Epoxy-Clay Nanocomposites: Influence of the Clay Surface Modification on Structure

B. Rýznarová,[1,2] J. Zelenka,[3] F. Lednický,[4] J. Baldrian[4]

[1]*Institute of Polymeric Materials, University of Pardubice, Nám. Čs. Legií 565, 53210 Pardubice, Czech Republic*
[2]*Polymer Institute BRNO s.r.o., Tkalcovská 36/2, 65649 Brno, Czech Republic*
[3]*Synpo a.s., S. K. Neumanna 1316, 53207 Pardubice, Czech Republic*
[4]*Institute of Macromolecular Chemistry Academy of Sciences of the Czech Republic, Heyrovského nám. 2, 16206 Prague, Czech Republic*

ABSTRACT: In this article, the effect of four different clay surface modifiers on the structure of epoxy-clay nanocomposites was studied. Various organoclays were prepared via cation exchange reaction between inorganic cations naturally occuring in the clay gallery and different alkylammonium ions. Epoxy-clay nanocomposites were prepared by *in situ* intercalative polymerization using a hardener of polyoxypropylenediamine type. It was found that various clay surface modifiers exhibit different catalytic effect on curing of epoxy inside the clay gallery as observed by measuring of the gel time with dynamic mechanical analysis. This was confirmed by monitoring the change in the *d*-spacing by wide angle X-ray scattering performed *in situ* during curing. Morphology of the cured systems was probed by transmission electron microscopy (TEM) and wide angle X-ray scattering (WAXS). The degree of dispersion observed by TEM and WAXS corresponds with achieved mechanical properties of cured composites. © 2008 Wiley Periodicals, Inc. J Appl Polym Sci 109: 1492–1497, 2008

Key words: nanocomposites; organoclay; modification; structure

INTRODUCTION

Various material properties of epoxy resins can be modified by dispersing inorganic fillers like layered silicates in the epoxy matrix. It was proven[1–4] that such improvements are strongly dependent on the extent of silicate layer separation in the polymer matrix. Silicate clays, originally occuring in the form of micron-sized aggregates, can be dispersed in polymer matrix in three forms[5]: aggregates, intercalated layered nanostructures, and exfoliated platelets. The last form leads to the so-called nanocomposites, where individual silicate layers are uniformly dispersed in the polymer matrix. This uniform dispersion enables preservation of the high surface area of the clay particles and thus creates a large interfacial area between the polymer and the nanoparticle which leads to a significant improvement of material properties.

Most frequently, layered silicates are on the basis of montmorillonite (MMT), naturally occuring clay mineral consisting of octahedral alumina sheets inserted between two tetrahedral silicate sheets. Stacking of the layers by van der Waals forces leads to regular galleries between the layers characterized by *d*-spacing. Isomorphic substitution of Al^{3+} by Mg^{2+} ions generates negative charge on individual layers which is counterbalanced by Na^+ or Ca^{2+} ions in the clay gallery.[6,7] To enhance the compatibility with polymer and aid the dispersion of clay nanolayers in polymer matrix, organic modification of the clays has been found to be useful.[8] This modification can be achieved via cation exchange reaction between inorganic ions naturally occuring in between the layers and organic cations, such as alkylammonium ions.

Epoxy-clay nanocomposites can be successfully prepared by *in situ* intercalative polymerization. Important factor for this synthesis is a difference between curing rates of epoxy resin inside and outside clay gallery.[9–13] Various organic ions can have different catalytic effect on curing of the intragallery epoxy. Therefore, by selecting suitable hydrophobic ion, intragallery and extragallery polymerization can proceed with comparable rates, facilitating clay exfoliation.

In this article, various types of organic ions differing in their polarity and functionality were selected and its effect on the degree of dispersion of silicate layers in epoxy matrix as well as resulting properties of epoxy-clay nanocomposites were studied.

TABLE I
Determination of the Amount of Clay Surface Modifier

Organoclay	Degree of clay surface coverage (%)
A	78
B	87
C	70
D	66

EXPERIMENTAL

Materials

Low molecular weight epoxy resin CHS-EPOXY 520 (Spolchemie, Czech Republic) based on diglycidyl ether of bisphenol A (DGEBA) was used as a matrix. Single organoclays were prepared via cation exchange reaction of sodium ions of Cloisite Na$^+$ (supplied by Southern Clay Products, USA) with bis(2-hydroxyethyl)methyloctadecyl ammonium chloride (denoted hereafter as organoclay A), with dimethyloctadecylphenyl ammonium chloride (organoclay B), with dimethyloctadecyloctyl ammonium chloride (organoclay C) and with methyldioctadecyl ammonium chloride (organoclay D). A polyetheramine, Jeffamine D400 from Huntsman (USA) was used as a hardener.

