



# Highly exfoliated epoxy/clay nanocomposites: Mechanism of exfoliation and thermal/mechanical properties



Zhang Ying<sup>a,b</sup>, Li Xianggao<sup>a</sup>, Chen Bin<sup>c,\*</sup>, Chen Fei<sup>c</sup>, Feng Jing<sup>c</sup>

<sup>a</sup>School of Chemical Engineering and Technology, Tianjin University, Tianjin 300072, China

<sup>b</sup>School of Applied Chemistry, Shenyang University of Chemical Technology, Shenyang 110142, China

<sup>c</sup>School of Materials Science and Engineering, Shenyang University of Chemical Technology, Shenyang 110142, China

## ARTICLE INFO

### Article history:

Available online 9 May 2015

### Keywords:

Epoxy  
Nanocomposites  
Exfoliation  
Mechanical properties

## ABSTRACT

Highly exfoliated epoxy/clay nanocomposites have been fabricated via a new “acetone-clay slurry compounding” approach. Transmission electron microscopy (TEM) observation displayed the clay platelets uniformly dispersed and highly exfoliated in the entire epoxy matrix. The mechanism of exfoliation has been explored by monitoring the change of morphology of organoclay during each stage of processing with X-ray diffraction (XRD). It revealed that organoclay platelets had exfoliated in epoxy prepolymer prior to the curing reaction. Differential scanning calorimeter (DSC) test indicated that incorporation of organoclay resulted in a significantly increase in  $T_g$  of the resultant nanocomposites, which is attributed to the highly exfoliation structure and the stronger interfacial interaction. Flexural tests performed at both room temperature (RT) and higher temperature (80 °C) showed the flexural strength of the nanocomposites decreased slightly with increasing clay loading at RT, while it exhibited a remarkably enhancement with increasing clay content at 80 °C.

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## 1. Introduction

In the last two decades, polymer–clay nanocomposites have attracted steadily growing interest from both industry and academia [1–3] since Toyota researcher successfully developed nylon6/clay nanocomposites with enhanced mechanical and/or physical properties at very low clay loading (usually less than 5 wt%) [4,5]. Generally these nanocomposites can be roughly classified into two categories: one is intercalated nanocomposites and the other is exfoliated. An intercalated nanocomposite, in which the silicate is well-dispersed in a polymer matrix with polymer chains inserted into silicate layers that retain their lateral order, and exfoliated nanocomposites where the silicate platelets become fully separated or delaminated, essentially individually dispersed in the polymer matrix. It has been widely accepted that the exfoliated nanocomposites are more desirable than intercalated ones because delaminated clay layers have high aspect ratios and contribute most to the properties of nanocomposites. However, complete exfoliation (especially highly and disorderly exfoliation) of clay is difficult and has become a challenging task in this fields.

Epoxy thermosets are used in a variety of applications, such as adhesives, anticorrosive coatings and electronic encapsulates or in

composites in the transportation and aviation industry [6]. Incorporation of layered silicates into epoxy is promising approach to improve and diversify the properties of the materials and has been investigated intensively [7,8]. In order to achieve epoxy/clay nanocomposites with highly exfoliated structure, many factors that may influence the extent of exfoliation have been explored, including the nature of clay [9], the kinds of curing agent [10–12], the curing profile [10,13–15] and the processing methods [16–20]. However, most of these attempts were found to have little impact on the final nanocomposites structure. In most cases, only intercalated structures were obtained, accompanying by agglomeration of large clay particles in epoxy matrix. Albeit of some results declared achievements of exfoliation, in fact, they were the ordered exfoliation with an enlarged  $d$ -spacing (usually more than 6 nm and the 001 peak disappeared on XRD pattern) but clay layers remained its original paralleled tactoids structure [21–25].

To render hydrophilic clay layers become compatible with epoxy, the organic surfactants (all kinds of organic ammonium ions) are usually employed to modify the clay by ion-exchange reactions. The properties of organic modifiers such as polarity, acidity, and functionality have much influence on the structure and properties of epoxy/clay nanocomposites [21,26–30]. In the case of quaternary and tertiary alkyl ammonium organic modifier, the organoclay usually has a poor dispersion in epoxy, and

\* Corresponding author. Tel.: +86 24 89388092; fax: +86 24 89388153.  
E-mail address: [bchen63@163.com](mailto:bchen63@163.com) (C. Bin).

aggregation occasionally formed because the alkyl chains of the modifier have no strong affinity with aromatic and polar epoxy. They can only lead to a slightly increase in *d*-spacing but not to an exfoliation. When primary and secondary alkyl ammonium used as surfactants, the catalytic action derived from their high Bronsted acidity on curing behavior of epoxy is considered to make the intragallery polymerization at a faster rate compared to extragallery polymerization. Therefore, an ordered exfoliated structure with an enlarged *d*-spacing was usually formed [21]. In the case of hydroxyl-substituted quaternary ammonium ions modifier, a mixture of ordered and disordered exfoliation can be obtained due to the formation of stronger hydrogen-bond between modifiers and epoxy [16]. The modifiers bearing reactive amino groups such as protonated polyoxypropylene diamine were also adopted to enhance compatibility between organoclay and epoxy. Theoretically, the driving force produced by reaction between modifiers (amino groups) and epoxy would facilitate the penetration of epoxy into the organoclay gallery and consequently leading an exfoliation. However, only intercalation but no exfoliation was observed [31,32]. It is supposed that most of these reactive amino groups were hidged between the dry clay layers and have little chance to contact with epoxy molecules.

