5. Results and discussions

The synthetic procedure used for nanocomposite preparation was achieved in two stages: The first includes the intercalation of epoxy and the hardener to the organically modified MMT. The second stage includes the curing of intercalated epoxy resin.

An organically modified silicate was prepared by a cation exchange reaction between the sodium cation in MMT and dimethyl benzyl hydrogenated tallow ammonium chloride. The presence of these alkylammonium cations in the interlayers (galleries) renders the hydrophilic character of MMT and increases its organophilic nature, i.e. increases its swelling in organic solvent and improves the wetting characteristics of the polymer. Accordingly, the long chain alkylammonium in the MMT tends to attract epoxy and hardener, which fa-

cilitates its migration into the clay layers. As the curing reaction proceeds, the adsorbed epoxy reacts with amine in the interlayer resulting in an increase in the interlayer space. An improvement in the properties of the resulting composite materials would be expected.

All previous work confirms that the formation of exfoliated clay nanocomposites is dependent on the nature of the alkylammonium-exchanged clays. Long alkyl chains between the galleries allow new organic species to diffuse between the layers more easily and progressively exfoliate the clay. The exfoliation of the clay in a polymer matrix requires the driving force of polymerization to overcome the attractive electrostatic force between the negatively charged silicate layers and the gallery cations. Preintercalation of epoxy into clay interlayer prior to curing reaction should facilitate the exfoliation. It is worth noting that the inorganic exchanged forms of MMT such as Na-MMT are hydrophilic and not readily swelled by epoxy resin, making intragallery curing impossible. Therefore, a conventional composite in that case is formed.

TGA data (Fig. 1) shows that for a composite (60 wt.%), there is no weight loss up to 250 °C. The single step at this temperature corresponds to polymer decomposition. The lack of a weight decrease at a temperature lower than 250 °C indicates that there is no release of any molecules from the host during heating. The total weight loss recorded at 250 °C is 40%, which amounts to a 1:1.5 ratio of organic/MMT. The amount of organic/MMT in the other composites corresponds to the initial feed of MMT in the nanocomposites.

The XRD pattern of the APA powder (Fig. 2A) shows a silicate (001) reflection at  $2\theta = 4.8^\circ$ . This silicate reflection corresponds to a layer d-spacing of 18.4 Å. This indicates that there is an increase of  $\approx 9$  Å from the van der Waals gap of Na-MMT. The XRD of cured

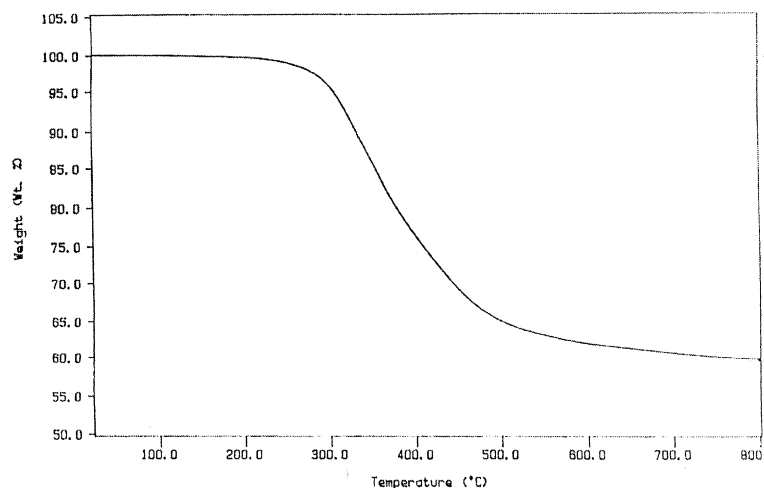


Fig. 1. TGA of cured epoxy-MMT nanocomposite (60 wt.% MMT).

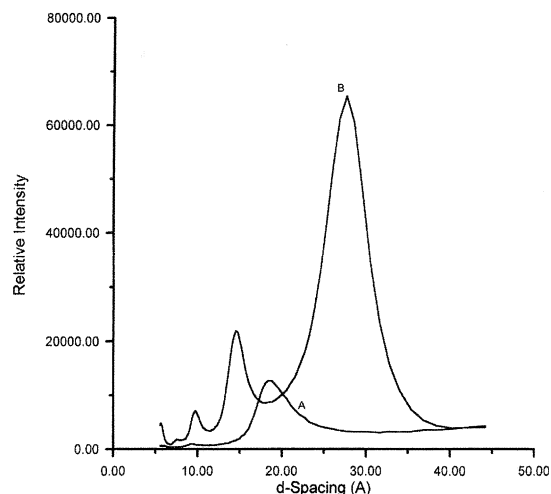


Fig. 2. XRD patterns for (A) claytone, (B) compression molded sample of claytone-epoxy nanocomposite containing 60 wt.% MMT.

