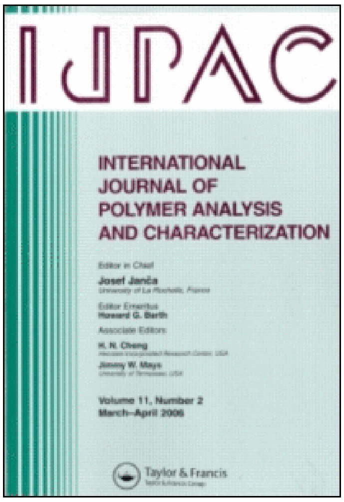


International Journal of Polymer Analysis and Characterization
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713646643

New Nanocomposites Based on Epoxy Resins Reinforced with Modified Montmorillonite

Sorina-Alexandra Gârea[a]; Alina Nicolescu[b]; Calin Deleanu[c]; Horia Iovu[a]
[a] Department of Polymer Science and Engineering, Faculty of Applied Chemistry and Materials Science, Polytechnic University of Bucharest, Bucharest, Romania [b] Institute of Macromolecular Chemistry "Petru Poni, " Iasi, Romania [c] Institute of Organic Chemistry, Romanian Academy, Bucharest, Romania

To cite this Article Gârea, Sorina-Alexandra , Nicolescu, Alina , Deleanu, Calin and Iovu, Horia(2010) 'New Nanocomposites Based on Epoxy Resins Reinforced with Modified Montmorillonite', International Journal of Polymer Analysis and Characterization, 15: 8, 497 — 508

To link to this Article: DOI: 10.1080/1023666X.2010.520906

URL: http://dx.doi.org/10.1080/1023666X.2010.520906

International Journal of Polymer Anal. Charact., 15: 497–508, 2010
Copyright © Taylor & Francis Group, LLC
ISSN: 1023-666X print
DOI: 10.1080/1023666X.2010.520906

NEW NANOCOMPOSITES BASED ON EPOXY RESINS REINFORCED WITH MODIFIED MONTMORILLONITE

Sorina-Alexandra Gârea,[1] Alina Nicolescu,[2]
Calin Deleanu,[3] and Horia Iovu[1]
[1]*Department of Polymer Science and Engineering, Faculty of Applied Chemistry and Materials Science, Polytechnic University of Bucharest, Bucharest, Romania*
[2]*Institute of Macromolecular Chemistry "Petru Poni," Iasi, Romania*
[3]*Institute of Organic Chemistry, Romanian Academy, Bucharest, Romania*

New nanocomposites based on diglycidyl ether of resorcinol (DGER) and modified montmorillonite were synthesized. The montmorillonite was modified with some protonated adducts synthesized by reacting different aromatic and aliphatic epoxies with cyclohexylamine. The chemical structure of the adducts was investigated by ^{1}H-NMR and ^{13}C-NMR. The quantity of organic cations exchanged between the silicate layers and the adducts and also the thermal stability of these modified compounds were determined from thermogravimetric analyses. The nanocomposite structure was confirmed by X-ray diffraction and transmission electron microscopy. Dynamic mechanical analysis showed that the modifier of the clay strongly influences the glass transition temperature of the nanocomposites.

Keywords: DMA; Epoxy; Montmorillonite; Nanocomposites; TEM; TGA; XRD

INTRODUCTION

Epoxy-layered silicate nanocomposites have been the source of much attention in both academic and industrial research due to their excellent flame retardancy, thermal stability, good mechanical properties, and chemical resistance.[1–4]

At present, there are several strategies for polymer-clay nanocomposite synthesis, like sol-gel technology, in situ intercalative polymerization,[5,6] intercalation of polymer or prepolymer from solution, melt intercalation,[7] and heterophase polymerization in aqueous media.[8–13] The main important step in the nanocomposite synthesis consists in organophilization of clay in order to improve the compatibility with epoxy resins.[14] Otherwise, the polymer and the clay will form a two-phase system with a low interface between the two components.[15] The main methods used for clay modifications consist in cation exchange reactions, silane grafting, and adsorption of polar polymers.[8] There are many factors, such as charge density of layered silicate, cationic exchange capacity (CEC) of clay, curing condition (curing agent

Submitted 5 July 2010; accepted 3 August 2010.

Correspondence: Sorina-Alexandra Gârea, Department of Polymer Science and Engineering, Faculty of Applied Chemistry and Materials Science, Polytechnic University of Bucharest, 149 Calea Victoriei, 010072 Bucharest, Romania. E-mail: garea_alexandra@yahoo.co.uk

concentration, curing temperature, curing degree, epoxy resin-curing agent ratio), and swelling time of clay, that exhibit some important influence on the synthesis and final structures of nanocomposites.[16–21]

The aim of this study was to investigate the influence of new modifiers on the structure of nanocomposites. The organophilic clay (modified montmorillonite, MM) used as reinforcing agent in nanocomposite synthesis was obtained by the cationic exchange process between unmodified clay (CloisiteNa) and some new protonated adducts synthesized by reacting low molecular weight aromatic and aliphatic epoxy resins (diglycidylether of bisphenol F (DGEBF), triglycidylether of triphenilol methane (TGETPM), diglycidylether of polydimethylsiloxane (DGEPDMS), and diglycidylether of butanediol (DGEBD) with cyclohexylamine (CA).

