J MATER SCI **41** (2006) 2929–2937

Mechanical and barrier properties of epoxy polymer filled with nanolayered silicate clay particles

T. P. MOHAN, M. RAMESH KUMAR, R. VELMURUGAN*
Composites Technology Centre, Indian Institute of Technology Madras, Chennai, 600 036, India
E-mail: rvel@iitm.ac.in

The diglycidyl ether of bisphenol A (DGEBA) epoxy resin system filled with organo clay (OC) and unmodified clay (UC) were processed separately by two different curing agents. Triethylene tetramine (TETA) and Diaminodiphenyl methane (DDM) hardeners were used as curing agents. The nanocomposites were processed by shear mixing at different clay concentrations (1, 2, 3 ,5 and 10 wt%). The OC and UC were characterized by x-ray diffraction (XRD) technique. The morphology of the nanocomposites was obtained by XRD and Transmission Electron Microscopy (TEM). Bending and Impact tests conducted on these materials revealed that the organo clay filled epoxy resin showed good improvement in property over unmodified clay filled epoxy composites. The mass uptake of the nanocomposites was studied in the acid, base and water mediums. It is observed that the mass uptake in the acid medium is higher than in other mediums. The equilibrium mass uptake in all the mediums for nanocomposites was found to be lower compared to neat epoxy polymer system.

1. Introduction

Polymer filled with nanoclay particles has gained a significant interest in the recent years. The increased strength, toughness, heat distortion temperature and barrier properties paved the way for this material to find the application in the automotive to aerospace industries. The improvement in the property is attributed due to the large surface area, high aspect ratio (diameter/thickness) and high crystallinity of the clay nano particles [1, 2]. In order to find suitable application in high performance areas like aerospace, marine etc, the knowledge of this new class of materials in the corrosive environments is essential.

The barrier property of the polymer with nanoclay particles is reported for the various thermoset and thermoplastic materials. The barrier property of the nanocomposites has increased to great extent due to the presence of hard nanolayer which hinders the diffusion of solvent molecules and also increases the tortuosity path which makes the diffusion of solvent molecule a time consuming process. It is further observed that diffusion of the solvent molecule differs in intercalated and exfoliated nanocomposite. The exfoliated nanocomposite structure restricts the diffusion path more when compared to the intercalated structure or conventionally filled micro composites [3–6].

The epoxy/clay system placed in the water environment is studied [7]. It is stated that water molecules strongly interact with the specific polar groups of the epoxy matrix and also detach the matrix resin from the reinforcement in the composite material which degrade the properties like young modulus, glass transition temperature and hardener degradation etc. The epoxy/clay system in the acid and base medium was studied by Wang and co-workers [8]. They have stated that the mass uptake in the acid environment is higher than that in the water and base medium.

This work mainly deals with the study of micro and nano scale clay particle, filled individually in the epoxy polymer and the effect in each condition. The epoxy/clay nano(micro) composites are processed under different curing conditions namely hot and cold curing. The mass uptake in the water, acid and base medium is studied. The properties of the nanocomposites in the corrosive medium with the effect of process condition, particle size and distribution are studied in detail.

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*Author to whom all correspondence should be addressed.

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DOI: 10.1007/s10853-006-5164-4

2. Experimental details

2.1. Materials

The matrix material is the DGEBA epoxy system. The room and high temperature curing agents namely Triethylene tetramine (TETA) and Diaminodiphenyl methane (DDM) are used for curing of the epoxy resin system. The epoxy and the curing agents are obtained from CIBA Ltd., Basle (Switzerland). Organo clay and unmodified clay are used as reinforcement in the epoxy system. The organo clay nanoparticle is the alkyl quaternary ammonium clay available from Southern Clay Products Inc, Gonzales, Texas (USA).The unmodified Na^+ bentonite clay is obtained from Ennore clays and Mudds Ltd, Chennai (India).

2.2. Nanocomposite synthesis

The nanocomposites consisting of the organo clay in the epoxy system are processed by two different means to study of effect of processing conditions in the properties of bulk material. The room temperature processing consists of mixing of clay of 1, 2, 3, 5 and 10 wt% in the epoxy resin system by means of shear mixer. The mechanical shear mixer rotates at ∼1000 rpm in the epoxy clay solution. The mixing is done until the clay particles are uniformly distributed in the matrix resin. During mixing the clay particles induces the viscosity besides the resins viscose nature. This viscose force favors the separation of nanoclay platelets thereby favoring the formation of intercalation/exfoliation in the matrix. 10 wt% of TETA hardener is added for curing the epoxy resin. During the hot curing conditions, the epoxy resin is initially heated to 120°C for 1 h. The clay is then gently added in to the resin bath and mixed using shear mixer until uniform dispersion of clays takes place in the matrix medium. Though the viscosity of the resin mixing is relatively slower than the room temperature curing conditions, the clay platelets will easily separate by means of easy diffusion of the polymer monomers inside the clay galleries due to high operating temperature. The 25 wt% of the DDM hardener is added at 80°C and maintained at this temperature for 4 h until it is fully cured. The nanocomposite specimens processed by the above mentioned process are tested for the characterization and property studies.