epoxy-MMT (Fig. 2B) shows a reflection at  $2\theta = 3^\circ$  ( $d_{001} = 29.4 \text{ \AA}$ ) with no peaks observed for residual organophilic at  $d_{001} = 18.4 \text{ \AA}$ . Consequently, the thickness of epoxy resin residing within the interlayer spacing is equal to  $11 \text{ \AA}$  which can be determined by subtracting the thickness of the organophilic silicate ( $18.4 \text{ \AA}$ ) from the observed  $d_{001}$  spacing ( $29.4 \text{ \AA}$ ). The reflections observed at  $2\theta = 3^\circ, 5.7^\circ, 8.6^\circ$  correspond to the (001), (002), (003) reflections of the epoxy-intercalated phase, respectively.

X-ray diffraction patterns for epoxy-MMT 60 wt.% are shown in (Fig. 3a,b) with the incident beam perpendicular and parallel to the fractured surface samples respectively. When the beam was directed perpendicular to the fractured surface, two arcs symmetrically arranged on each side of the central spot which was produced by the undeviated beam. This confirms a highly ordered multilayered structure. The arrows near 30 and  $70 \text{ \AA}$  indicate that cured epoxy exists between the MMT layers. Increasing the  $d$ -spacing suggests a high degree of adsorption of epoxy and hardener that is held by van der Waals forces. Since the interlayer surface is organophilic and has a great tendency to adsorb organic molecules, an exfoliated nanocomposite is achieved.

It has been established on the basis of electron microscopy studies [15] that the stacks of parallel layers (lamellae), with an average of about 10 lamellae, form a primary particle (10 nm). Association of these several primary particles which are nearly parallel, joined together laterally, form micro-aggregates (few hundreds of nm). Finally, a large number of primary particles and micro-aggregates, form an aggregate (0.1–10  $\mu\text{m}$ ).

Toyota's researchers described in their patent [12] a procedure to prepare an epoxy-MMT composite con-

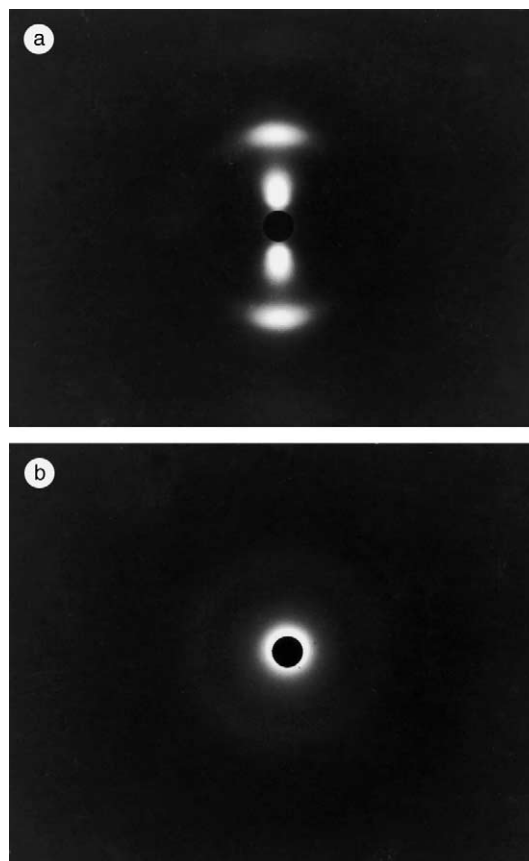


Fig. 3. X-ray diffraction pattern of epoxy-MMT (60 wt.%) when the incident beam (a) perpendicular to the surface, (b) parallel to the surface.

taining only 5.3% MMT using a modified MMT derived from aminolauric acid. The patent narrates that the X-ray diffractometry of a molded nanocomposite material gave no peak attributable to the (001) plane of MMT. This indicates that the individual layers of MMT were uniformly dispersed in the polymer. However, it has been pointed out [16] that these data do not justify the formation of nanocomposite materials. Also, Moet and Akelah [5] have mentioned that the interlamellar expansion is possible without disaggregation of MMT. Therefore, evidence by SEM is necessary to unveil the morphological hierarchy of the resulting compressed molded composite.

