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ORIGINAL PAPER

A new method for preparing completely exfoliated epoxy/clay nanocomposites: nano-disassembling method

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Abstract Completely exfoliated epoxy/clay nanocomposites with comprehensive high performance were successfully prepared using Nano-disassembling method. In this method, nano-SiO_2 was added into the montmorillonite and epoxy mixture system as disassembler to interact with montmorillonite (MMT). By means of the strong interaction between nanoscale particles, the MMT layers were completely disassembled into elemental nanometric mono-platelets. These mono-platelets took interlacing arrangement with the disassembler particles in the resultant nanocomposites. Mechanical testing and thermal analysis results indicated that the epoxy/MMT nanocomposites prepared by the Nano-disassembling method displayed dramatic improvements in multiple properties over conventional epoxy/organo-MMT nanocomposites. At the optimal MMT content of 5 phr, tensile modulus and tensile strength increased by 64.2 and 52.3%, respectively. Flexural modulus enhanced by 7.1%, flexural strength by 14.6% and notch impact strength by 37.7%. Glass transition temperature and thermal decomposition temperature moved to higher temperatures by 10.1 and 5.7 °C, respectively.

Keywords Montmorillonite · Nanocomposites · Complete exfoliation · Mechanical properties · Thermal properties

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Introduction

The booming space, aviation, and submarine building industries are starving for lightweight materials with comprehensive high performance. Polymer/layered silicate (PLS) nanocomposites are considered to be promising materials. They not only retain polymer merits such as light total weight and high chemical resistance, but also obtain impressively enhanced mechanical, thermal, and barrier properties due to the incorporation of layered nanomaterials [1–4]. Based on the exfoliation degree of layered silicates in polymers, PLS nanocomposites are usually classified into ''intercalated'' type and "exfoliated" type, with the latter vastly superior in performance to the former [4]. Unfortunately, it is still difficult to obtain completely exfoliated PLS nanocomposites, and this situation is especially serious in the preparation of epoxy/clay nanocomposites [5].

Some strategies have been raised to solve this problem. The most commonly used one is to modify clays with organic additives in a hope that the improved compatibility between hydrophobic polymer and hydrophilic clay layers can facilitate intercalation-exfoliation. However, due to the intrinsic drawback of the conventional "intercalation-exfoliation" mechanism [6], intercalated structures or intercalated and partially exfoliated mixture structures are actually obtained in most cases [1–7]. Therefore, there is a need to get out of the traditional mode and create new methods for making completely exfoliated structures.

There are strong energy fields around nanoscale particles [8]. When nanoscale particles approach one another, strong interactions between them will be generated. These interactions are promising for use to disassemble clay layers. However, there have not been any reports on studies in this aspect. In this study, while MMT and epoxy were mixed together, small amounts of nano-SiO_2 was added in as nano-disassembler to interact with MMT. The MMT layers were completely disassembled, and thus completely exfoliated epoxy/o-MMT nanocomposites were successfully prepared.

Experimental

Materials

The epoxy resin was diglycidyl ether of bisphenol A (DGEBA) E51, provided by Nuoxin Chemicals, Hebei province, China. The curing agent and accelerator were methyl tetrahydrophthalic anhydride and 2-ethyl-4-methylimidazole, respectively; both were commercial products of chemically pure grade and purchased from Shikoku chemical Co., Japan. Two types of clay fillers were used for nanocomposite preparation. One is MMT with a cation exchange capacity (CEC) of 90 meq/100 g and the other one is the DK1 commercial organo-montmorillonite (o-MMT), both from Fenghong chemical Co. Inc., Zhejiang province, China. The nano-disassembler was nano-SiO_2 (30 nm in diameter) supplied by Nachen Co., Beijing, China.

Nanocomposite preparation

Preparation of epoxy/MMT nanocomposites with the Nano-disassembling method was conducted by mixing epoxy resin, 80 phr (parts per hundreds of resin) curing agent, 1 phr accelerator, nano-disassembler, and MMT. The mixture was stirred at ambient temperature for 0.5 h to obtain a transparent and homogenous system. Then the system was injected into a steel mould and degassed for 0.5 h in vacuum. Finally, the mixture was cured at 90 °C for 2 h and 150 °C for 2 more hours. With this process, the epoxy/MMT nanocomposites containing 2, 4, 5, 6, 8, and 10 phr MMT were prepared. The weight ratio of nano-disassembler and MMT was 1:1. Hereafter, the epoxy/MMT nanocomposites prepared with the Nano-disassembling method are designated as N-d epoxy/MMT nanocomposites.