2.3. Characterization and property studies

X-ray diffraction (XRD) was preformed for the clay particles to study the interlayer separation. It was carried out with a scanning rate of 2°/min with CuKα radiation ($\lambda = 1.541$ Å) operating at 30 KV and 15 mA. Thin foils of about 100–200 nm thick specimens were made for Transmission Electron Microscopy using Philip electron microscopy instrument operating at 200 KV. Inorder to carry out the mass uptake in the acid, base and water medium, five specimens in each medium were prepared with the dimension of 50 × 50 × 3 mm and kept in the beakers containing 0.1 N of H_2SO_4 acid and NaOH base solutions. After certain interval of days the samples were taken, dried with a paper towel and weight was measured by using analytical scales. 3-point bending tests were carried according to ASTM D-790, and the Izod impact tests were carried according to ASTM D-256.

3. Results and discussion

3.1. Morphology of nanocomposite

The XRD pattern for the organo clay (OC) and the unmodified clay (UC) is shown in Fig. 1. It is seen that the basal spacing for the organo clay is ∼17 Å and for the unmodified clay is 13 Å. This shows that the interlayer distance for the organo clay is higher than that of the unmodified clay. The presence of organo ion in the interlayer gallery region of OC causes higher d-spacing than the unmodified clay. The organo ion tends to attract the polymer and as a result of this, the matrix polymer can easily penetrate in to the interlayer gallery region of the organo clay and form nanocomposites by dispersing the nanolayers in the matrix. This nanocomposite formation is absent in the unmodified clay filled polymer. The hydrophilic nature of Na^+ in interlayer region of UC restricts the penetration of polymers in to the interlayer gallery, and this leads to the formation of conventional particle filled composites [9]. The XRD pattern of epoxy with OC and UC fillers synthesized at RTC and HTC were shown in Figs 2–5. In Fig. 2 of room temperature cured epoxy-OC

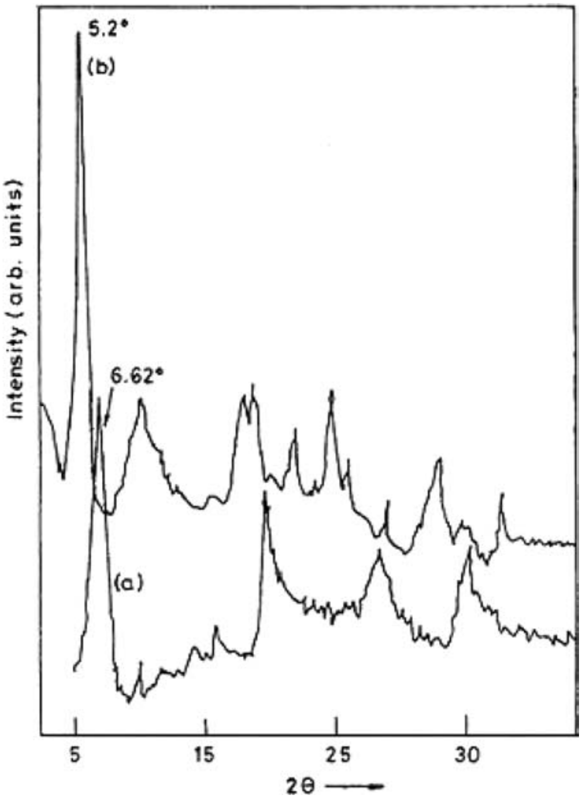


Figure 1 XRD pattern of (a) Na^+- Bentonite and (b) Organoclay.

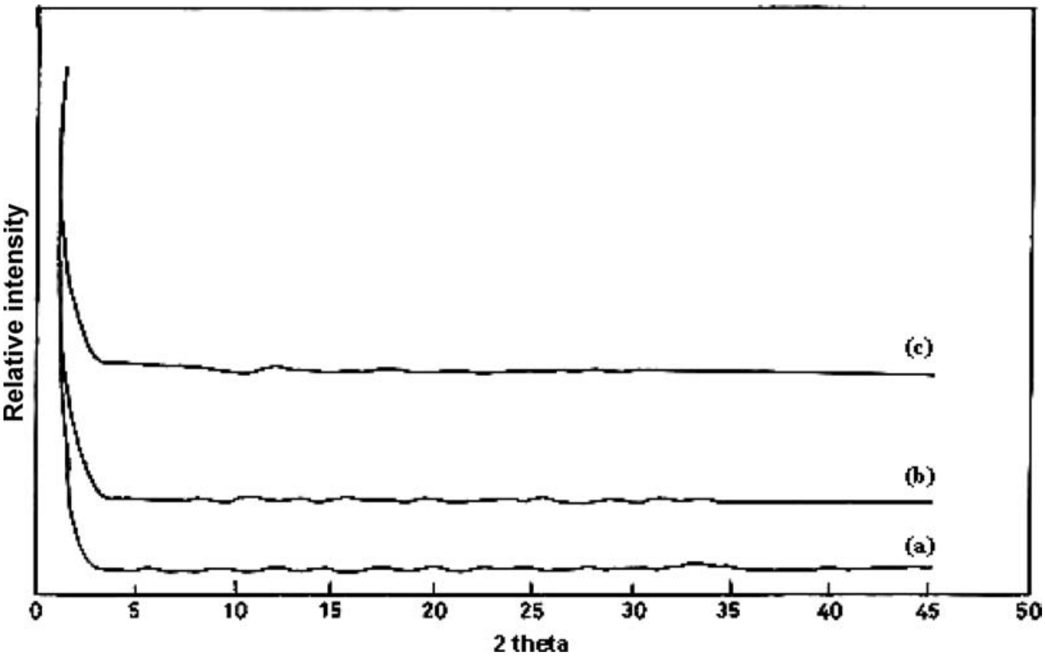


Figure 2 XRD pattern of RTC epoxy with (a) 1 wt% OC, (b) 2 wt% OC and (c) 10 wt% OC.