EXPERIMENTAL SECTION

Materials

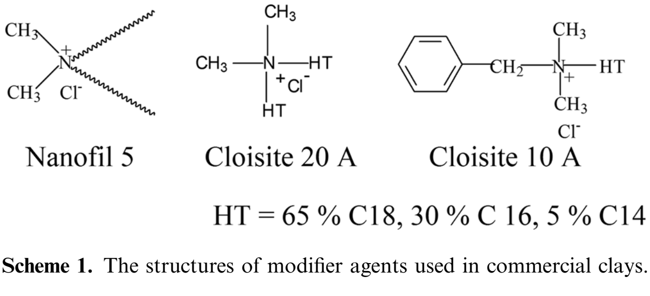
Diglycidylether of resorcinol (DGER), diglycidylether of bisphenol F (DGEBF), triglycidylether of triphenilol methane (TGETPM), diglycidylether of polydimethylsiloxane (DGEPDMS), and diglycidylether of butanediol (DGEBD) epoxy resin types were supplied by Fluka and used as received. Cyclohexylamine (CA) was received from Fluka and used without further purification. Jeffamine D230 (used as cross-linking agent) was supplied by Huntsmann. CHROMASOLV tetrahydrofurane (THF) type was supplied by Fluka.

The unmodified montmorillonite clay (CloisiteNa-ClNa) with a 92.5 mequiv./100 g clay cationic exchange capacity (CEC) and commercial modified clays (Cloisite 10 A, Cloisite 20 A) were supplied by Southern Clay Products (Texas, USA). Nanofil 5 is another modified clay received from Sud-Chemie. The chemical structures of modifier agents used in the commercial clays are shown in Scheme 1.

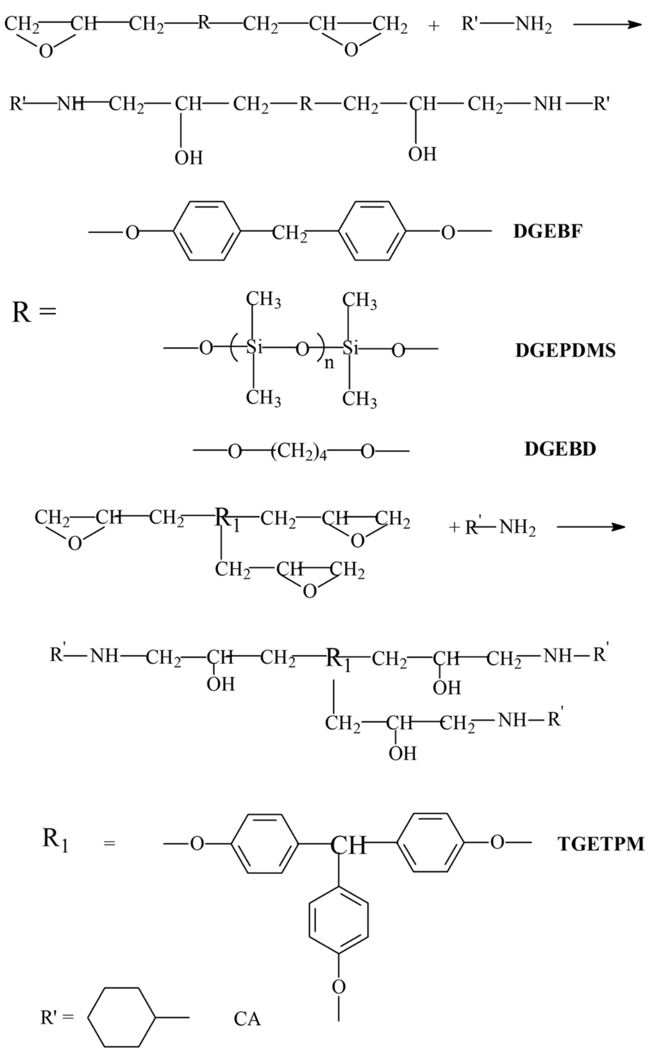
Adducts Synthesis

The adducts were synthesized by reacting different epoxy resin types with a stoichiometric amount of monoamine (CA). The synthesis steps are shown in Scheme 2.

First 5 g of epoxy resin were dissolved in 8 mL THF in a 100 mL glass flask equipped with reflux condenser, dropping funnel, and magnetic stirrer. The mixture was heated at 60°C and continuously stirred. Then the amine was added dropwise.



Scheme 1. The structures of modifier agents used in commercial clays.



