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Preparation and characterization of epoxy composites filled with functionalized nano-sized MCM-41 particles

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Abstract Mono-dispersed nano-sized MCM-41 (M (with template)) particles were synthesized by sol–gel reaction. The effect of interface modification on the properties of epoxy composites was investigated. Modifications were carried out either by substituting silanol groups on the surface or in the mesopore channels into amine (M-NH_2), calcinating mixture template in the mesopore channels (M (without template)), or recalcinating them at higher temperature to remove silanol groups (–OH) in the mesopore channels or on the surface (CM). Transmission electron micrograph results showed that the dispersing of MCM-41 nanoparticles was not influenced by the modification, while –NH_2 group indeed modified the mesopore channels or the surface of MCM-41 particle by using IR, XRD, and N_2 adsorption–desorption. In addition, tensile tests suggested that M-NH_2 nanoparticles could simultaneously provide epoxy matrix with strengthening and toughening effects. However, due to the different interfacial structures between the fillers and the matrix, the mechanical properties of the composites filled by M-NH_2 were much better than those of composites filled by MCM-41 (without template), MCM-41 (with mixture template), and CM.

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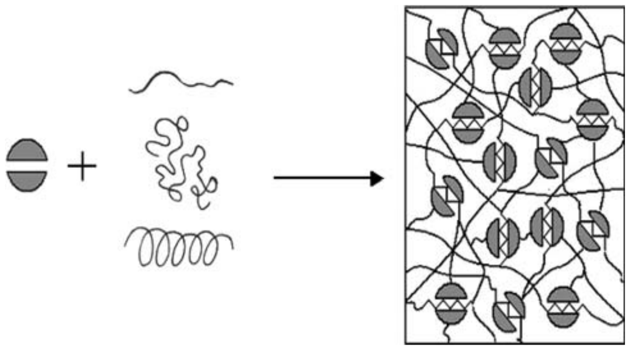
Introduction

Organic–inorganic composites are of considerable interest and importance because they give rise to a synergy between the inorganic particles and the polymer matrix in which they are dispersed [1]. So far most of the nanocomposites reported are reinforced by nano-sized mineral materials, metal, precipitated metal, and non-metal oxides, such as PE/clay [2], vinyl chloride-acrylonitrile copolymer/nano-SiO_2 [3], EP/nano-SiO_2 [4], EP/Ag [5]. The challenges in this area of high-performance polymers are to obtain significant improvement in the interfacial adhesion between the polymer matrix and the inorganic additives, and to realize a homogeneous dispersion of the additives in the polymer matrix.

These two main problems have been solved by adding nano-sized mesoporous MCM-41 as fillers in our previous studies [6]. Ordered mesoporous MCM-41 materials consist of extended inorganic or inorganic–organic hybrid arrays with exceptional long-range ordering, highly tunable textural and surface properties, and controllable pore size and shape. It is expected that a polymer could either be introduced directly or produced by in situ polymerization of organic monomers inside the mesopores. One of the advantages of this method is that the micro-structure of the interface between the matrix and the pore openings of the fillers could be easily tailored. The physical entanglement of the polymer chain ends could not only increase the miscibility between the matrix and the filler, but also form a novel nanonetwork composite (see Scheme 1). The aggregation of the fillers was highly suppressed in the composites filled with MCM-41 particles.

In our previous studies, we used polymer-filled porous MCM-41 as a nanofiller to design polypropylene-based nanocomposite. The results of tensile tests showed that



Scheme 1 Model analogy novel nanonetwork composite

different flexible polymer-filled mesoporous MCM-41 nanoparticles could simultaneously provide polypropylene with both strengthening and toughening effects at rather low filler content [6].

The aim of this current study is to investigate the effect of surface modification for nano-sized mesoporous MCM-41 fillers on the properties of epoxy resins' composite, especially on the mechanical properties. Nano-sized mesoporous MCM-41 were synthesized by sol–gel reaction to get uniform size and uniform dispersing. Their surfaces were then modified by substituting silanol groups for other functional groups to some extent. In our previous paper, we have reported the best medium and the proper amount of coupling agent for the MCM-41 modification [7]. In this paper, we compared different fillers, M (without template), M (with template), CM, and M-NH_2 at the same filler content and the emphasis was how the nature of the interface affected the properties of the epoxy resins composites.

Experimental

Materials

Tetraethylorthosilicate and Cetyl trimethylammonium bromide (CTAB) were supplied by shenyang Xinxi Chemical Co. Ltd and Beijing Zhonglian Chemical Co. Ltd, respectively; epoxy of bisphenol A type (E-44) used was purchased from WuXi Epoxy Co Ltd; low molecular weight polyamide was used as a curing agent for epoxy resin. All chemicals were used as received.