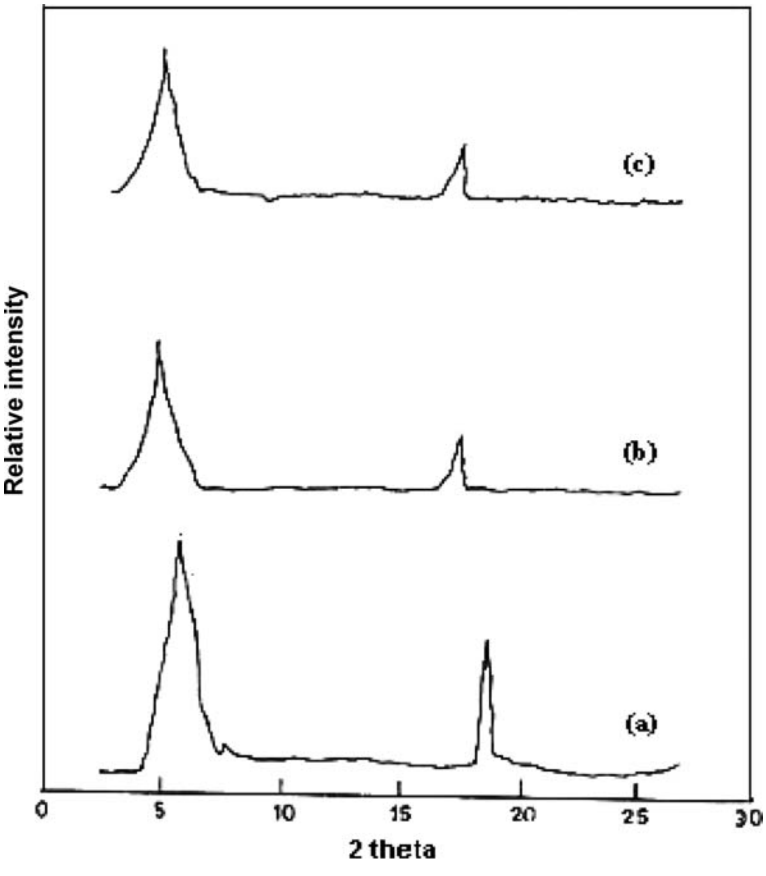


Figure 3. XRD pattern of RTC epoxy with (a) 1% UC, (b) 3% UC and (c) 10% UC.

nanocomposites, the 001 basal reflection of OC is absent, which indicates that the clay layers are completely exfoliated or the interlayer distance is more than 70 Å. In Fig. 3 of room temperature cured epoxy-UC composites, there is very negligible change in the d-spacing of UC and this shows that the UC filled epoxy act as conventional micron scale particle filled polymer composites. Fig. 4 shows the diffraction pattern of epoxy with OC series

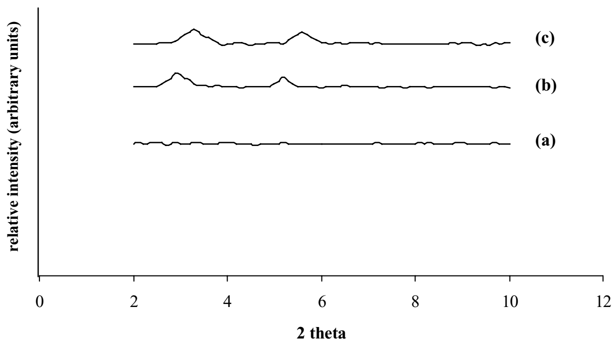


Figure 4 XRD pattern of HTC epoxy with (a) 2% OC, (b) 3% OC and (c) 10% OC.

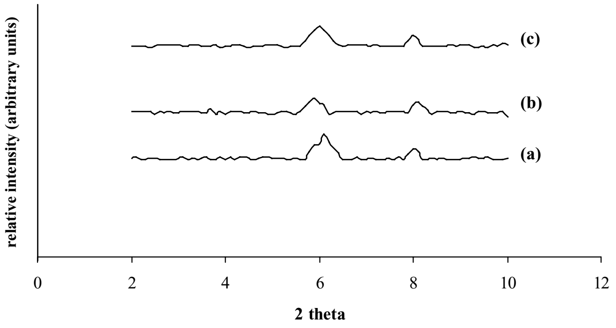


Figure 5 XRD pattern of HTC epoxy with (a) 1% UC, (b) 3% UC and (c) 10% UC.