Scheme 2. The chemical reactions for adduct synthesis.

The reaction mixture was stirred for 5 h. For adducts based on aliphatic epoxy resins, extra time of 10 h at room temperature is required. The THF was removed from the final products using a rotavapor.

Synthesis of Organophilic Montmorillonite (MM)

First, the adducts were transformed in a protonated form. A certain amount of adduct was dissolved in 12 mL mixture (THF = 3 mL, H_2O = 9 mL), and then a given quantity of hydrochloric acid (37%) was added.

The organophilization step of montmorillonite was done by a cationic exchange process between unmodified montmorillonite (ClNa) and protonated adducts. The protonated adducts were added to a certain quantity of unmodified montmorillonite already swollen in hot deionized water for 1 h and kept at 80°C for 4 h. Then the organophilic montmorillonite was isolated and washed with hot deionized water until no chloride ions were detected by one drop of 0.1 molL^{-1} $AgNO_3$ solution. The product was dried for two days at 110°C and then was ground to produce powder.

Synthesis of Epoxy-Montmorillonite Nanocomposites

An amount of DGER epoxy resin (4 g) was introduced into a glass vessel at 80°C and sonicated for 5 min using an ultrasonic device. Then a certain amount of organophilic montmorillonite (5% wt. to epoxy resin) was added and the mixture was sonicated for 9 h in order to allow the epoxy chains to swell the clay network. After this period of time, the mixture was degassed for a few minutes and a stoichiometric amount of curing agent (Jeffamine D 230) was added. The final mixture was degassed for 5 min and poured into a Teflon mold. It was then cured for 3 h at 75°C and post-cured for 10 h at 100°C. Following this procedure, more types of nanocomposites were synthesized using different MM (Cl-DGEBF-CA, Cl-TGETPM-CA, Cl-DGEPDMS-CA, Cl-DGEBD-CA) or commercial montmorillonite (Cloisite 10 A, Cloisite 20 A, Nanofil 5) as reinforcing agent.

Characterization

Fourier transform-infrared (FT-IR) spectra were registered on Shimadzu 8900 equipment using 40 scans and 4 cm^{-1} resolution. The samples were analyzed from KBr pellets. ^1H-NMR and ^{13}C-NMR spectra were recorded on Brucker 400 MHz equipment, using $CDCl_3$ as solvent and tetramethylsilane as an internal standard. X-ray diffraction (XRD) analysis was performed on a Shimadzu XRD 6000 Diffractometer. Transmission electron micrographs were recorded on a Philips CM 120 ST using an acceleration voltage of 100 kV. Thin specimens of about 50–100 nm were cut from nanocomposite blocks using an ultramicrotome equipped with a diamond knife at ambient conditions.

The value of the glass transition temperature (T_g) of the cured epoxy-organophilic clay nanocomposites was estimated from the maximum of tan δ-temperature curve. Dynamic mechanical analysis (DMA) measurements were run on a Tritec 2000 (Triton Technology) in a single cantilever bending mode, at a heating rate of 5°C/min, a frequency of 1 Hz, and 0.05% strain.

Thermogravimetric analyses were run on a Mettler Toledo TGA/SDTA 851^e. Samples of 15 mg were heated from 50° to 800°C at a scanning rate of 10°C/min under a constant nitrogen flow of 45 mL/min.

RESULTS AND DISCUSSION

Epoxy-Amine Adducts

In the nanocomposite synthesis, an important role is played by the surface modifier of the clay. This decreases the surface energy of the layered silicate in order to diminish the electrostatic interactions between the silicate layers and thus to favor the diffusion. Pinnavaia and Beall[16] proved that the long chains like octadecylammonium cations exhibit positive action for the synthesis of epoxy-clay nanocomposites. However, due to the nonpolar nature of their alkyl chain, octadecylammonium cations exhibit poor compatibility with the epoxy matrix.

An important goal of our work was to synthesize some adducts for modifying the montmorillonite used as a reinforcing agent in nanocomposites, the adducts being more compatible with the epoxy matrix. The main idea was to improve the separation of silicate layers in order to obtain a nanometric dispersion. The chemical structures of the adducts were confirmed by ^{1}H-NMR and ^{13}C-NMR.

^{1}H-NMR analysis. From ^{1}H-NMR spectrum of DGEBF-CA adduct (Figure 1(b)) one may notice that a change of the proton signal of the methine group in the epoxy ring occurred. In the DGEBF structure (Figure 1(a)) this signal appeared at 3.3 ppm, being shifted to about 3.9 ppm in the adduct spectrum (Figure 1(b)), which is proof for the hydroxyl group formation by opening of the epoxy rings. The totally absence of the signal at 3.3 ppm in the DGEBF-CA adduct shows that all epoxy groups reacted with CA. Similar results were obtained from ^{1}H-NMR spectra of the other adducts.