Synthesis and surface modification of mesoporous MCM-41

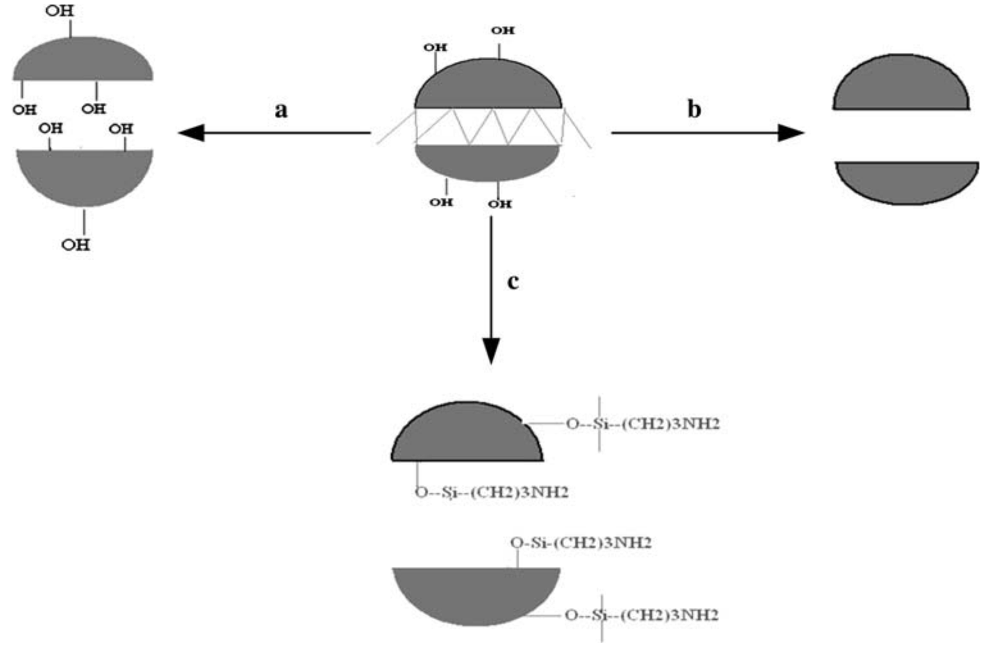
Synthesis of mesoporous MCM-41

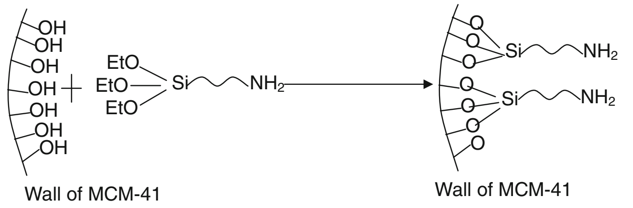
The nano-sized mesoporous MCM-41 particles were prepared in an aqueous phase by sol–gel method. A triblock copolymer (Pluronic F_{127}, molecular weight = 11,500) was added as an assistant surfactant and dispersant to prevent the agglomeration of the particles [6].

The as-synthesized powder was named as M (with template).

The as-synthesized powder was used for substituting the surface silanol group. The surface modification was illustrated in Scheme 2.

Scheme 2 (**a**) Calcinations (560 °C, 6 h) (**b**) Calcinations (560 °C, 6 h; 800 °C, 2 h). (**c**) APTES (-aminopropyl-triethoxysilane)





Scheme 3 The chemical reaction of amine groups with silanol groups of MCM-41

Calcinations of the synthesized mesoporous MCM-41 nanoparticles

Mesoporous MCM-41 nanoparticles were full of silanol groups (Si–OH) on the surface or in the mesopore channels. It had been demonstrated that all physisorbed water could be removed by heating at 373 K for a prolonged period. Except a small amount of isolated silanol groups, most of silanol groups could be removed by condensing water between two silanol groups over 878 K [8].

The as-synthesized MCM-41 nanoparticles [M (with template)] were subjected to calcinations in air at 833 K for 6 h to remove the organic templates. The powder was named as M (without template), and then the M (without template) powder was heated to 1,073 K for 2 h to remove silanol groups on the surface and in the inner-channel, which was named as CM.

Inclusion of amine groups onto MCM-41 surface and mesopore channels

We have found the best medium and the proper amount of coupling agent for the MCM-41 modification in our previous work [7]. The procedures were as follows. One gram of MCM-41 (without template), 50 mL dry hexane, and 5.0 mL 3-aminopropyltriethoxysilane were placed in a 100 mL round bottom flask. The mixture was stirred and refluxed at 343 K for 12 h under the protection of nitrogen atmosphere. The white solid was washed repeatedly with ethanol and then dried at 353 K for 12 h. 3-Aminopropyl functional MCM-41 was named as M-NH_2. The chemical reaction was illustrated in Scheme 3.

Composite preparation

MCM-41 powders and modification of MCM-41 powders were added into liquid epoxy by portion, and then they were dispersed into epoxy resin by ball mill. The resin mixtures were degassed until most of entrapped bubbles were removed completely after mixing. Forty parts per hundred resin of curing agent were gently mixed into the resin mixtures until they dissolved uniformly. The mixtures were cured in a preheated mold at 70 °C for 3 h followed by post-cured at 125 °C for 2 h.