For comparison, conventional epoxy/o-MMT nanocomposites were prepared using DK1 o-MMT according to the procedure described in ref [9]. The epoxy/o-MMT nanocomposites containing 2, 4, 5, 6, 8, and 10 phr o-MMT were prepared.

Characterization

X-ray diffraction (XRD) experiments were performed on a D/MAX-2500+/PC diffractometer equipped with a Cu Kα and operated at 40 kV and 30 mA. Data were collected in the range of 2θ from 2° to 10° at the scanning rate and step size of 1.0°/min and 0.02°, respectively.

The internal structures of the samples were inspected with transmission electron microscopy (TEM) using a JEM-2010 operated at 120 kV voltage.

Mechanical property tests were performed on a universal material testing machine (Instron 5567) at ambient temperature. At least six speciments were tested for each sample. The tensile modulus and tensile strength were measured according to ASTM D638-96. The flexural modulus and flexural strength were measured according to ASTM D 790M, and the notch impact strength according to ASTM D-256.

The tensile, flexural, and impact fracture morphologies were investigated by means of scanning electronic microscopy (SEM) using a KYKY-2800 operated at an accelerating voltage of 20 kV.

Glass transition temperature (T_g) was determined by a STA449C multipurpose thermal analyzer using differential scanning calorimetry, with the samples heated under argon atmosphere from 25 to 150 °C at a heating rate of 10 °C/min.

Thermal decomposition temperature (T_d) was measured on a STA449C multipurpose thermal analyzer using thermogravimetric analysis, with the samples heated under argon atmosphere from 30 to 600 °C at a heating rate of 10 °C/min.

Results

XRD patterns (Fig. 1) were recorded to determine the structures of the composites. The MMT and DK1 o-MMT exhibit 001 diffraction peaks at 5.8° and 4.4°, respectively. As for the 5 phr conventional epoxy/o-MMT nanocomposites, the

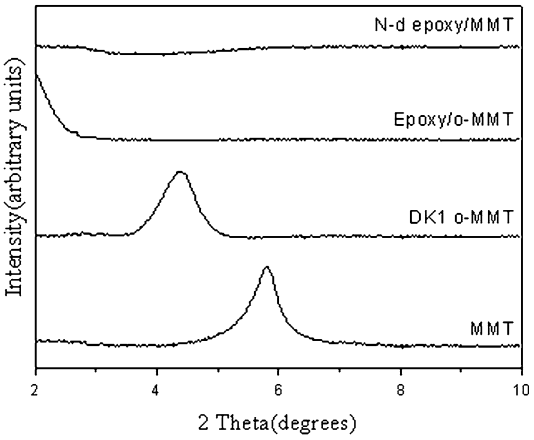

Fig. 1 XRD patterns of MMT, DK1 o-MMT, 5 phr conventional epoxy/o-MMT nanocomposite, and 5 phr N-d epoxy/MMT nanocomposite 70 × 58 mm (600 × 600 DPI)

diffraction peak shifts towards a lower angle beyond the capacity of the instrument. The diffraction curve representing the 5 phr N-d epoxy/MMT nanocomposites is approximately parallel to the base line in the entire measuring range. As calculated from the Bragg equation, the interlayer spacing of the MMT and DK1 o-MMT was 1.5 and 2.0 nm, respectively; the interlayer spacing of the o-MMT in the conventional epoxy/o-MMT nanocomposite was larger than 2.0 nm; no periodical-ordered structure was present in the N-d epoxy/MMT nanocomposite. These data indicate that the interlayer spacing of MMT was enlarged after organic modification and further enlarged after the o-MMT was incorporated into epoxy, but the ordered layered structure of MMT was still maintained in the conventional epoxy/o-MMT nanocomposite. However, in the N-d epoxy/MMT nanocomposite, the MMT lost its layered structure.

