Alternative Synthetic Routes to Epoxy Polymer – Clay Nanocomposites using Organic or Mixed-Ion Clays Modified by Protonated Di/Triamines (Jeffamines)

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Summary: The use of homoionic organic clays and mixed-ion organic/inorganic clays modified by di- or triamines (Jeffamines), which are being used as epoxy resin curing agents, in the synthesis of polymer nanocomposites has been studied in this work. Our aim is to enhance polymer crosslinking and interfacial adhesion in the nanocomposite structure by utilizing the functionality of the di/triamines on the surface of clay nanolayers and by reducing the organic modifier via formation of homostructured mixed-ion organic/inorganic clays. The results show that the use of homoionic organic clays exchanged with relatively short chain di- or triamines and mixed-ion organic/inorganic clays partially exchanged (ca. 35%) with long chain diamines resulted in intercalated structures with enhanced thermo-mechanical properties (Young's Modulus, Storage Modulus). On the other hand, homoionic organic clays exchanged with long chain diamines and triamines resulted in exfoliated nanocomposites but with compromised mechanical properties due to the plasticizing effect of the long chain amine modifiers.

Keywords: di/triamines (Jeffamines); epoxy resin; nanocomposites; organic and mixed-ion clays; thermo-mechanical properties

Introduction

Polymer – layered silicate nanocomposites (PLSN) usually exhibit improved physical and performance properties in comparison to pristine polymers and conventional composites, due mainly to their unique phase morphology and the interfacial properties provided by the highly dispersed silicate nanolayers in the polymer matrix. Loadings of only $\sim$5 wt.% exfoliated silicate nanoparticles in PLSN materials result in significant enhancement of mechanical properties (modulus, strength, thermal expansion coefficient), barrier properties, thermal stability, resistance to solvent swelling, flammability resistance and ablation performance [1–5]. However, the reinforcement of the polymer matrix is compromised by the presence of the organic modifiers of clays due to the introduction of dangling chains of monoamine modifiers (e.g. octadecyl ammonium ions) that reduces the degree of polymer crosslinking and weakens interfacial adhesion. In addition, utilization of large quantities of modifiers, which are usually quaternary ammonium ion surfactants, induces economical and environmental issues. Our approach has been on the utilization of protonated diamines (Jeffamines) both as clay modifiers and as epoxy curing agents [6] and also on the use of homostructured mixed organic/inorganic cation exchanged smectite clays (e.g., montmorillonite) in which both the organic and the inorganic cations co-occupy the gallery surfaces of the clay, thereby dramatically reducing the amount of organic

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modifier needed to access the galleries for nanocomposite formation [7]. In the present work further improvement has been attempted by the use of triamines with variable size in order to benefit both from the large volume/size for efficient clay platelets separation with minimum amount of modifier and from the functionality of the free amino-groups of the triamine which have not been bound to the clay surface.

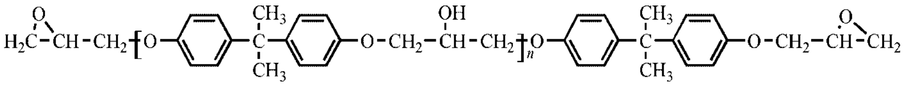
Table 1.
Epoxy-clay nanocomposite samples.

Nanocomposite Sample	Clay Modifier*
3%H$^+$-PGW	–
3%H$^+$-PGW_100%D400	100%D-400
3%H$^+$-PGW_35%D2000	35%D-2000
3%H$^+$-PGW_100%D2000	100%D-2000
3%H$^+$-PGW_35%D4000	35%D-4000
3%H$^+$-PGW_100%D4000	100%D-4000
3%H$^+$-PGW_100%T403	100%T-403
3%H$^+$-PGW_100%T5000	100%T-5000

*Refers to % ion-exchange of clay protons with alkylammonium ions of the respective di/triamine.

Experimental Part

The inorganic clay was a Na$^+$-montmorillonite (PGW) with a CEC = 1.45 meq/gr provided by Nanocor. The epoxy resin was a diglycidyl ether of bisphenol A (EPON 826) with an epoxide equivalent weight (EEW) ~187 supplied from Hexion.