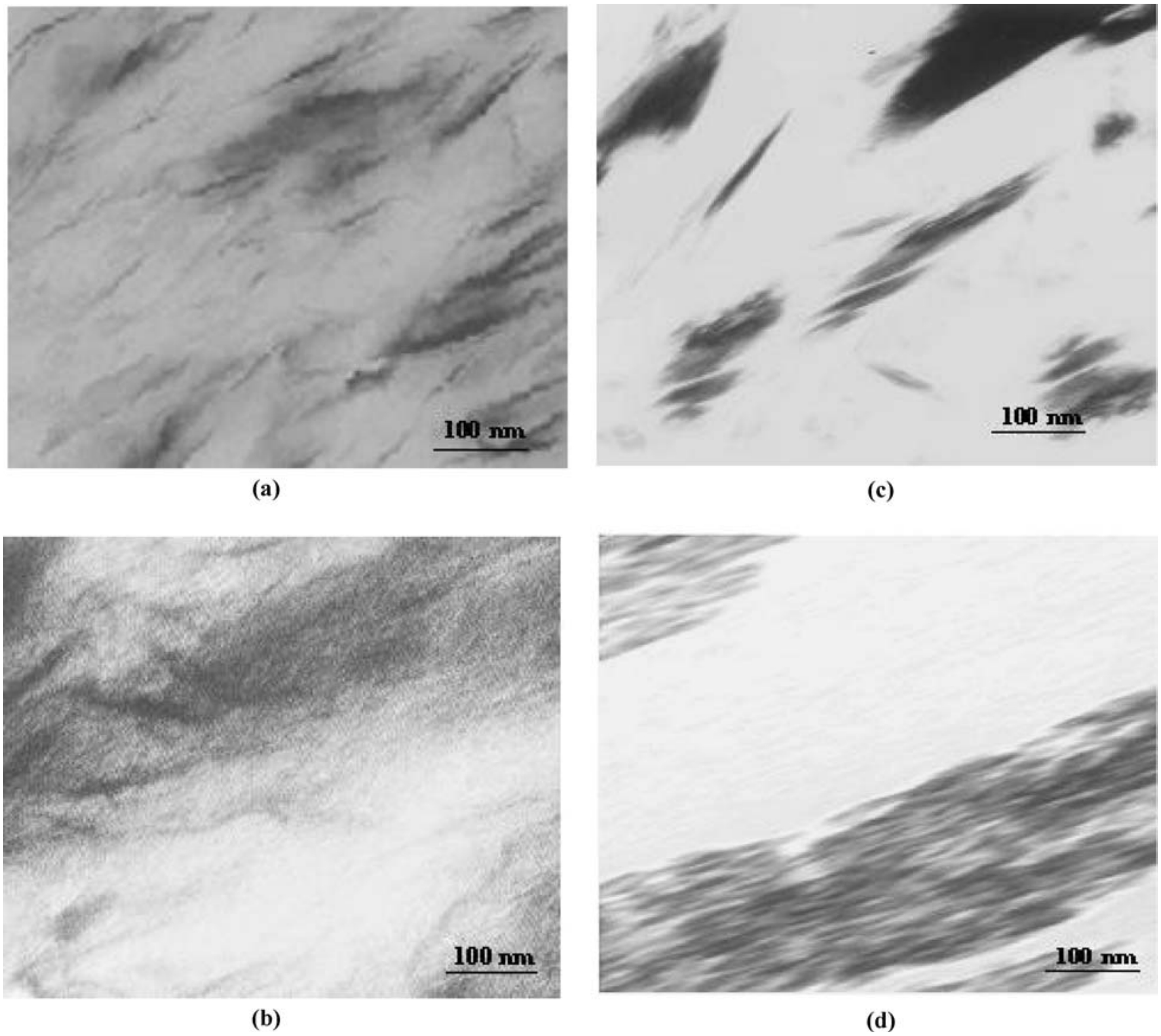
under high temperature cured condition. It is seen that upto 2 wt% of OC, there is no sharp diffraction peak which indicates that clay layers are dispersed by forming exfoliated structure in the epoxy matrix. As the wt% of OC increases further, the diffraction pattern shows the formation of intercalated nanocomposites. The d-spacing of clay layers in the polymer matrix is 30.43 Å and 26.74 Å, for 3 wt% and 10 wt% of OC contents respectively. Fig. 5 of high temperature cured epoxy-UC composites show that there is very negligible change in the d-spacing of UC, which shows that the UC filled epoxy act as conventional micron scale particle filled composites. The morphology of nanocomposites filled with modified clay particles is seen in Fig. 6. TEM picture shows that the distribution of clay particles is uniform in the polymer matrix for both the room temperature cured (RTC) and high temperature cured (HTC) nanocomposites at 2 wt% of OC content. It is seen that at higher clay content (10 wt%), the clay layers were agglomerated, or forming intercalated structure. The distribution of clay particles depends on processing time, processing temperature, mechanical mixers, curing agent, nature of matrix material and the clay particles used [10].

3.2. Flexure properties

It is seen that the incorporation of fillers in the polymer matrix has considerable effect in the flexural properties. It is known that the flexural strength decreases as the filler content increases. The flexural modulus of the epoxy filled with organo and unmodified clay particles under different processing condition are shown in Figs 7 and 8. The organo clay filled epoxy has better improvement in the flexural modulus than that of the unmodified clay filled epoxy. The important parameter which affects this property by incorporating such fillers is the quality of interface in the composites, i.e., the adhesive strength and the interfacial stiffness of the composite medium. These two factors play a crucial role in stress transfer and the elastic deformation from the matrix to the fillers [11]. This is very much applicable to the nano particle filled polymers, due to high surface area of the organo clay filler which increases the contact area to the matrix and imparts high portion of interface. If the interface is poor between the matrix and fillers, there is very less chance for the fillers to carry the load and results in less modulus which is seen for the unmodified clay filled epoxy polymer. As a result of this, the unmodified clay filled composite cannot have good strength than that of the matrix material. But in the nanocomposites, due to the enhanced interfacial property owing to their large surface area of fillers, the increased property is observed which reveals that stresses are effectively transferred through the interface.