The above results are further confirmed by TEM inspection, as shown in Fig. 2. It can be seen clearly that in the 5 phr conventional epoxy/o-MMT nanocomposites, the MMT platelets exists in the form of layered stacks with the interlayer spacing of approximately 4 nm, exhibiting an ordered structure (Fig. 2a). This morphology indicates that the o-MMT in the conventional epoxy/o-MMT nanocomposite still retained the ordered layered structure, although its interlayer spacing was increased due to the intercalation of many polymer chains into MMT galleries. However, in the 5 phr N-d epoxy/MMT nanocomposites (Fig. 2b), MMT mono-platelets are completely separated from one another and the distance between them exceeds 100 nm. The separated MMT mono-platelets took interlacing arrangement with the nano-SiO_2 particles. Obviously, the addition of nano-SiO_2 promoted complete exfoliation of the MMT layers. This effect could be caused by the van der Waals forces generated between the nano-SiO_2 nanoparticles and the surface layers of MMT. These forces exceeded the Coulomb forces existing in MMT galleries, so the MMT layers were completely disassembled into nanoscale mono-platelets. Therefore, we term the nano-SiO_2 as nano-disassembler and the new method as Nano-disassembling method.

Five mechanical properties of the two kinds of nanocomposites were tested and compared (Fig. 3). At every fixed filler content, the N-d epoxy/MMT

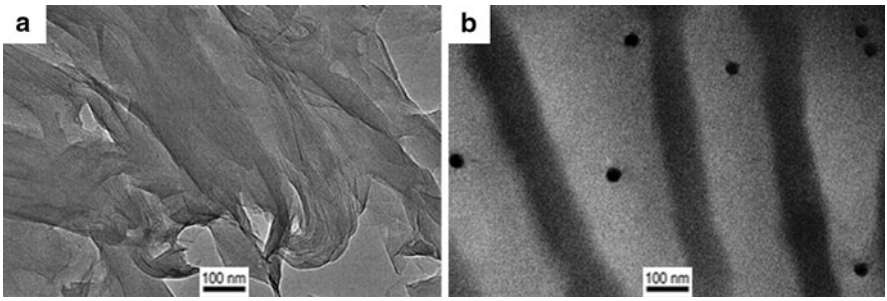

Fig. 2 TEM micrographs corresponding to **a** 5 phr conventional epoxy/o-MMT nanocomposite and **b** 5 phr N-d epoxy/MMT nanocomposite 170 × 56 mm (300 × 300 DPI)

nanocomposites displayed dramatic improvements over the conventional epoxy/o-MMT nanocomposites in all the properties. The 5 phr N-d epoxy/MMT nanocomposite demonstrated the best properties and showed the greatest improvements by yielding: (1) an increase of 64.2% in tensile modulus, (2) an increase of 52.3% in tensile strength, (3) an increase of 7.1% in flexural modulus, (4) an increase of 14.6% in flexural strength, and (5) an increase of 37.7% in notch impact strength. These data suggest that the N-d epoxy/MMT nanocomposites are comprehensively and substantially superior in mechanical properties to the conventional epoxy/o-MMT nanocomposites.

Figure 4 shows the tensile, flexural, and impact fracture morphology of the two nanocomposites containing 5 phr fillers. The conventional epoxy/o-MMT nanocomposite exhibits moderately rough fracture surfaces (Fig. 4 on the left). Its cracks, although displaying some deflection, stretch mainly in one direction. This morphology indicates that the stress in the material was dispersed to some extent, and that the load energy was partially dissipated during crack propagation. The N-d epoxy/MMT nanocomposite displays very rough fracture surfaces (Fig. 4 on the right). Its cracks are fine, close, short, twisting, varying in shape, and scattered in various directions. This morphology indicates that the stress in the material was effectively dispersed to various directions in manifold forms, that load energy was considerably dissipated by many factors during crack propagation, and that some cracks terminated due to lack of energy. Therefore, the performance of the N-d epoxy/MMT nanocomposites is significantly higher than that of the conventional epoxy/o-MMT nanocomposites.

Furthermore, thermal properties of the two kinds of nanocomposites were tested and compared (Fig. 5). At every fixed filler content, the N-d epoxy/MMT nanocomposites displayed dramatic improvements over the conventional epoxy/o-MMT nanocomposites in both T_g and T_d. The 5 phr N-d epoxy/MMT nanocomposite demonstrated the highest properties and showed the biggest improvements by yielding a T_g increase of 10.1 °C and a T_d increase of 5.7 °C. These data suggest that the N-d epoxy/MMT nanocomposites are comprehensively and substantially superior in thermal properties to the conventional epoxy/o-MMT nanocomposites.