^{13}C-NMR analysis. The chemical structures of the adducts were also confirmed from ^{13}C-NMR spectra. For DGEBF-CA adduct, the new signal at 67 ppm assigned to the carbon atom with hydroxyl substituent proves the opening of the epoxy ring and thus the adduct formation (Figure 1(d)).

Modified Montmorillonites

FT-IR analysis. The clay organophilization step was performed through the cationic exchange reaction between protonated adducts and clay and was first noticed from FT-IR spectra. In Figure 2 one may observe the FT-IR spectra of some MM with protonated adducts (Cl-adduct).

The appearance of the new peaks at 2925 and 2854 cm^{-1}, which correspond to C-H stretching vibration from CH$_2$ groups, the new peak at around 1458 cm^{-1},

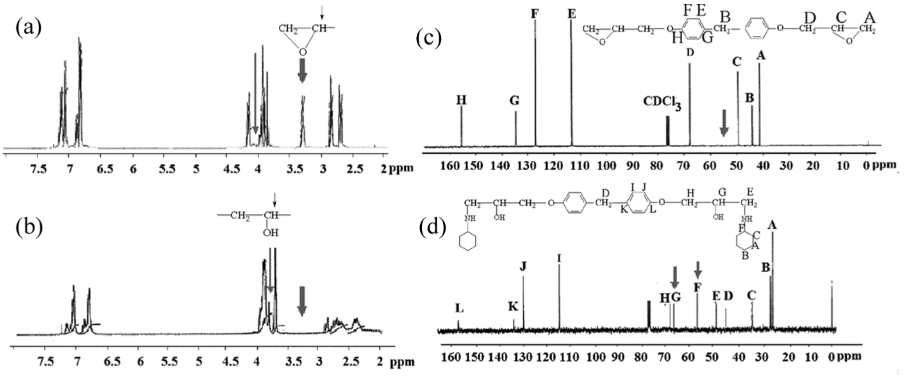


Figure 1. (a) ^{1}H-NMR spectra of DGEBF, (b) DGEBF-CA adduct, (c) ^{13}C-NMR spectra of DGEBF, and (d) DGEBF-CA adduct.

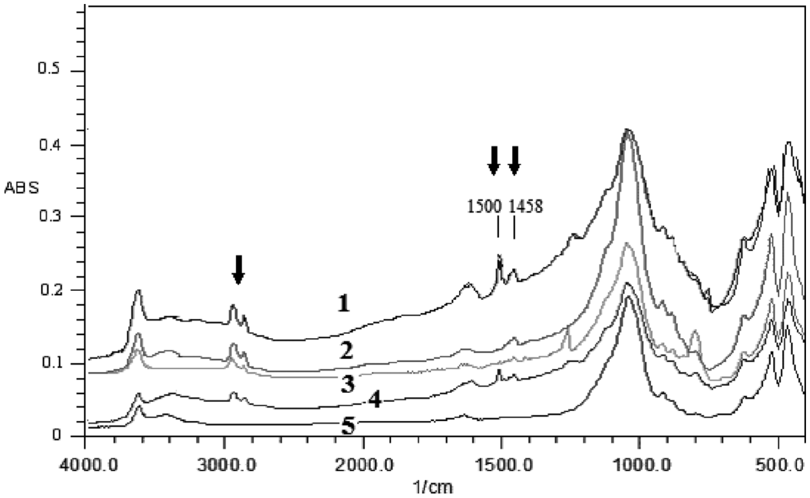


Figure 2. (1) FT-IR spectra of different MM: Cl-DGEBF-CA, (2) Cl-DGEBD-CA, (3) Cl-DGEPDMS-CA, (4) Cl-TGETPM-CA, and (5) and unmodified clay ClNa.

which is assigned to the in-plane C-H bending vibration from CH_2 groups, and the peak at 1500 cm^{-1} assigned to the aromatic C-H stretching vibration is the first proof that the exchange process took place.

XRD analysis. The most important argument for the silicate layers intercalation by protonated adducts was revealed by the X-Ray diffraction (XRD) analysis which gives the value of the basal distance between silicate layers (Table I).

From Table I, one may notice that the basal distance of MM is always higher than of the unmodified clay. This means that all the new protonated adducts were successfully intercalated between the silicate layers during the cationic exchange process. The commercial MM with quaternary ammonium salts exhibits high basal distances (19–25 Å) due to the long hydrophobic chains, which include 14–18 carbon atoms.