The curing agent was an aliphatic polyoxypropylene diamine (Jeffamine D-230, Mw = 230) and the organic clay modifiers used were polyoxypropylene diamines (D-400, D-2000, D-4000) and triamines (T-403, T-5000) (Jeffamines) provided by Huntsman.

The homoionic organic clays and the mixed-ion inorganic/organic clays were prepared by ion exchange of the inorganic clay (H$^+$-clay) with the desired amount of protonated diamines or triamines. In the case of the mixed-ion clays the concentration of onium ions in the reaction mixture was adjusted to achieve the desired degree of protons exchange on the clay surface, while for the homoionic organic clays a small excess of onium ions to that required for 100% ion-exchange of protons was added in the solution. The pristine glassy epoxy polymer was synthesized by mixing of EPON 826 prepolymer with the curing agent diamine D-230 followed by appropriate outgassing and curing at 75 °C for 3 h and 125 °C for another 3 h in N_2 atmosphere. The epoxy-clay nanocomposites containing 3 wt.% clay (on silicate basis) were prepared by pre-mixing of the clay with epoxy precursors at 60 °C for 1 h followed by the addition of curing agent and subsequent curing under conditions similar to those for the pristine epoxy polymer. The synthesized nanocomposite samples are presented in Table 1, while more detailed description of experimental techniques can be found in previous reports [6,7]. The designation 3% H$^+$-PGW_35% D2000 indicates that the composite contained three weight percent protonated montmorillonite clay and that 35% of the protons on the exchange sites of the clay were neutralized by reaction with 0.35 equivalents of Jeffamine D-2000.

Results and Discussion

Homoionic organic clays exchanged with long chain diamines (D-2000, D-4000) and triamines (T-5000) resulted in exfoliated nanocomposites as indicated from the XRD patterns of the respective nanocomposite samples in Figure 1. The long backbone chain of these di/triamines provided sufficient space and highly organophilic environment for the epoxy prepolymer to be inserted between the layers resulting in enhanced formation of epoxy polymer

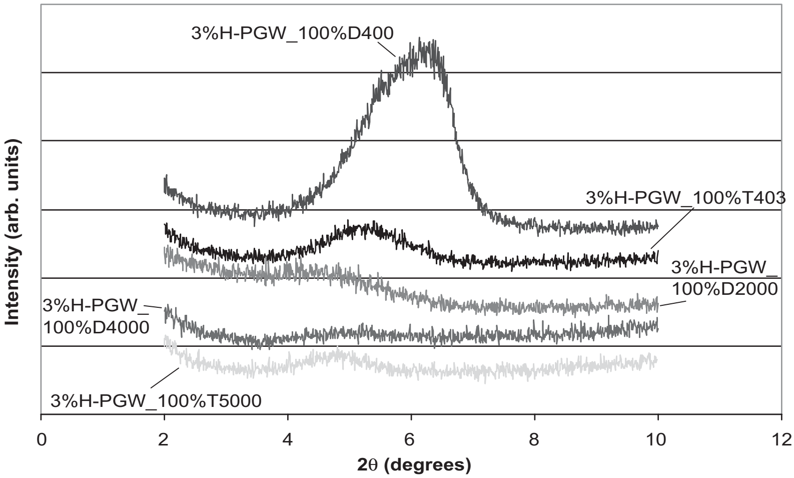


Figure 1.
XRD patterns of epoxy – clay nanocomposites synthesized by the use of homoionic organic clays exchanged with short chain diamine (D-400) and triamine (T-403), and long chain diamines (D-2000, D-4000) and triamine (T-5000).

network in the intragallery space [6]. When smaller chain amines were used as clay modifiers the resulting nanocomposite structure depended on the type of Jeffamine used; the diamine D-400 modified clay resulted in intercalated nanocomposite while the triamine T-403 modified clay induced an almost exfoliated structure, as it can be revealed from the respective XRD patterns in Fig. 1.