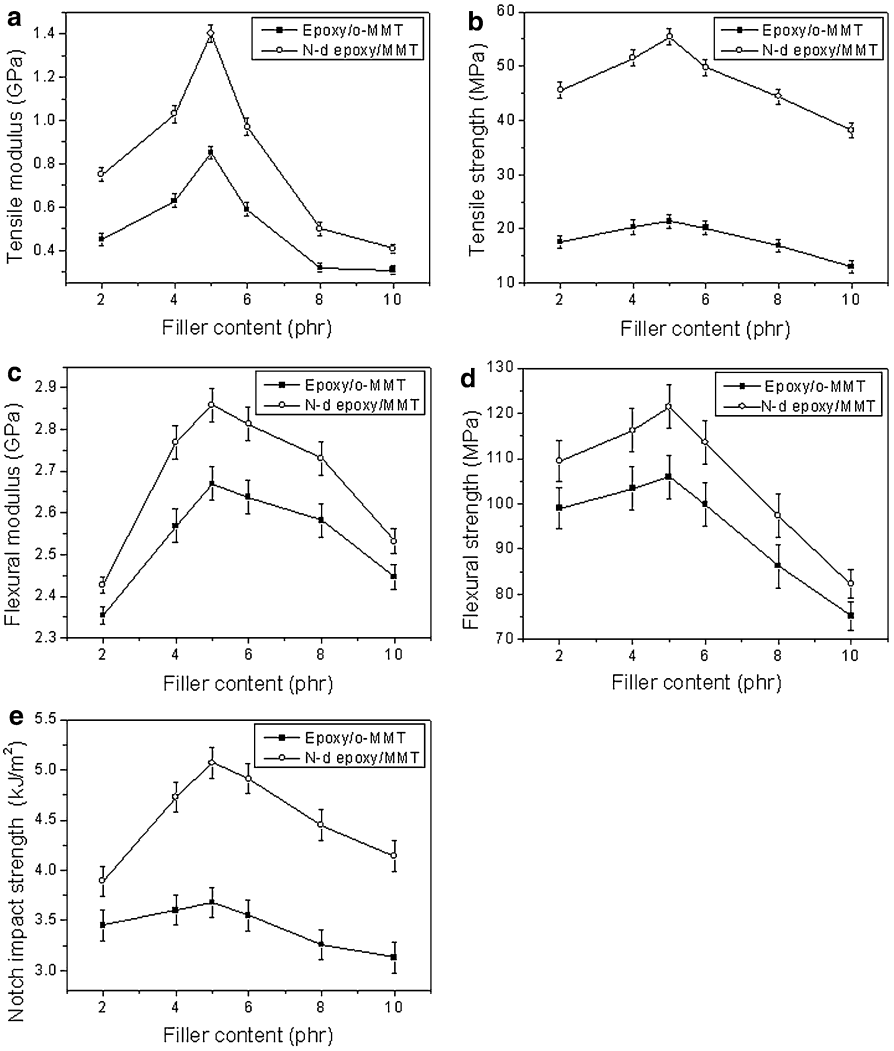

Fig. 3 Mechanical properties of conventional epoxy/o-MMT nanocomposites and N-d epoxy/MMT nanocomposites: **a** tensile modulus, **b** tensile strength, **c** flexural modulus, **d** flexural strength, and **e** notch impact strength 170 × 210 mm (600 × 600 DPI)

Discussion

In the "intercalation-exfoliation" mechanism, hydrophilic clay was usually modified by surfactants to increase its compatibility with hydrophobic epoxy, thus intercalating more epoxy into interlayer regions [9, 10]. In a subsequent cross-linking reaction, the increase of conformation entropy drives the exfoliation of clay layers. However, the cross-linking reaction mainly occurs in the curing stage. In this