Figs 9 and 10 show the strain at break for the epoxy filled with organo modified and unmodified clay under different processing conditions. It is well known that the filler content reduces the strain at break, due to the hard and rigid nature of the fillers. The deformation of the pure polymer is drastically affected by the presence of these fillers [12]. This in turn decreases the composite strain of the composites at break. However, Figs 9 and 10, show that the organo clay particle filled epoxy polymer experiences high strain to break for clay up to 3 wt%. This increase in strain suggests that these nanoparticles are able to introduce some additional mechanism to failure and energy absorption without affecting the matrix deformation. These particles may act as crack stoppers by pinning the cracks. It is seen that the filler content above 3 wt% decreases the failure strain. Here the fillers dominate and they reduce the matrix deformation considerably. The failure strain for the unmodified filled clay particles continuously decreases as the clay content increases after 3 wt% irrespective of the process conditions.

Figs 11 and 12, show the flexure strength for epoxy filled organo and unmodified clay particles. The strength for the epoxy filled with organo clay particles increases continuously up to the 3 wt% of filler and further addition of clay decreases the strength. The distribution of the particles in the matrix is an important factor to be considered in this case. The stress distribution around the particles increases the stress concentration of the propagating crack which in turn induces relative early failure. This is very much seen in the higher filler content. At higher filler content (above 3 wt%), the chance for agglomeration is high which induces more stress distribution. It is evident from Fig. 6 that the distribution of nanoclay is good at lower



(a) (c)

(b) (d)

Figure 6 TEM morphology of epoxy/clay nanocomposites: (a) epoxy with 2% OC under RTC condition, (b) epoxy with 2% OC under HTC condition, (c) epoxy with 10% OC under RTC condition and (d) epoxy with 10% OC under HTC condition.

filler content and at higher filler content the agglomeration dominates in the matrix. This factor demonstrates the importance of the particle distribution. The nanoparticle reinforcement enhances the surface area of contact to the matrix, and thereby enhancing the stress transfer between both parts and results in improved strength, modulus and failure strain. The unmodified clay filled epoxy shows the decrease in the strength than the matrix material. The possible reason is due to the poor interfacial property owing to their micron scale filling, high stress concentration which paved the way for less load transfer from the matrix to the filler.

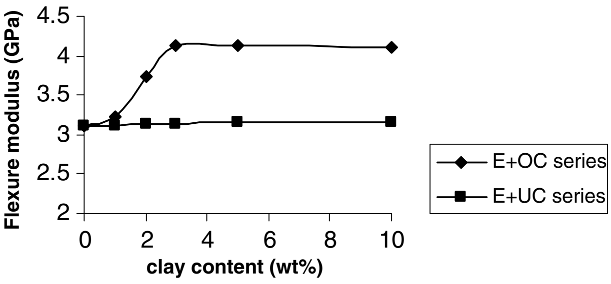


Figure 7 Flexural modulus of epoxy/clay series for HTC composites.

3.3. Impact properties

Impact test under Izod impact method of un-notched specimens are high speed fracture tests measuring the energy to break the specimens under high strain rate conditions. The energy measured in this test is the energy required to create a crack and the energy required to propagate the crack. Generally un-notched specimen will have high impact energy than notched specimen. This is also due to the stress concentration which occurs at the tip of the notched specimen. The same effect is seen in the un-notched specimen if the particle agglomeration is large. This effect is

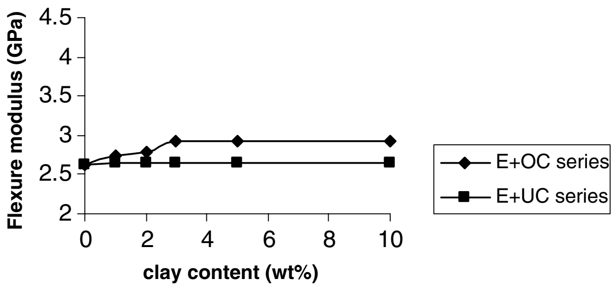


Figure 8 Flexural modulus of epoxy/clay series for HTC composites.

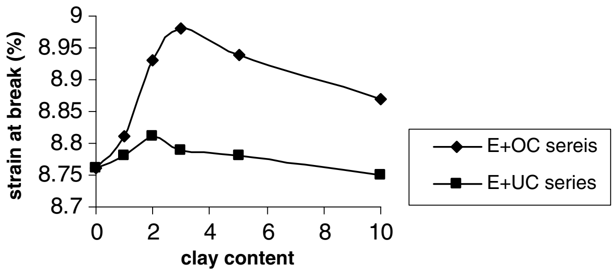


Figure 9 Strain at break of epoxy/clay series for HTC composites.

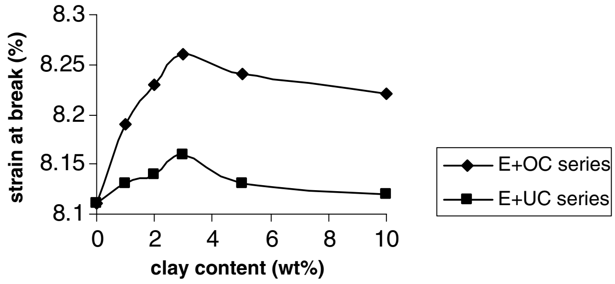


Figure 10 Strain at break of epoxy/clay series for RTC composites.