The reason for all the efforts mentioned above have failed to achieve highly exfoliation of epoxy/clay nanocomposites is mainly due to the preparation process and the dispersion-curing-exfoliation mechanisms of epoxy thermoset. As reported by most researches, the common process for epoxy nanocomposites synthesis is as follows: dry organoclay powder and epoxy prepolymer was firstly mixed by mechanical blending under heating for a long time. In order to make organoclay uniformly dispersed in epoxy matrix, sonication was often employed after or while blending. At this stage, the organoclay dispersed in epoxy matrix in the form of micro-particles and meanwhile epoxy prepolymer molecules will permeate into clay galleries and the *d*-spacing of the organoclay was broadened by 1–2 nm. However, organoclay platelets would remain its original ordered tactoids, almost no exfoliation occurred in this step. When adding a hardener to the mixture and heated under a proper temperature profile, the curing reaction would occur intragallery and extragallery simultaneously. The elastic force exerted by curing reaction of epoxy molecules inside the clay galleries should gradually enlarge the *d*-spacing of clay to some extent which mainly depended on the compatibility between epoxy and organoclay. However, further delamination of clay tactoids becomes difficult since the viscosity of the system increases dramatically with the increase of the extent of curing process [33] and finally it became hardened when the gelation occur. This means that the exfoliation of clay relies on the high extent of curing, however, the high extent of curing will in turn harden the resulting materials, which prevent the further exfoliation of the clay. Obviously, highly exfoliated epoxy/clay nanocomposites can hardly be achieved via conventional dry organoclay powder compounding method. Therefore, to acquire highly exfoliation, the clay platelets must be well dispersed and highly exfoliated in the epoxy prepolymer prior to curing reaction rather than during the curing. In view of this thought, in our previous study [34], we simply reported a new approach to prepare epoxy/clay nanocomposites: 2,4,6-tris-(dimethylaminomethyl) phenol (DMP-30), which is a promoter of epoxy curing and has very good compatibility with epoxy, is first protonated and then employed as a modifier for modification of pristine clay. Instead of drying up organoclay as usual, the modified organoclay was prepared in the form of acetone-clay slurry and then directly mixing with epoxy prepolymer. By using the method, well-dispersion and highly disordered exfoliated structure epoxy-clay nanocomposites was achieved. Shortly after our report, Wang Ke et al. reported a similar “slurry-compounding” method [35,36], by

which they also successfully achieved highly exfoliated epoxy/clay nanocomposites. Here an intensive study for the distinct mechanism of clay exfoliation, which is very different from the conventional ones [9,21,33], and the mechanical/thermal properties of the nanocomposites has also been presented.

## 2. Experimental

### 2.1. Materials

Sodium montmorillonite, Cloisite Na<sup>+</sup> with cation exchange capacity (CEC) of 92.6 meq/100 g was from Southern Clay. Epoxy resin (EPON 828) was product of Shell Co. 2,4,6-tris-(dimethylaminomethyl) phenol (DMP-30), with a purity of 95% and Polyoxypropylene diamine (Jeffamine D230, denoted J230) used as curing agent, were ordered from Aldrich.

### 2.2. Preparation of organophilic clay and epoxy/clay nanocomposites

10 g pristine clay was dispersed into 1500 mL of distilled water at 80 °C. Protonated form of DMP-30 was prepared by slowly dropping 60 ml 0.24N HCl solution (14.4 mmol) into 4.2 g (15 mmol) DMP-30 in 100 ml distilled water under a magnetic stirring. Slight excess of DMP-30 was added to guarantee only one reactive group of DMP-30 turned into a cation. The solution was then poured into the hot clay/water suspension and stirred vigorously for 8 h at 80 °C. A pale yellow precipitate formed and was isolated by filtration and washed several times with hot distilled water until no chloride was detected in the filtration by one drop of 0.1N AgNO<sub>3</sub> solution. The modified clay (M-clay) was then washed with acetone for several times to replace the water in the M-clay. The acetone/M-clay slurry was directly added into desired amount of epoxy, stirring at 80 °C under reduced pressure for 2 h. During the process, the reaction between modifiers and epoxy would occur and acetone was removed. When the mixtures were cooled down to 50 °C, a stoichiometric amounts of curing agent (J230) corresponding to 100% of epoxy resin content was added and blended for 10 min using a magnetic stirrer. The mixture was then out-gassed in a vacuum oven at 60 °C for a short period of time and then cast into a Teflon mold. The sample was cured at 75 °C for 2 h and post-cured at 120 °C for 8 h.

### 2.3. Characterization

TEM was used to observe the dispersion of clay layers in the polymer matrix. The sample specimens of approximately 80 nm in thickness were microtomed with a diamond knife using a Leica Ultramicrotome at room temperature. TEM images were obtained from a Japan JEOL JEM-1011 microscope operating at 200 kV in bright field mode.

X-ray diffraction (XRD) patterns were obtained on a Germany BRUKER D8 ADVANCE diffractometer with Cu K $\alpha$  X-ray radiation and a curved crystal graphite monochromator, operating at 40 kV and 100 mA. The scanning range was 2–10° (2 $\theta$ ) with a scanning speed and the step size of 1°/min and 0.02, respectively.

DSC measurements were carried out under a nitrogen gas atmosphere in a Perkin-Elmer Diamond thermal analyzer. The samples were first heated to 150 °C and kept for 5 min (to remove any previous processing history), then cooled to 30 °C, and finally heated to 150 °C again. The heating and cooling rates for all runs were 20 °C/min. The *T<sub>g</sub>* values determined according to ASTM E1356-08 were obtained from the reversible heat flow curve.

Flexural properties were performed on a USA INSTRON 5869 electronic testing instrument according to ASTM D790-07. Samples were cast into specimens of 80 × 10 × 4 mm<sup>3</sup> and tested at a crosshead speed of 2 mm/min. The surfaces of the samples

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