SEM photographs in Figs. 4–6 clearly prove that the samples are homogenous with no phase separation between silicate layers and epoxy matrix with excellent apposition between the layers and the polymeric matrix. At the macrometer scale ( $\times 100$ ), in Fig. 4, the graph shows clearly the layered structure where bulk epoxy may be adsorbed providing a good adhesion between the MMT layers and the epoxy matrix. Hence, the technique

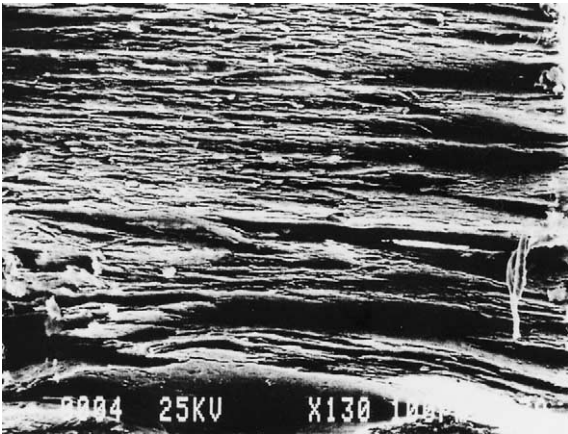


Fig. 4. Scanning electron micrograph of epoxy-MMT ( $\times 130$ ).

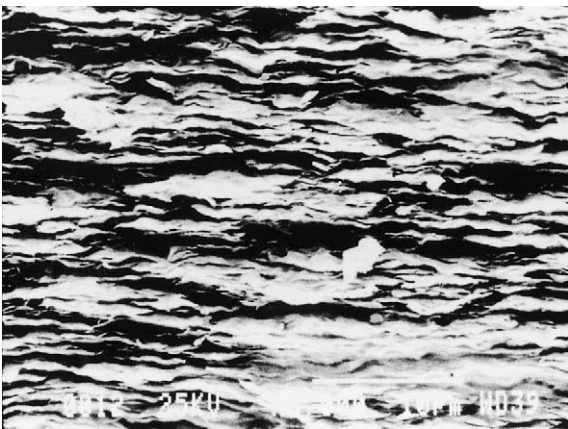


Fig. 5. Scanning electron micrograph of epoxy-MMT ( $\times 3,000$ ).

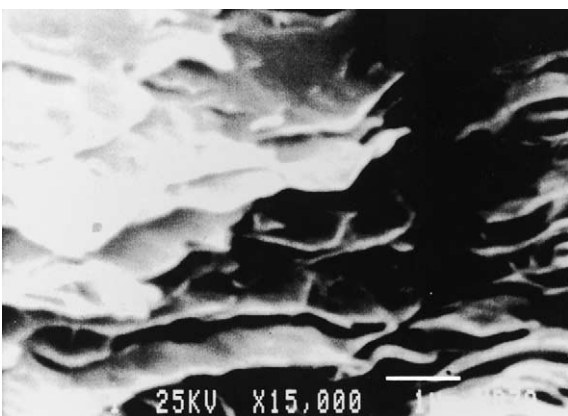


Fig. 6. Scanning electron micrograph of epoxy-MMT ( $\times 15,000$ ).

leads to breakdown of the agglomerate and improves the particle matrix interaction by using a good solvent and mixer. This reassembles to nodular-layered structures with thickness 1–3  $\mu\text{m}$ . At the micrometer scale a layered supercluster is observed in Fig. 5. The thickness of these superclusters is in the range 200–500 nm with an average thickness of 300 nm and oriented parallel to the surface of the specimen. Associations of these superclusters form the nodular structures that have been observed on the fracture surface of the compression-molded sample. At the nanometer scale (Fig. 6) ( $\times 15,000$ ) these superclusters show oriented smaller subunits (clusters) with a thickness in the range 50–120 nm. Therefore, it can be concluded that the composite has a special layered structure at all scales and the plane of the layers orient parallel to the surface of the specimen. The uniqueness of this system is this layered structure.