Sample preparation

Dried organoclays were swollen in the epoxide resin, dispersed in it using high shear forces and mixed with a stoichiometric amount of a hardener. Final mixtures containing 6 wt % of organoclays were degassed in a vacuum oven for 1 h and cast into molds. All samples were subsequently cured for 24 h at 23°C, 1 h at 40°C, 4 h at 60°C, 20 h at 80°C and postcured for 30 min at 80°C and 6 h at 130°C.

Methods

Thermogravimetric analysis

Thermogravimetric analysis (TGA) was conducted on a Perkin–Elmer Thermogravimetric Analyzer TGA 7 in the temperature range from 40 to 800°C in air. The heating rate was 10°C/min.

Wide angle X-ray scattering

Wide angle X-ray scattering (WAXS) studies were carried out using a powder diffractometer HZG/4A (Freiberger Präzisionsmechanik GmbH, Germany) and monochromatic Cu Kα radiation. The diffractograms were scanned in the 2θ range from 1.4° to 10°.

Dynamic mechanical analysis

Dynamic mechanical properties were measured using Dynamic mechanical analysis (DMA) device

(Ares, Rheometric Scientific). The heating rate was 3°C/min in the temperature interval from −50 to 250°C, with frequency 1 Hz.

The gel times of prepared nanocomposites were measured in multiwave mode at different temperatures (80, 100, 110, 120, and 130°C) and frequencies (1, 2, 4, 8, 16, 32 rad/s) by the same device.

Tensile testing

Tensile testing was performed at room temperature on an universal testing machine Zwick/Roell Z 050. The crosshead speed was 0.5 or 2 mm/min with 5-kN load cell with the use of an extensiometer Multi-Xtens (Zwick/Roell). Lower testing speed was used for modulus measurements.

Transmission electron microscopy

Ultrathin sections (60 nm) of the prepared nanocomposites were cut with an ultramicrotome Ultrotome III (LKB, Sweden) equipped with a diamond knife. Transmission electron microscopy (TEM) of ultrathin sections was performed with a microscope JEM 200CX (JEOL, Japan) with acceleration voltage 100 kV.

RESULTS AND DISCUSSION

Characterization of organoclays

To characterize prepared organoclays, TGA and WAXS studies were performed.

TGA experiments were performed to evaluate the degree of clay surface coverage by modifying ions. Supposing that the thermal decomposition of organoclay takes place only in organic modifier as was reported previously by Xie et al.,[14] the weight loss during heating is proportional to the amount of organic modifier. Calculated values of the degree of clay surface coverage by modifying ions are listed in Table I.

Using TGA, deintercalation behavior of modifying ions was investigated. The weight losses of respective organoclays measured isothermally for 6 h at 130°C are summarized in Table II. It is obvious that almost no deintercalation takes place as the weight losses are less than 1 wt % of organoclay. We can

TABLE II
Deintercalation Behavior of Prepared Organoclays
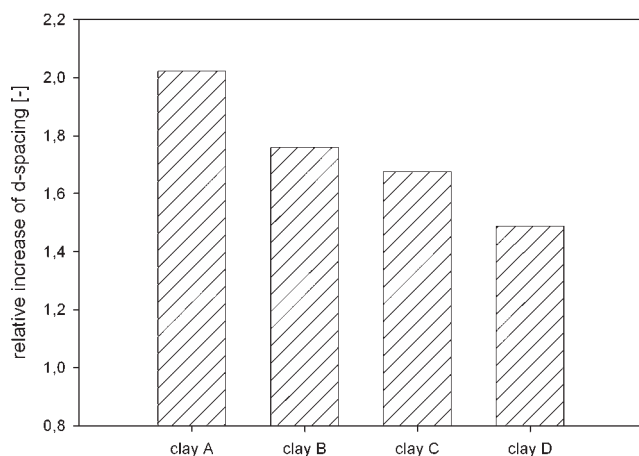
Organoclay	Isothermal weight loss (%)
A	0.19
B	0.79
C	0.29
D	0.23

Figure 1 Intercalation ability of prepared organoclays.