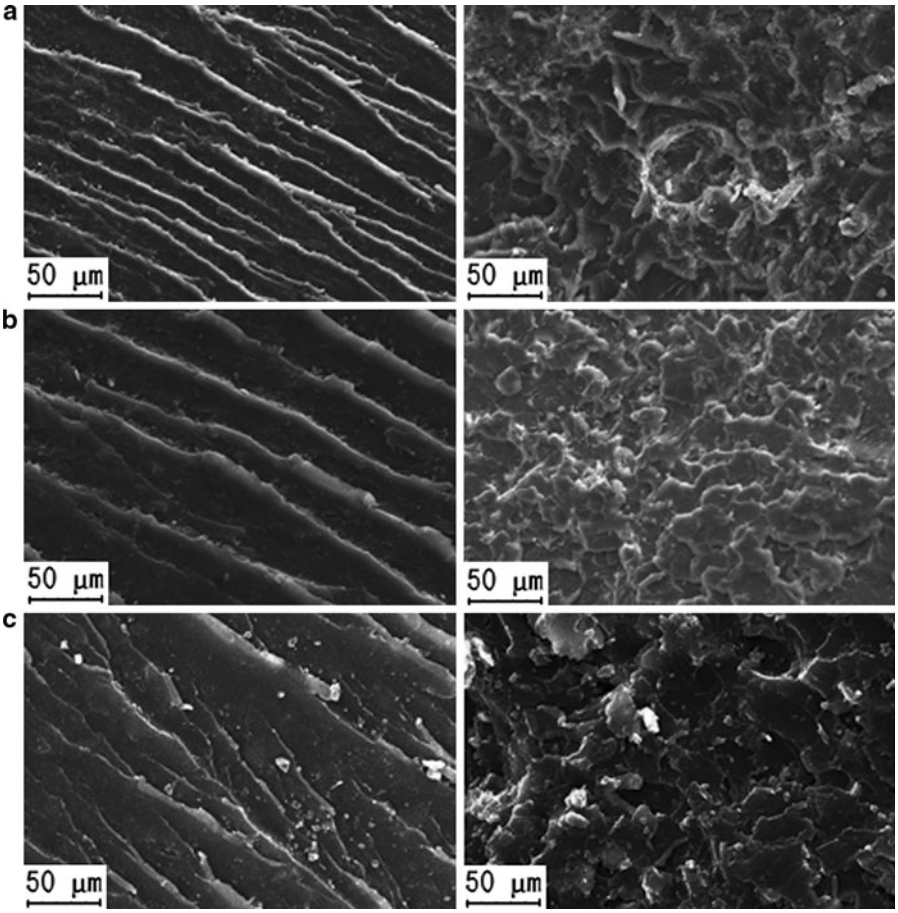

Fig. 4 SEM micrographs showing **a** tensile, **b** flexural, and **c** impact fracture surfaces for: 5 phr conventional epoxy/o-MMT nanocomposite (*left*) and 5 phr N-d epoxy/MMT nanocomposite (*right*) 170 × 165 mm (300 × 300 DPI)

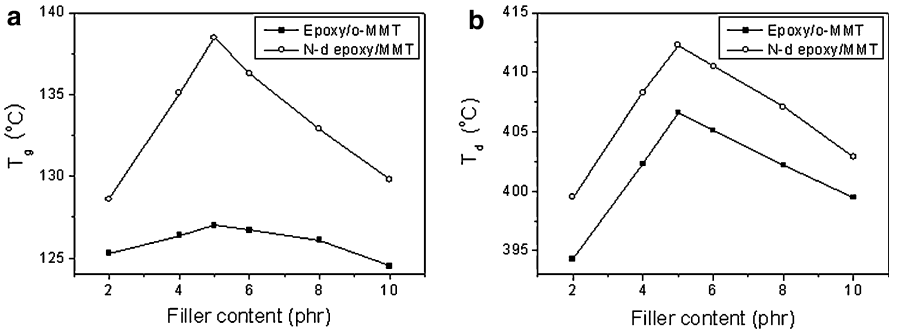

Fig. 5 Thermal properties of conventional epoxy/o-MMT nanocomposites and N-d epoxy/MMT nanocomposites: **a** T_g, **b** T_d 69 × 28 mm (600 × 600 DPI)

stage, the viscosity of the mixture system increases rapidly and shearing is frequently absent, so the intercalated epoxy can only swell clay tactoids to a limited degree and cannot obtain proper conditions for further exfoliation of them [6, 10]. Therefore, the ordered structure of clay layers is still maintained in most cases, and real completely exfoliated epoxy/clay nanocomposites are difficult to obtain [2, 6, 10, 11]. This drawback is common to all the conventional methods that depend on the "intercalation-exfoliation" mechanism. In contrast, The Nano-disassembling method performs natural and direct disassembling to MMT layers by means of the attractive forces between nano-SiO_2 particles and MMT layers. Thus, completely exfoliated epoxy/MMT nanocomposites with comprehensive high performance can be obtained.