Thermogravimetric analysis. Thermogravimetric analysis was used to measure the quantity of organic cations exchanged between the silicate layers and

Table I. The basal distance of ClNa and different types of MM

Clay type	Basal distance
ClNa	11.8
Cl-DGEBF-CA	16.5
Cl-TGETPM-CA	15.2
Cl-DGEPDMS-CA	14.7
Cl-DGEBD-CA	15.1
Cloisite 10 A	19.2
Cloisite 20 A	23
Nanofil 5	25

Table II. Data from TGA and DTG tests for different MM

Modified montmorillonite (MM)	Quantity of organic cations exchanged (meq/100 g clay)	T_{onset} (°C)
Cl-DGEBF-CA	50	250
Cl-TGETPM-CA	29	250
Cl-DGEPDMS-CA	41	240
Cl-DGEBD-CA	50	220

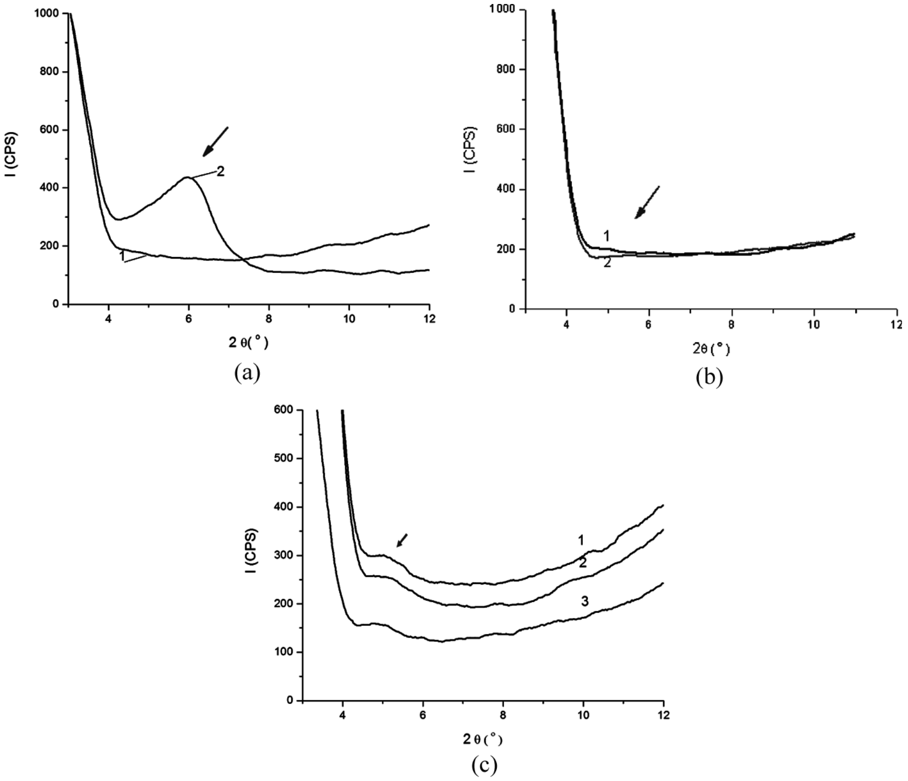
the protonated adducts and to test the thermal stability of organic modifier. From TGA data (Table II), one may observe that the quantity of organic cations exchanged is between 41 and 52 meq/100 g clay, apart from TGETPM-CA adduct, for which only 29 meq/100 g clay were exchanged, probably due to the high volume of the adduct.

The organic cations based on protonated adducts show a different thermal stability, which depends on the nature of epoxy resin used for the adduct synthesis. The epoxy-amine adducts based on aromatic epoxy resins (DGEBF, TGETPM) exhibit higher thermal stability than the adducts based on aliphatic epoxy resins. Thus, the initial decomposition temperature (T_{onset}) exhibits a higher value for the aromatic adduct (250°C) than for the aliphatic ones (DGEPDMS-CA and DGEBD-CA).

Epoxy-Montmorillonite Nanocomposites

XRD analysis. As one may notice from Figure 3(a), the best result was obtained for the epoxy system including MM with DGEBD-CA adduct. In this case, no peak assigned to the basal distance is observed, which means that the basal distance of the clay significantly increased; it is hard to say if an exfoliated or intercalated structure is obtained. Therefore, further TEM analysis is required. For the epoxy system including MM with DGEPDMS-CA adduct, the peak corresponding to the basal distance still exists, indicating a lower compatibility of this MM with DGER.

Figure 3(b) shows the XRD spectra of the nanocomposites including MM with adducts based on aromatic epoxy components (TGETPM, DGEBF) and monoamine (CA). As one may observe, the peak assigned to the basal distance does not exist. The disappearance of the XRD peak assigned to the basal distance indicates that the MM with aromatic adducts give a higher compatibility to the epoxy matrix (DGER), thus enhancing the probability of cross-linking reaction to occur within the silicate galleries, which will lead to further separation of the silicate layers on greater distances. This will also require further TEM analysis to accurately establish the hybrid structure. For the hybrid materials, which include commercial MM with quaternary ammonium salt (Cloisite 10 A, Cloisite 20 A, Nanofil 5), the peak assigned to the basal distance still exists, showing a lower compatibility of this MM type with DGER than the MM with DGEBD-CA and aromatic adducts (DGEBF-CA, TGETPM-CA) but similar to MM based on DGEPDMS-CA.