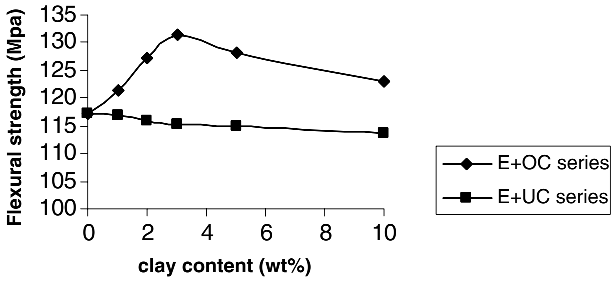


Figure 11 Flexural strength of epoxy/clay series for HTC composites.

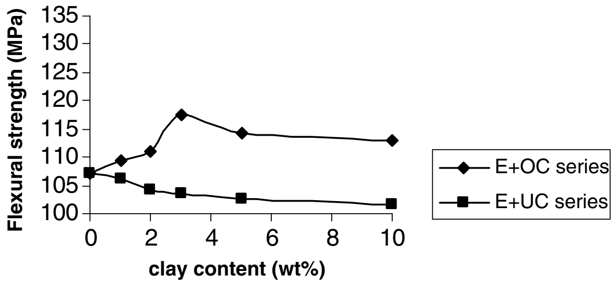


Figure 12 Flexural strength of epoxy/clay series for RTC composites.

usually seen in the large filler content which acts as stress concentrators within the matrix.

The impact results of the clay filler in the epoxy polymer at different process condition are seen in Figs 13 and 14. It is seen that in the HTC, the OC filler increases the impact strength up to 3 wt%, and on further addition of the clay the impact property decreases but above the property of the matrix material. The decrease in impact strength at high filler content is due to the agglomeration in the polymer matrix. The addition of UC in epoxy polymer decreases the impact strength than that of the neat epoxy. Similar results are obtained for the room temperature cured epoxy polymer that is filled with OC and UC particles. The impact test result shows that the nanocomposites exists better improvement in impact property than micron scale filled UC composites.

The SEM fracture surface of nanocomposites that is shown in Fig. 15 gives some idea of improved impact properties. Fig. 15 (a) of RTC epoxy shows that the fracture surface is smooth. This indicates that the resistance of the material under crack propagation is less and leads to brittle failure. However, on the addition of 3 wt% of OC, the crack surface becomes rough, which indicates that the crack propagation is difficult. The crack propagation could have increased the torturous path and leads to high strength [13]. The impact property doesn't show any good improvement for UC filled polymer composites. The impact strength decreases as the UC clay content increases in the matrix. Such low impact strength for epoxy with the UC filler content is due to the agglomeration, large particle size of the filler, etc.

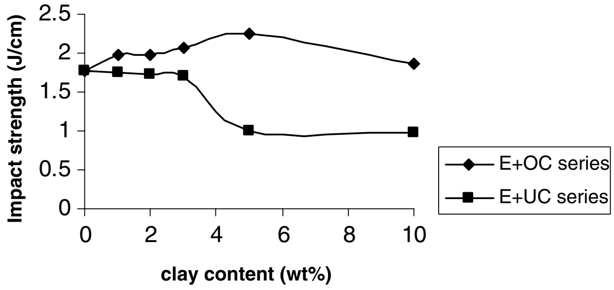


Figure 13 Impact strength of epoxy/clay series for HTC composites.

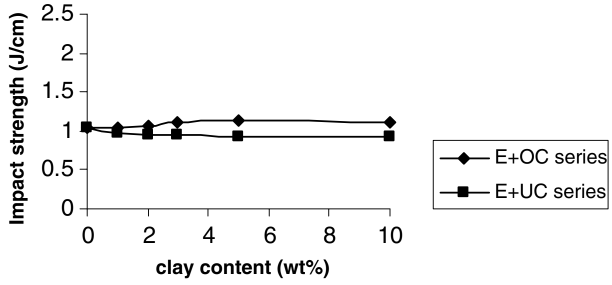


Figure 14 Impact strength of epoxy/clay series for RTC composites.