In order to fully characterize the nanocomposite material, TEM of a microtomed section of compression molded samples was examined. A typical TEM image of the epoxy-clay nanocomposite containing claytone is shown in Fig. 7. A face-face morphology like seawater waves with high orientation can be observed. This morphology is correlated with the morphology obtained by SEM. At low magnification Fig. 7a (micro scale)

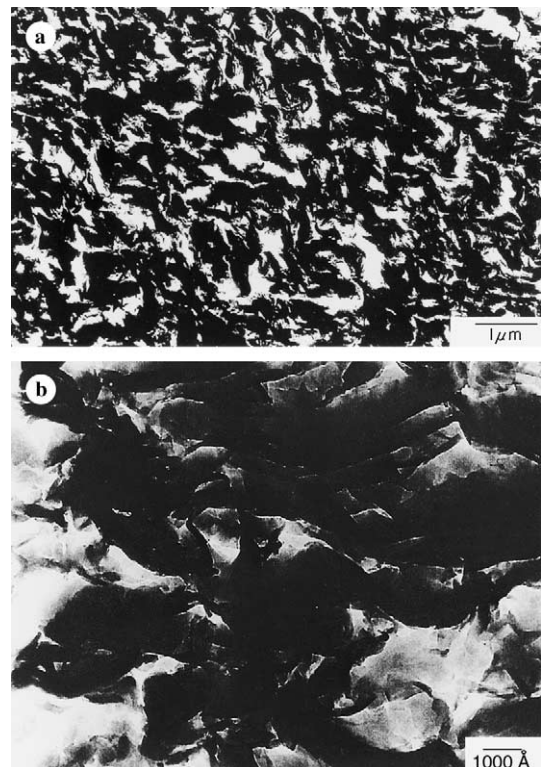


Fig. 7. Transmission electron micrograph of microtome section prepared from compression molded samples (a) low magnification, (b) high magnification.

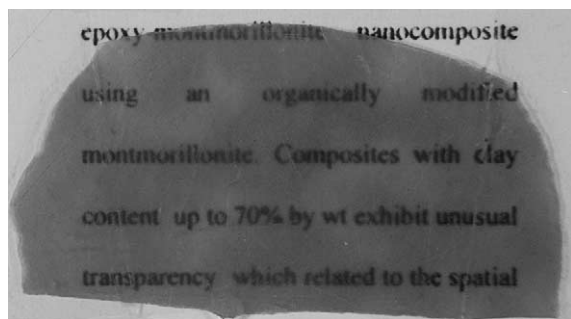


Fig. 8. Transparency of epoxy-MMT (60 wt.% MMT) nanocomposite.

photograph provides unambiguous evidence for the oriented layered structure and reveals that the agglomerate clay has been dispersed by the epoxy into packets (supercluster) with size range (0.3–0.5  $\mu\text{m}$ ). At high magnification, Fig. 7b (nanoscale), the dark lines are intersections of clusters of the composite with thickness 50–100 nm. It would be reasonable to suggest that to achieve this ultra high ceramic content in this nanocomposite a high level of oriented stacking is necessary. Also, the process conditions and the arrangement of the inorganic clay in the nanocomposite, which could vary from isotropic dispersion to oriented stacking, have great effects.

Although the hybrids contain clay up to 70 wt.%, the compressed molded samples are transparent as is ordinary epoxy resin (Fig. 8). This fact is explained by the molecular level dispersion of MMT of a size smaller than the wavelength of visible light. This result is very encouraging since improved or novel properties of the composite material would be expected with homogenous dispersing size going down to such a nanometer level.

The hardness of the composite (60 wt.%) was measured using Vickers test. The measurements are carried out for five samples. The DPH values calculated using Eq. (1) are 10–13 and 10–29  $\text{kg/mm}^2$  for the epoxy resins the end composite respectively.

## 6. Conclusions

Nanostructured MMT has been successfully dispersed into an epoxy matrix. The agglomeration of MMT particles has been reduced significantly, as evidenced from the morphology studies. The synthetic approach involves intercalation of epoxy resin within an organically modified MMT, followed by curing of the crosslinked network. The driving force for reduction of

particle agglomeration was known, so this work demonstrates one practical way to obtain exfoliated nanoscale particles of MMT and homogenous epoxy/MMT nanocomposite with high content of MMT up to 70 wt.%. The hybrid had a special structure in which MMT was dispersed homogeneously and dispersed parallel to the surface. Although the hybrids include up to 70 wt.% of MMT, the materials are as transparent as ordinary epoxy. This fact is explained by the molecular level dispersion of MMT of a size smaller than the wavelength of visible light. The reinforcement provided by the silicate layers at 60 wt.% loading was manifested by an improvement in hardness properties.

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