(a) (b) (c)

Figure 3. XRD spectra of different hybrid materials: (a) DGER/Cl-DGEBD-CA/D 230 (1), DGER/Cl-DGEPDMS-CA/D 230 (2); (b) DGER/TGETPM-CA/D 230 (1), DGER/DGEBF-CA/D 230 (2); (c) DGER/Nanofil 5/D 230 (1), DGER/Cloisite 10 A/D 230 (2), DGER/Cloisite 20 A/D 230 (3).

TEM analysis. The final structure of the hybrids is provided by TEM analysis registered on an ultramicrotomed section. Despite the high initial basal distance of Cloisite 10 A (19.2 Å), the epoxy system based on Cloisite 10 A exhibits an intercalated nanocomposite structure. The TEM images at different magnifications show that the silicate layers are kept parallel, being intercalated by polymer on distances of 35 Å. This is due to a low compatibility between the MM with quaternary ammonium salts and the epoxy matrix (DGER). This aspect was also confirmed for the hybrids with Cloisite 20 A and Nanofil 5 as reinforcing agents (Figure 4(a) and Figure 4(b)).

The epoxy system including MM with DGEBF-CA adduct may be considered as an intercalated nanocomposite, the silicate layers exhibiting a distance of 80 Å between them (Figure 5(a)). By comparison with the hybrids based on commercial MM, the distance between silicate layers increased, which proves that the DGEBF-CA adduct enhanced the compatibility of the clay towards the epoxy matrix, thus favoring the cross-linking process to occur within the silicate galleries.

Figure 5(b) shows the TEM image of hybrid material including MM with TGETPM-CA. One may notice different zones with different distances between

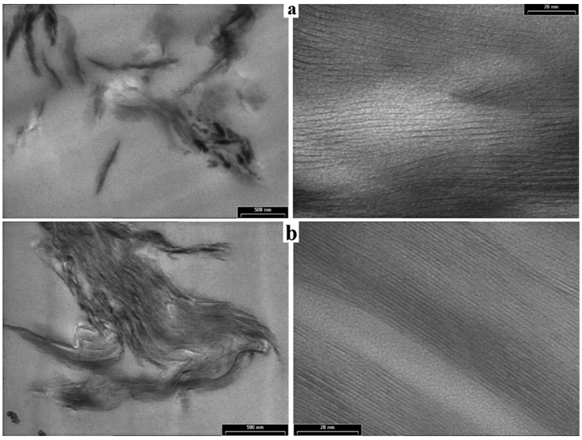


Figure 4. TEM images at different magnifications for hybrid materials that include commercial modified montmorillonites: (a) Nanofil 5, (b) Cloisite 20 A.

silicate layers (80 Å and normal) and even zones in which the silicate layers kept the initial distance before the cross-linking process occurred. This may be explained by the incomplete exchange process of cations between ClNa and TGETPM-CA adduct, not all the sodium ions being exchanged with the cations from the protonated adduct. Thus the diffusion of the epoxy matrix between the unmodified silicate layers is hindered.

In the case of the epoxy systems including MM with adducts obtained from aliphatic resins, the best results from the point of view of clay dispersion were obtained for MM with DGEBD-CA, followed by DGEPDMS-CA. From Figure 5(d), one may observe two distinct zones: one (zone A) characterized by 100 Å distance

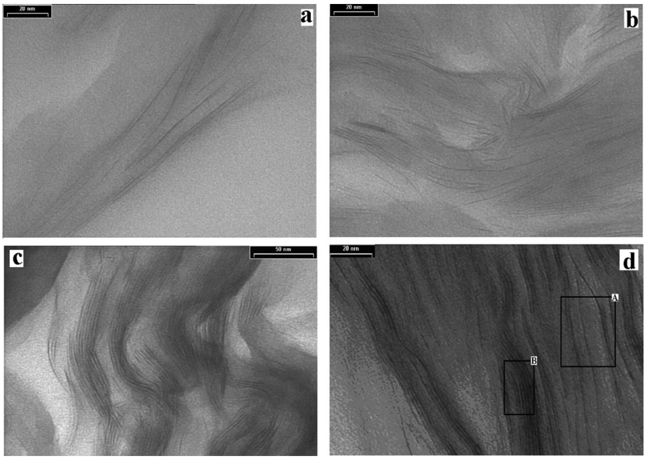


Figure 5. TEM images of hybrid materials including different modified montmorillonites: (a) Cl-DGEBF-CA, (b) TGETPM-CA, (c) Cl-DGEPDMS-CA, (d) Cl-DGEBD-CA.

between silicate layers and another one (zone B) in which the silicate layers are separated by relatively low distances. Therefore in the case of DGER/Cl-DGEBD-CA/D230 hybrid, the intercalated nanocomposite structure coexists with a conventional composite structure (Figure 5(d)).