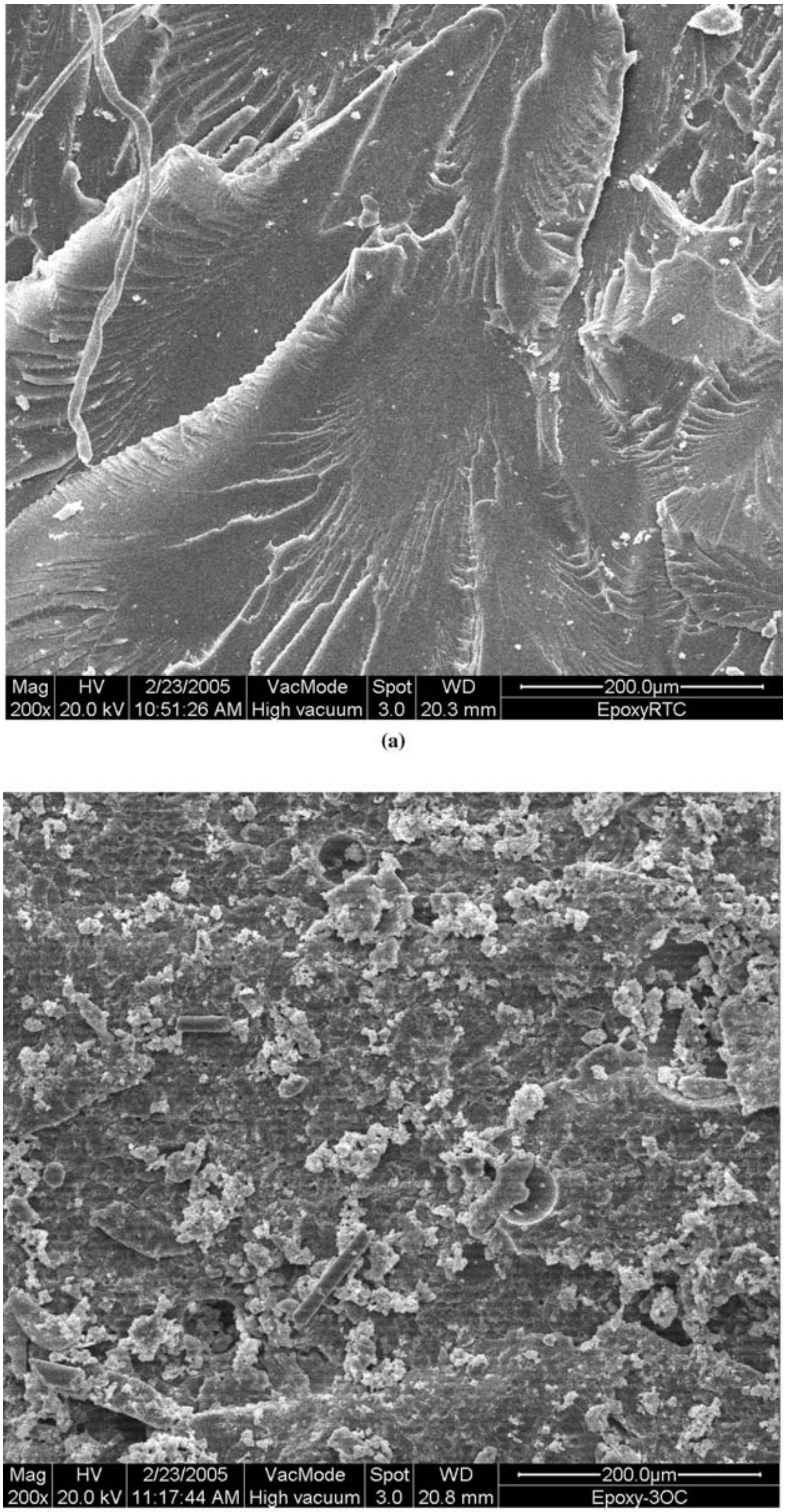


Figure 15 Impact fracture surface of (a) pure epoxy and (b) E + 3%OC.

3.4. Barrier properties

Fig. 16 shows the water mass uptake for epoxy filled with OC and UC at different process conditions. The equilibrium mass uptake for epoxy is 2.23 wt% and 3.17 wt% at HTC and RTC conditions respectively. On addition of 10 wt% OC, the equilibrium mass uptake reduces to 1.28 wt% and 1.5 wt% for HTC and RTC conditions respectively. This shows that mass uptake under HTC conditions is less than RTC condition. This large mass uptake for RTC is due to

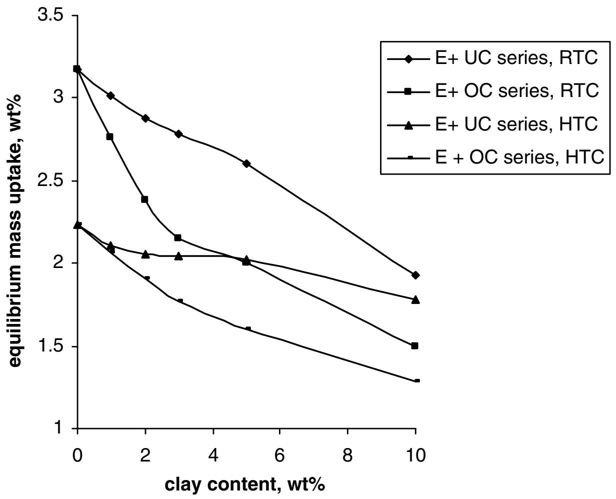


Figure 16 Equilibrium mass uptake of epoxy/clay series in water medium.

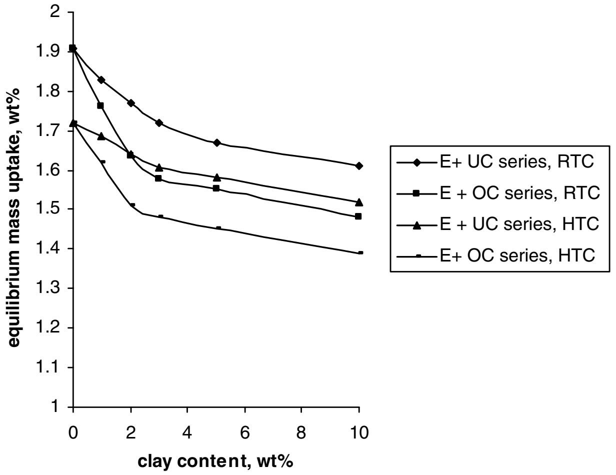


Figure 17 Equilibrium mass uptake of epoxy/clay series in base medium.

the existence of porosity during process condition. The free pore volume can easily take up the water molecules and increases the mass uptake. The addition of 10 wt% UC shows the equilibrium mass uptake of 1.78 wt% and 1.93 wt% for HTC and RTC respectively. This shows that the mass uptake is more in UC filled polymer than in OC filled polymer. The existing hydrophilic nature of UC causes this mass improvement.