Figure 2 Influence of clay surface modifier on gel time.

conclude that the thermal stability of all organoclays is not affected by the curing temperature.

The intercalation ability of the prepared organoclays was also investigated by the WAXS measurements. Relative increase in d-spacing expressed as ratio of the d-spacing after and before swelling by epoxy is depicted in Figure 1. All types of organic modification significantly promote intercalation of the epoxide between silicate layers as indicated by the increase in the d-spacing after swelling. The highest increase was found for the organoclay A which indicates the best compatibility of the modified clay with the epoxy resin due to the presence of the hydroxyl functionalities. In addition, hydroxyl groups may react with epoxy groups of the prepolymer leading to attachment of the polymer chains on the clay surface and therefore expanding clay gallery. The smallest increase in the interlamelar spacing was observed for organoclay D and was probably caused by high hydrophobicity of the modifier D.

Exfoliation of organoclays in epoxy resin

Using dynamic mechanical analysis in the multiwave mode, influence of various clay surface modifiers on gel time was studied. The gel time for each temperature was determined according to the Winter's criterion[15] as an instant in time when the loss angle tan δ became independent of frequency ω. The dependence of the gel time on the temperature can be described by Arrhenius relation:[16,17]

$$t_{gel} = A \cdot e^{[E_a/RT]} \quad (1)$$

where t_{gel} is the gel time, E_a is the activation energy, A is the preexponential factor, R is the gas constant, and T is the temperature in Kelvin.
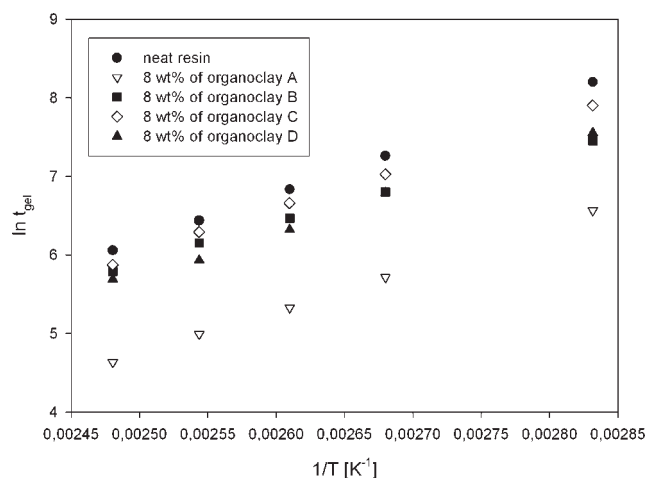
Because of the high viscosity needed, this experiment was performed on samples containing 8 wt % of organoclay. As is shown in Figure 2, all samples fulfill the Arrhenius equation that means linear dependence of $\ln(t_{gel})$ versus $1/T$. According to this equation, the slopes of the lines in Figure 2 are equal to the activation energies of the crosslinking reaction and the y-intercepts are equal to the preexponential factors. Thus, from these data the activation energies and preexponential factors of the studied systems were determined and its values are summarized in Table III. From Figure 2 it is obvious, that all systems filled with 8 wt % of organoclay show reduced gel times in comparison with the neat epoxy. The presence of clay nanoparticles may have an influence on the values of activation energy and preexponential factor. The lower are the values of activation energy and the higher are the values of preexponential factor, the faster the curing reaction will be. The differences between the values of activation energy and preexponential factor at the same organoclay loading can be attributed to the different catalytic effect of the alkylammonium ions on curing of epoxy resin. The order of gel times for given organoclays is in good accordance with the change of the d-spacing measured during curing by "in situ" WAXS. In Figure 3, changes in the d-spacing are plotted against the curing time for 50°C. Organoclay A providing

TABLE III
Activation Energy and Preexponential Factor of Pure Epoxy and Epoxy-Clay Nanocomposites