Poor results were recorded for hybrids based on MM with DGEPDMS-CA adduct, the distances between the silicate layers being very low (30 Å). This may be explained by taking into account on one hand the lower compatibility of the MM with the DGER polymer matrix and on the other hand the small volume of the adduct, which does not lead to a significant increase of the distance between two silicate layers and thus the penetration of the epoxy resin within the gallery is diminished.

Dynamic mechanical analysis (DMA). The effects of the surface modification of montmorillonite on the properties of nanocomposites are currently under investigation. The effect of organophillic montmorillonite on the glass transition temperature (T_g) of the epoxy-based composites reported in the literature is controversial.[22–26] A decrease in T_g for organophilic montmorillonite-epoxy nanocomposite has been reported.[22] An increase in the T_g has also been noted.[23]

From DMA tests, by comparing the pure epoxy (DGER/D230) and conventional composite (DGER/ClNa/D230) curves with those obtained for the intercalated and exfoliated nanocomposites, one may observe that the value of glass transition temperature (T_g) is shifted to lower temperatures. The pure epoxy resin and conventional composite exhibit the same value of T_g(85°C). Thus, we may assume that the shift in T_g may be assigned to the presence of the clay modifier. A small decrease of the T_g value was registered for the hybrid including Cl-DGEPDMS-CA (83°C). A more significant decrease of T_g was observed for the hybrid based on Cl-DGEBD-CA (with 7°C). Also, in the case of hybrids based on MM with aromatic adducts, the decrease of T_g is significant (8°C for Cl-TGETPM-CA and 10°C for Cl-DGEBF-CA).

The DMA results are in good agreement with those from TEM images. As the MM is more compatible with the polymer matrix, the T_g decreases. The increase in the compatibility with the epoxy matrix leads to the penetration of a higher concentration of epoxy resin, which is then homopolymerized in the presence of the clay's modifier, which acts as a catalyst. The unreacted cross-linking agent will behave like a plasticizer, decreasing the T_g.

Not every clay's modifier that includes groups capable of homopolymerizing the epoxy resin may lead to the homopolymer formation. A significant aspect is the compatibility between the resin and the clay. Even if the clay contains a modifier with groups capable of homopolymerizing the epoxy resin (e.g., amino, hydroxyl) but the compatibility with the resin is very low, the penetration of the resin within the silicate galleries is diminished, and thus the formation of homopolymer occurs at a low level. This fact was observed for the hybrids based on MM with DGEPDMS-CA adducts. The silicate layers exhibit low distances between them, providing a low compatibility between the resin and the clay. The quantity of the formed homopolymer depends on the concentration of the resin that penetrates between the silicate layers. Thus the modification of the final structure is not so significant and therefore the decrease of T_g is quite low (2–3°C).

CONCLUSIONS

Exfoliated and intercalated nanocomposites were produced based on DGER as a polymer matrix and modified montmorillonite obtained by a cationic exchange process between the unmodified clay (ClNa) and protonated adducts synthesized from the reaction of different aliphatic and aromatic epoxy resins with cyclohexylamine. The selection of the compatibilizing agent for the montmorillonite is an essential step in the synthesis of epoxy-montmorillonite nanocomposites. The enhanced compatibility of MM towards the epoxy matrix allows further diffusion of the epoxy resin in a higher concentration within the silicate gallery and thus the cross-linking process to occur inside the gallery, which will increase the chance to finally obtain epoxy-montmorillonite nanostructures.

The MM with epoxy-amine adducts obtained from epoxy resins including aromatic rings and exhibiting a low oligomer concentration show a much higher compatibility with the epoxy matrix (DGER) than the MM based on quaternary ammonium salts, commercially available. The concentration of the hydroxylic groups and the high-volume groups from the epoxy-amine adducts plays an important role in synthesis of the epoxy-montmorillonite nanocomposites.

The best results were obtained by using adducts based on aromatic epoxy resins (DGEBF and TGETPM) including bulky benzene rings and with a low concentration of oligomers. For the hybrid material including MM with DGEPDMS-CA adducts, the diffusion of the epoxy matrix was not favored, and intercalated structures with low distances between the silicate layers were finally obtained.

The compatibilizing agent of montmorillonite significantly influences the T_g value of the obtained hybrids. As the modifier exhibits a higher compatibility towards the epoxy resin, this may homopolymerize more easily within the silicate galleries, and thus a lower cross-linking density of the final cured resin is achieved with a direct consequence for T_g value.