Additionally, the Nano-disassembling method has several merits in preparation procedure. Firstly, it doesn't require any organic modifications to MMT layers, which not only avoids the complicated synthesis process and the high cost involved [12], but also prevents the thermal property decrease caused by introduced surfactants [13, 14]. This may partly explain the experimental results that the T_g and T_d of N-d epoxy/MMT nanocomposites were higher than those of the conventional epoxy/o-MMT nanocomposites. Secondly, in the mixing stage, it only needs stirring at ambient temperature for 0.5 h, rather than at high temperatures (80, 120 °C, etc.) for 2 h, 12 h, or even longer as described in many reports [2, 10–16]. Thirdly, it employs a two-phase curing that is simpler than the widely used three-phase curing [10, 11, 15, 16]. Obviously, the Nano-disassembling method is suitable for application in industrial production of epoxy nanocomposites with comprehensive high performance, as it is convenient, time-sparing, energy-saving, and environmentally benign.

Conclusions

A new and convenient method for preparing completely exfoliated epoxy/clay nanocomposites with comprehensive high performance has been developed, termed Nano-disassembling method. This method utilizes the interaction between nanoscale particles to achieve complete exfoliation of clay layers. Compared with the epoxy/o-MMT nanocomposites prepared by conventional method, the epoxy/MMT nanocomposites prepared by the Nano-disassembling method exhibited dramatic improvements in tensile modulus, tensile strength, flexural modulus, flexural strength, notch impact strength, glass transition temperature, and thermal decomposition temperature. This study opens a new pathway for the preparation of completely exfoliated polymer/layered silicate nanocomposites with high performance.

References

1. Nam BU, Son Y (2010) Evaluations of PP-g-GMA and PP-g-HEMA as a compatibilizer for polypropylene/clay nanocomposites. Polym Bull 65:837–847
2. García-López D, Gobernado-Mitre I, Merino JC et al (2009) Properties of polyamide 6/clay nanocomposites processed by low cost bentonite and different organic modifiers. Polym Bull 62:791–800

3. Okada A, Usuki A (2006) Twenty years of polymer-clay nanocomposites. Macromol Mater Eng 291:1449–1476
4. Koo CM, Kim SO, Chung IJ (2003) Study on morphology evolution, orientational behavior, and anisotropic phase formation of highly filled polymer-layered silicate nanocomposites. Macromolecules 36:2748–2757
5. Wang L, Wang K, Chen L et al (2006) Preparation, morphology and thermal/mechanical properties of epoxy/nanoclay composite. Composites A 37:1890–1896
6. Wang K, Wang L, Wu JS et al (2005) Preparation of highly exfoliated epoxy/clay nanocomposites by "slurry compounding": process and mechanisms. Langmuir 21:3613–3618
7. Becker O, Cheng YB, Varley RJ, Simon GP (2003) Layered silicate nanocomposites based on various high-functionality epoxy resins: the influence of cure temperature on morphology, mechanical properties and free volume. Macromolecules 36:1616–1625
8. Bishop KJM, Wilmer CE, Soh S, Grzybowski BA (2009) Nanoscale forces and their uses in self-assembly. Small 14:1600–1630
9. Pluart LL, Duchet J, Sautereau H (2005) Epoxy/montmorillonite nanocomposites: influence of organophilic treatment on reactivity, morphology and fracture properties. Polymer 46:12267–12278
10. Guo BC, Jia DM, Cai CG (2004) Effects of organo-montmorillonite dispersion on thermal stability of epoxy resin nanocomposites. Eur Polym J 40:1743–1748
11. Liu HZ, Zhang WA, Zheng SX (2005) Montmorillonite intercalated by ammonium of octaaminopropyl polyhedral oligomeric silsesquioxane and its nanocomposites with epoxy resin. Polymer 46:157–165
12. Wang ZC, Xu CL, Zhao YQ et al (2008) Fabrication and mechanical properties of exfoliated clay–CNTs/epoxy nanocomposites. Mater Sci Eng A 490:481–487
13. Wang JW, Qin SC (2007) Study on the thermal and mechanical properties of epoxy–nanoclay composites: the effect of ultrasonic stirring time. Mater Lett 61:4222–4224
14. Gao F (2004) Clay/polymer composites: the story. Mater Today 7:50–55
15. Liu WP, Hoa SV, Pugh M (2005) Fracture toughness and water uptake of high-performance epoxy/nanoclay nanocomposites. Compos Sci Technol 65:2364–2373
16. Lakshmi MS, Narmadha B, Reddy BSR (2008) Enhanced thermal stability and structural characteristics of different MMT-clay/epoxy-nanocomposite materials. Polym Degrad Stab 93:201–213