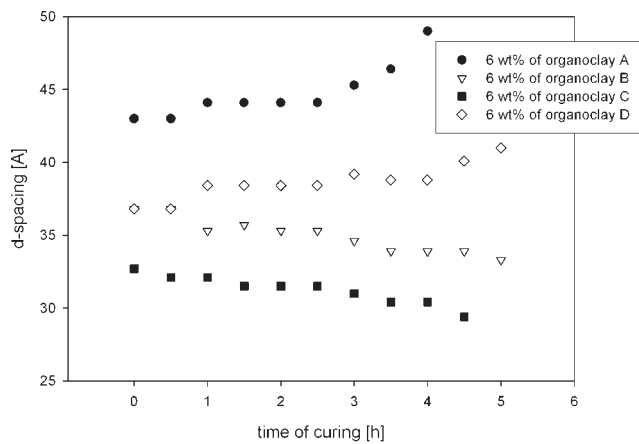| Sample	Activation energy (kJ/mol)	Preexponential factor
Neat epoxy	57.4	1.496×10^{-5}
Epoxy + 8 wt % of A	45.6	1.284×10^{-4}
Epoxy + 8 wt % of B	38.9	3.029×10^{-3}
Epoxy + 8 wt % of C	47.4	2.616×10^{-4}
Epoxy + 8 wt % of D	45.4	3.684×10^{-4}

Figure 3 Increase in the *d*-spacing during isothermal curing at 50°C.

the shortest gelation times (almost six times shorter than the neat epoxy) also promotes separation of the individual silicate layers to the highest extent indicating faster intragallery polymerization. As a result, the intragallery epoxy can cure fully before the extragallery epoxy reaches its gel point and the clay can exfoliate. Surprisingly, also in the case of organoclay D, we can observe short gelation times and high increase in the *d*-spacing during curing although initial intercalation ability of this organoclay was very low compared to the others. This increase in *d*-spacing can be attributed to the presence of H$^+$ ion in the modifier D which can catalyze intragallery polymerization. On the other hand, in the case of organoclay B and C, the decrease of the *d*-spacing during curing is observed suggesting faster extragallery polymerization leading to reverse stacking of clay nanolayers. These results confirm that protonated or functionalized forms of alkylammonium ions are more effective in facilitating clay nanolayer expansion than nonfunctionalized ions.
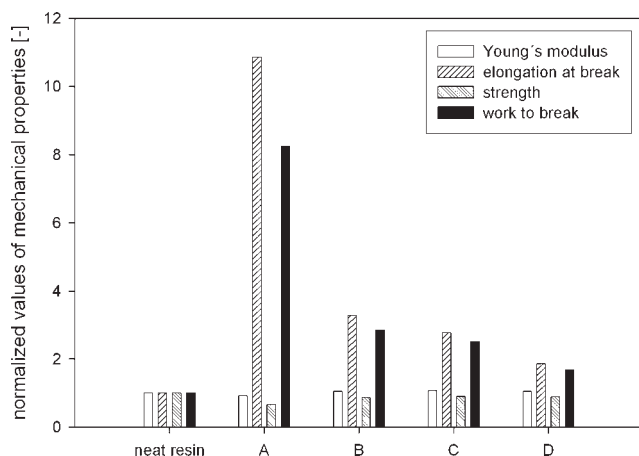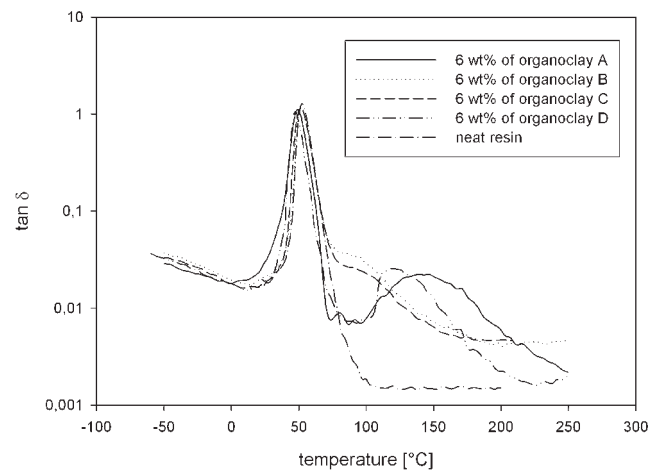

Figure 5 Temperature dependence of loss tangent for composites filled with 6 wt % of different organoclays.

Thermomechanical properties

Tensile properties of cured systems containing 6 wt % of organoclay were measured. As shown in Figure 4, all composites show substantial increase in elongation at break and toughness defined by work to break compared to the neat resin. The sequence of decreasing elongation at break corresponds to the intercalation ability of prepared organoclays and thus is related to the possibility efficiently exfoliate an organoclay in the polymer matrix. Exfoliated clay nanolayers possess very high specific surface area and the conformational effects of the gallery ions on polymer at the clay-matrix interface may contribute to the higher elasticity of composites containing exfoliated or partially exfoliated clay platelets.