REFERENCES

1. Faucheu, J., C. Gauthier, L. Chazeau, J. Y. Cavaille, V. Mellon, and E. B. Lami. 2010. Miniemulsion polymerization for synthesis of structured clay/polymer nanocomposites: Short review and recent advances. *Polymer* 51: 6–17.
2. Choudalakis, G., and A. D. Gotsis. 2009. Permeability of polymer/clay nanocomposites: A review. *Eur. Polym. J.* 45: 967–984.
3. Yasmin, A., J. J. Luo, J. L. Abot, and I. M. Daniel. 2006. Mechanical and thermal behavior of clay/epoxy nanocomposites. *Compos. Sci. Technol.* 66: 2415–2422.
4. Jitendra, K., K. Pandey, R. Reddy, A. P. Kumar, and R. P. Singh. 2005. An overview on the degradability of polymer nanocomposites. *Polym. Degradation Stab.* 88: 234–250.
5. Akat, H., M. A. Tasdelen, F. Prez, and Y. Yagci. 2008. Synthesis and characterization of polymer/clay nanocomposites by intercalated chain transfer agent. *Eur. Polym. J.* 44: 1949–1954.
6. Meneghetti, P., and S. Qutubuddin. 2006. Synthesis, thermal properties and applications of polymer-clay nanocomposites. *Thermochim. Acta.* 442: 74–77.
7. Samyn, F., S. Bourbigot, C. Jama, and S. Bellayer. 2008. Fire retardancy of polymer clay nanocomposites: Is there an influence of the nanomorphology? *Polym. Degradation Stab.* 93: 2019–2024.

8. Kiliaris, P., and C. D. Papaspyrides. 2010. Polymer/layered silicate (clay) nanocomposites: An overview of flame retardancy. *Prog. Polym. Sci.* 35: 902–958.
9. Lertwimolnun, W., and B. Vergnes. 2005. Influence of compatibilizer and processing conditions on the dispersion of nanoclay in a polypropylene matrix. *Polymer* 46: 3462–3471
10. Paul, D. R., and L. M. Robeson. 2008. Polymer nanotechnology: Nanocomposites. *Polymer* 49: 3187–3204.
11. Chakraborty, S., S. Kar, S. Dasgupta, R. Mukhopadhyay, S. Bandyopadhyay, M. Joshi, and S. C. Ameta. 2010. Study of the properties of in-situ sodium activated and organomodified bentonite clay-SBR rubber nanocomposites. Part I: Characterization and rheometric properties. *Polym. Test.* 29: 181–187.
12. Ladhari, A., H. B. Daly, H. Belhadjsalah, K. C. Cole, and J. Denault. 2010. Investigation of water absorption in clay-reinforced polypropylene nanocomposites. *Polym. Degradation Stab.* 95: 429–439.
13. Pavlidoua, S., and C. D. Papaspyrides. 2008. A review on polymer–layered silicate nanocomposites. *Prog. Polym. Sci.* 33: 1119–1198.
14. Liu, P. 2007. Polymer modified clay minerals: A review. *Appl. Clay Sci.* 38: 64–76.
15. Bandyopadhyay, J., and S. S. Ray. 2010. The quantitative analysis of nano-clay dispersion in polymer nanocomposites by small angle X-ray scattering combined with electron microscopy. *Polymer* 51: 1437–1449.
16. Pinnavaia, T. J., and G. W. Beall. 2001. *Polymer-Clay Nanocomposites*, pp. 57–96. New York: John Wiley.
17. Wang, Z., and T. J. Pinnavaia. 1998. Hybrid organic−inorganic nanocomposites: Exfoliation of magadiite nanolayers in an elastomeric epoxy polymer. *Chem. Mater.* 10: 1820–1826.
18. Chen, C., and D. Curliss. 2003. Processing and morphological development of montmorillonite epoxy nanocomposites. *Nanotechnology* 14: 643–648.
19. Salahuddin, N., A. Moet, A. Hiltner, and E. Baer. 2002. Nanoscale highly filled epoxy nanocomposite. *Eur. Polym. J.* 38: 1477–1482.
20. Lan, T., and T. J. Pinnavaia. 1994. Clay-reinforced epoxy nanocomposites. *Chem. Mater.* 6: 2216–2219.
21. Kornmann, X. 2001. Synthesis and characterisation of thermoset-layered silicate nanocomposites. Ph.D. diss., Lulea University of Technology. pp. 23–56.
22. Sun, Y., Z. Zhang, K. S. Moon, and G. P. Wong. 2004. Glass transition and relaxation behavior of epoxy nanocomposites. *J. Polym. Sci. Part B: Polym. Phys.* 42: 3849–3858.
23. Messersmith, P. B., and E. P. Giannelis. 1994. Synthesis and characterization of layered silicate-epoxy nanocomposites. *Chem. Mater.* 6: 1719–1725.
24. Preghenella, M., A. Pegoretti, and C. Migliaresi. 2005. Thermo-mechanical characterization of fumed silica-epoxy nanocomposites. *Polymer* 46: 12065–12072.
25. Lu, H., and S. Nutt. 2003. Restricted relaxation in polymer nanocomposites near the glass transition. *Macromolecules* 36: 4010–4016.
26. Zilg, C., R. Mulhaupt, and J. Finter. 1999. Morphology and toughness/stiffness balance of nanocomposites based upon anhydride-cured epoxy resins and layered silicate. *Macromol. Chem. Phys.* 200: 661–670.