The mixed-ion organic/inorganic clay with 35% exchange of protons with D-2000 onium ions resulted in an intercalated nanocomposite structure (Figure 2) with the d-spacing of clay tactoids being slightly higher than that of the inorganic H^+-clay based nanocomposite. However, in a previous study [7] we have shown that a 50% ion-exchanged clay with protonated diamine D-2000 was capable of forming

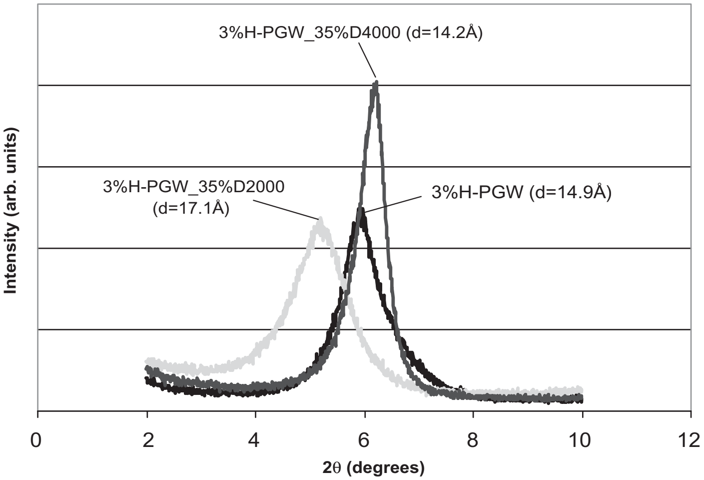


Figure 2.
XRD patterns of epoxy – clay nanocomposites synthesized by the use of homoionic inorganic clay (H^+-clay) and mixed-ion organic/inorganic clays partially exchanged (35%) with long chain diamines (D-2000 and D-4000).

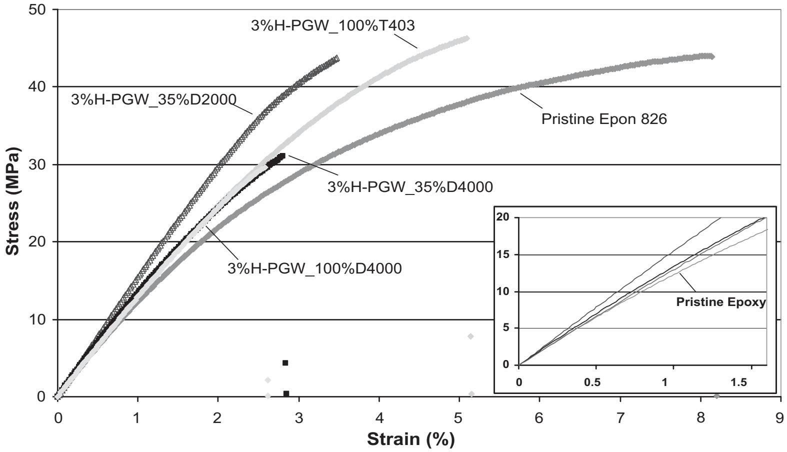


Figure 3.
Stress – strain curves of representative epoxy – clay nanocomposites. Inset: Enlargement of low strain region.

exfoliated epoxy – clay nanostructures, especially by the use of certain organic solvents during initial mixing of the clay and the epoxy precursor. The use of the larger diamine D-4000 at the same proton exchange percent (35%) had no additional benefit; on the contrary, the respective nanocomposite contained an almost non-intercalated clay phase similar to that in the case of the inorganic H^+-clay (Figure 2). This could be attributed to the inhomogeneity of the D-4000 partially exchanged clay sample due to the very long chain and the strong organophilic character of D-4000 that inhibited homogeneous diffusion through the clay galleries.

The tensile properties of the nanocomposites samples were not largely affected compared to those of the pristine epoxy as it was revealed by the stress – strain tests of the samples (Figure 3). This was more or less expected due to the glassy state of the epoxy. However, a small increase in elastic modulus (Young's modulus) was observed for all the nanocomposite samples indicating the enhanced stiffness of the composites. The 35% D-2000 exchanged mixed-ion clay and the homoionic T-403 exchanged clay showed the best tensile properties among the various nanocomposites. As a consequence, a small compromise was observed in the maximum strain at break (maximum elongation) of the nanocomposites, which was either way quite small in the pristine epoxy polymer (~8%).