Slight decrease of Young's modulus for the system filled with organoclay A can be attributed to the plasticizing effect of modifier A, which is consistent with the decrease of T_g observed by DMA. Because
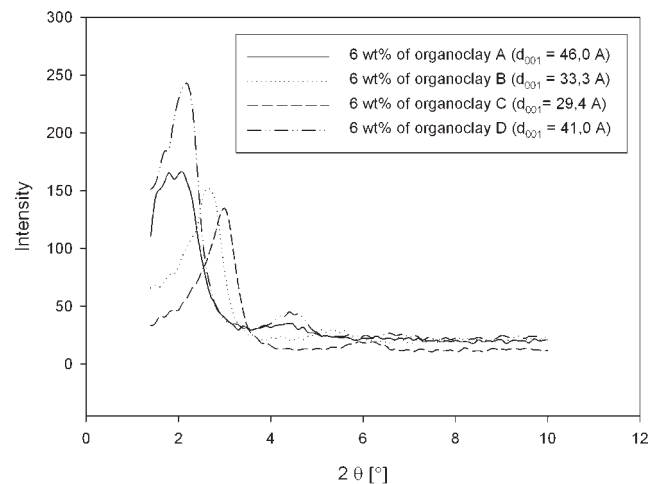

Figure 4 Tensile properties of cured composites containing 6 wt % of organoclay.

Figure 6 WAXS diffractograms of prepared composites with 6 wt % of organoclay.
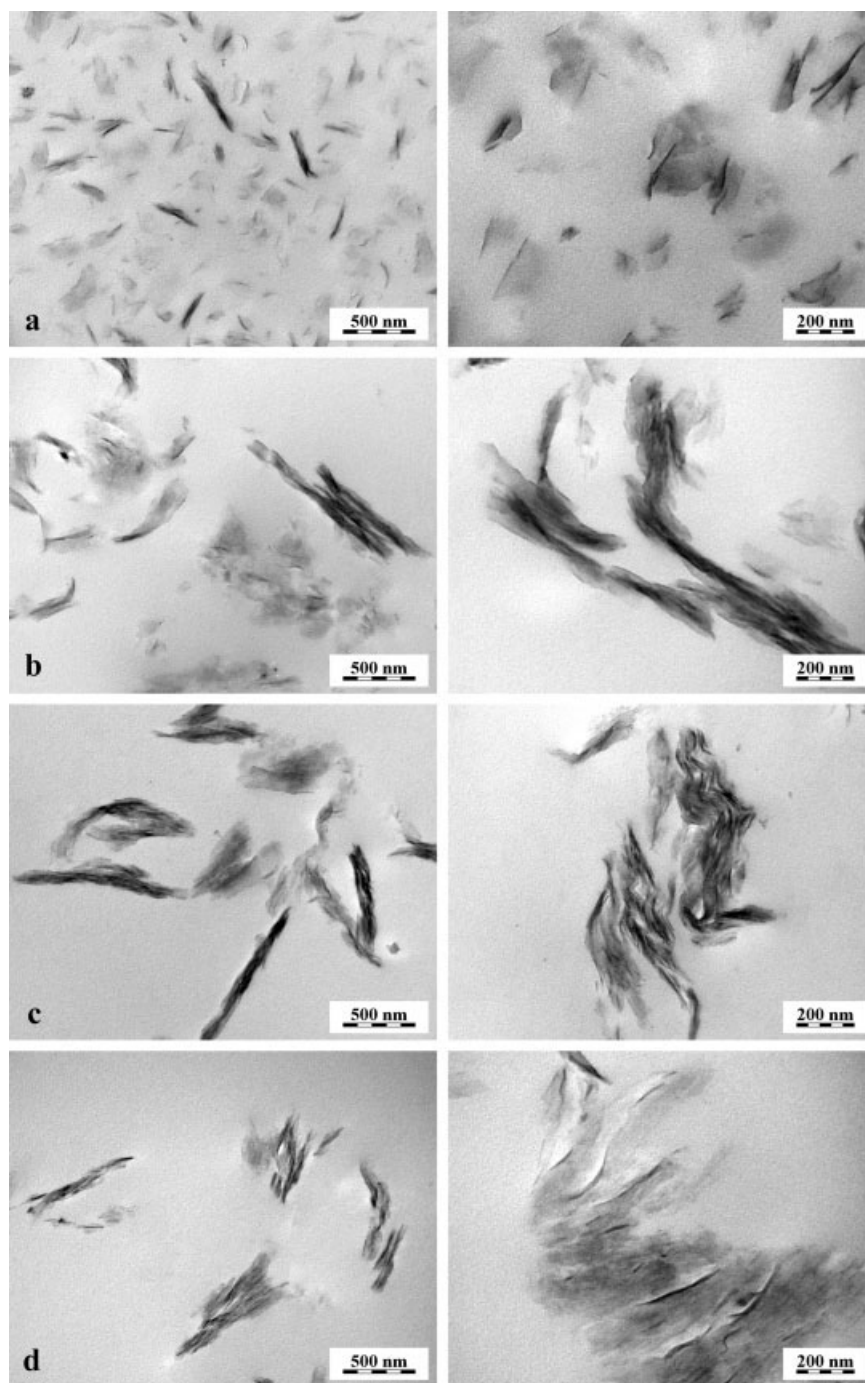
Figure 7 TEM images of prepared composites containing: (a) 6 wt % of organoclay A, (b) 6 wt % of organoclay B, (c) 6 wt % of organoclay C, (d) 6 wt % of organoclay D.