Fig. 17 shows the composites placed in the base medium. The equilibrium mass uptake for pure epoxy is 1.72 wt% and 1.92 wt% at HTC and RTC conditions respectively. On addition of 10 wt% OC, the equilibrium mass uptake decreased to 1.39 wt% and 1.48 wt% at HTC and RTC conditions respectively. On addition of 10 wt% UC, the mass uptake decreases to 1.52 wt% and 1.61 wt% at HTC and RTC conditions respectively. This shows the mass uptake on the addition of UC is higher than that of the OC filled epoxy, irrespective of the process conditions. This result shows that the mass uptake in the base medium is less than that of the water medium.

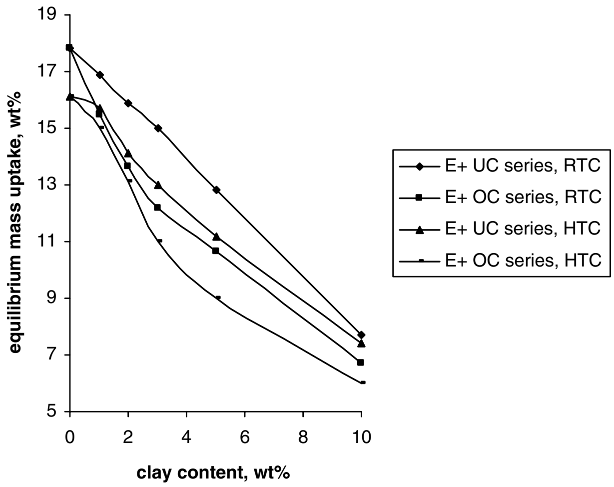


Figure 18 Equilibrium mass uptake of epoxy/clay series in acid medium.

Fig. 18 shows the acid mass uptake in the OC and UC filled composites. The equilibrium mass uptake for pure epoxy is 16.1 wt% and 17.8 wt% for HTC and RTC conditions respectively. On addition of 10 wt% OC it decreases to 6 wt% and 6.7 wt% at HTC and RTC respectively. But for 10 wt% UC addition, mass uptake decreases to 7.4 wt% and 7.71 wt% for HTC and RTC respectively. This result suggests that mass uptake in the acid medium is larger for nanocomposites than in the other two mediums. The addition of OC serves as good weight loss arrester in all the mediums than UC systems. The addition of OC increases the torturous path of the solvent medium, hinders the diffusion path and also decreases mass uptake in the polymer matrix [14]. This torturous path is relatively less in the case of UC filled composites and therefore comprises large mass uptake.

3.5. Relationship between toughness and modulus on the nanoparticle reinforcement

The behaviour of nanocomposites under bending and impact loading is shown in Fig. 19. The normalized impact energy and the flexure modulus are obtained

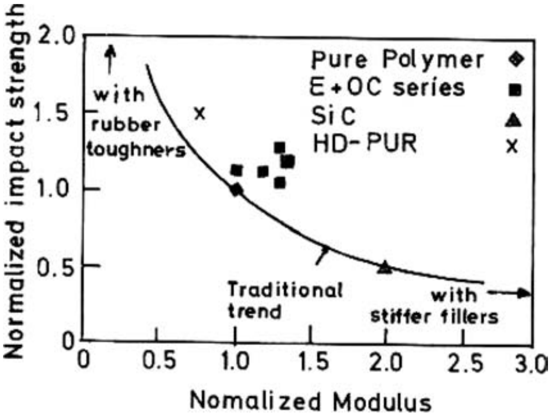


Figure 19 Normalized impact versus modulus of epoxy polymer filled with different fillers.

and compared in single scale. Assuming the normalized impact strength and bending modulus for the pure unfilled polymer matrix as 1.0, the effect of reinforcement is studied. It is seen that the rubber particles (eg. HD-PUR) filled polymers show higher impact energy sacrifying the modulus. The increased toughness is due to the shear yielding, crazing or by cavitation mechanisms [15]. On the other hand, by reinforcing hard phase ceramic particles like SiC, Al_2O_3, TiO_2 etc., [16] in the polymer matrix increases the modulus but with the loss of the impact toughness. These composites become more brittle and lower in impact strength. In order to improve both toughness and modulus the nano particles filled nanocomposite has formed. The nano particle reinforcement improves the properties from the expected traditional trend. This improved property is largely affected by the contents in the matrix, particle size and its distribution in the matrix. The epoxy filled with the organo clay processed under HTC condition reveals enhanced impact and modulus properties as seen in Fig. 19. The improved toughness by reinforcing such hard nano phase particles is due to some energy absorption mechanisms like crack pinning, crack arresting etc.

4. Conclusions

The epoxy/clay nanocomposites were successfully processed by using shear mixing, at different clay concentrations. The nanocomposites were processed by adding room temperature curing agent TETA and high temperature curing agent DDM. XRD pattern reveals that the organo clay has higher d-spacing than that of the unmodified clay. The morphology of the nanocomposites reveals that the clay nano layers are distributed in the matrix. Bending and Impact properties are good for the epoxy filled with the organo clay particles. The DDM cured nanocomposites showed better properties than TETA cured nanocomposites. Barrier property shows that the reinforcement of nano layers decreases the mass uptake considerably than that of the pure matrix. The nanocomposites placed in the acid medium shows high mass uptake than other medium.

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Received 2 August 2004
and accepted 13 July 2005