Dynamic mechanical analysis (DMA) tests were used to evaluate the reinforcement of epoxy provided by the homoionic organic clays and the mixed-ion clay homostructures. Figure 4a and b show the dependence of storage modulus and tanδ, respectively, on temperature for representative nanocomposite samples. As it can be seen from the curves addition of the homoionic organic D-4000 exchanged clay resulted in a small increase of storage modulus but also in a considerable decrease of T_g due to the plasticizing effect of the long chain diamine used as clay modifier. A similar effect was observed with the use of D-2000 and T-5000 as clay modifiers. On the other hand, the mixed-ion (35% exchanged with D-2000) clay induced a similar increase of the storage modulus without any significant compromise of the T_g. The strongest enhancement in the thermo-mechanical properties of the epoxy was provided by the organic clay fully exchanged with the relatively short chain diamine D-400 which resulted in a significant increase of storage modulus (~40%) with a slight decrease of T_g.

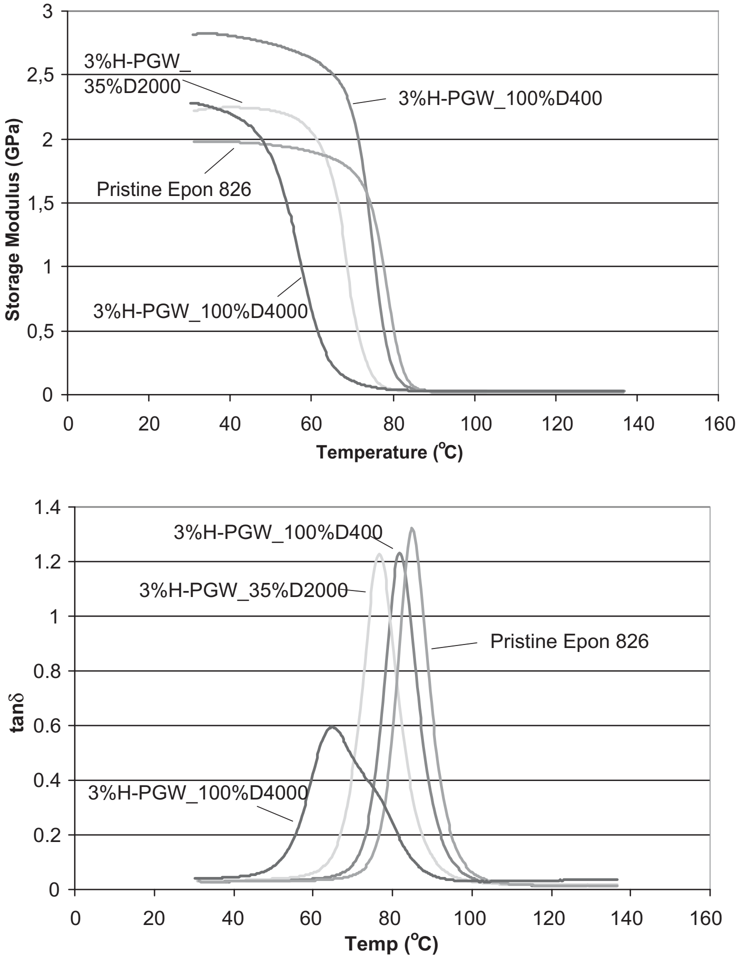


Figure 4.
(a) Storage Modulus and (b) tanδ vs. temperature curves of representative epoxy – clay nanocomposites.

Conclusions

Homoionic organic clays exchanged with long chain di/triamines (Jeffamines) result in the formation of exfoliated epoxy – clay nanocomposite structures which however show a compromise in the mechanical properties mainly by reducing the T_g of the glassy epoxy polymer due to the plasticizing effect of the large amine clay modifiers. Mixed-ion organic/inorganic clays with 35% exchange of protons with onium ions of relatively large di/triamines lead to intercalated structures with slightly improved thermo-mechanical properties compared to the pristine epoxy polymer. The use of fully exchanged clay with protonated relatively short chain di/triamine (D-400 or T-403) seems to be the most appropriate for inducing highly intercalated and partially exfoliated nanocomposite structures with significantly enhanced thermo-mechanical properties. The use of di/triamines as clay modifiers and their capability of acting also as epoxy cross-linking agents could reduce the steps in the production of epoxy – clay nanocomposites by performing the organo-functionalization of the clay in situ during the synthesis of the nanocomposite.

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