of the participation of the modifier A in the curing of epoxy, the incorporation of the modifier A may have more significant effect on T_g of epoxy, although its amount in the clay gallery in not the highest in comparison with other organoclays.

Figure 5 shows the plot of tan δ versus temperature. In the case of all composites, the dependence shows two maxima. The position of the first loss tangent peak (48–52°C) is almost the same for both filled systems and the neat epoxy and thus is related to the glass transition temperature of polymer. The difference between T_g of the neat epoxy and epoxy filled with 6 wt % of organoclay A is negligible and was probably caused by plasticizing effect of modifier A on curing of epoxy, as was discussed above. The occurrence of the second maximum was discussed[17,18] to be connected with lower mobility of epoxy network at the interface and thus indicates the degree of intercalation by epoxy. From Figure 5 it is obvious that the position of the second maxi-

mum depends on the type of organic modification which suggests an influence of the clay surface modifier on the mobility of interface. Hydroxyl functional groups of modifier A can react directly with the epoxide ring leading to strong immobilization of the epoxide near the interface. H^+ ions of modifier D cause faster curing of intragallery epoxy which leads to further diffusion of epoxy inside the gallery and promotes intercalation. The position of second maximum of organoclays B and C at lower temperatures indicates these modifications promote intercalation only to a small extent.

Morphology

The above-mentioned improvements of tensile properties of prepared composites are related to the degree of dispersion of organoclay layers in the epoxide matrix. Indirect evidence of the degree of dispersion can be provided by WAXS measurements on cured samples. WAXS diffractograms for all systems are depicted in Figure 6. From the position of the diffraction peak at lower diffraction angles we can assume that high degree of intercalation was achieved for all composites. The sequence of d-spacings of cured composites is in accordance with the catalytic activity of gallery ions as measured before by the means of *in situ* WAXS and DMA measurements of gel time.

Transmission electron microscopy visualizes directly the distribution of the clay platelets in nanocomposites. Figure 7 shows TEM micrographs of composites containing 6 wt % of organoclays. Clay particle distribution corresponds to the results calculated from WAXS measurements. At lower magnification, we can observe inhomogeneous distribution of clay particles separated by regions of pure matrix. The size and number of these aggregates for all samples differ from each other. The best dispersion was achieved in the composite filled with organoclay A, where exfoliated individual clay particles are visible at higher magnification. On the other hand, organoclay C provides the worst dispersion as the size of the aggregates is more than 200 nm, even under high magnification. Morphology observations prove the results obtained by DMA and WAXS measurements concerning the differences in the influence of clay surface modification on the exfoliation.

CONCLUSIONS

In this study, the effect of different clay surface modifiers on the structure of epoxy-clay nanocomposites was investigated. It was confirmed that the difference between curing rates inside and outside clay gallery is crucial for achieving high degree of dispersion of prepared nanocomposites. The difference between curing rates can be changed by selecting appropriate modification of a particular silicate clay. Protonated and functionalized forms of clay surface modifiers are able to catalyze intragallery polymerization of epoxy showing reduced gelation times, gradual increase in the d-spacing during curing and higher degree of dispersion leading to improved mechanical properties in terms of increased elongation at break and toughness. Systems prepared using nonfunctionalized alkylammonium ions are unable to catalyze intragallery polymerization, therefore extragallery polymerization proceeds faster and leads to only partially intercalated nanocomposites.

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