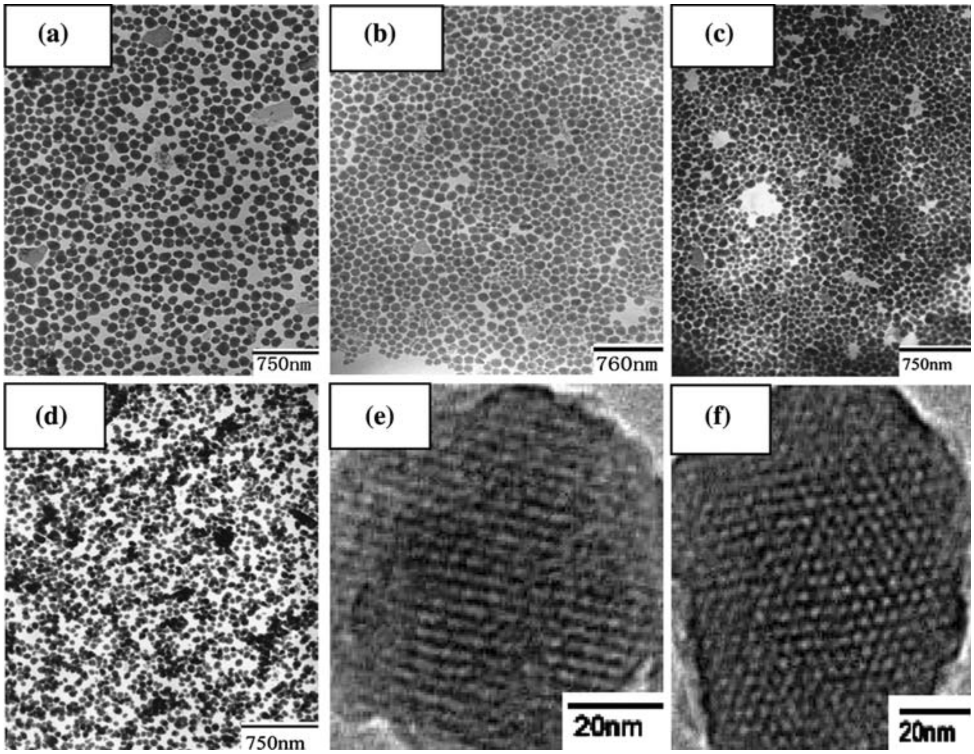


Fig. 1 TEM images of all samples. (**a**) MCM-41 (without template) (**b**) MCM-41 (with template) (**c**) CM (**d**) M-NH_2 (**e**) shows the MCM-41 (without template) side view, and (**f**) the front view

Characterization

N_2 adsorption–desorption isotherms at 77 K were conducted on micromeritics ASAP 2010 micropore analysis system. The samples were outgassed at 473 K for 4 h. X-ray diffraction patterns were recorded on D/max-2500PC X-ray diffractometer, using Cu K_a radiation at 50 kV and 200 mA with a scanning rate 1°/min by 0.01 steps. To identify the functional groups on the surface and mesopore channels of modified mesoporous MCM-41, FT-IR measurements were performed on Nicolet MNGNA-IR560 with 4 cm^{-1} resolution. The template and organic group content of the mesoporous MCM-41 nanoparticles were measured using a thermogravimetric analyzer (NETCH STA449C). The measurement was carried out under N_2 at a heating rate of 10 °C/min. The sizes of the nanoparticles were determined by a Philips EM420 transmission electron micrograph (TEM). To prepare the nanoparticle sample for TEM examination, the MCM-41 nanoparticles were dispersed in ethanol by an ultrasonic bath for 10 min. The average size of the primary particles was determined by measuring the sizes of ten randomly chosen particles. Room temperature tensile testing of the composites was done on an Instron1211 testing machine at a crosshead speed of 10 mm/min. The measurement was repeated five times for each type of sample and the average value was calculated.

Results and discussion

Preparation and modification of mesoporous MCM-41

In this study, nano-sized mesoporous MCM-41 particles with uniform diameters in the order of 80–100 nm, spherical shape, and that were mono-disperse were synthesized by our group to exclude the size and shape effects of fillers on composites (Fig. 1a, b). The dispersed MCM-41 nanoparticles were not influenced by the high-temperature treatment (Fig. 1c). This spherical morphology for M-NH_2 was preserved for the composite materials (Fig. 1d). No clear aggregates were observed and this indicates that chemical bonds were formed between the amine groups and the hydroxy group of the MCM-41 surface and the mesopore channels. Thus, indicating that effective dispersion of amine groups on the very high surface area spherical MCM-41 material was achieved. The TEMs in Fig. 1e, f showed the regular hexagonal array of uniform channels for MCM-41 with pore size about 3.6 nm agreed with nitrogen adsorption results.

The N_2 adsorption isotherm of the MCM-41 materials was typical of type IV with a steep increase at $P/P_0 = 0.3$–0.4 according to the IUPAC classification [8], as shown in Fig. 2. The textural properties of the mesoporous samples were collected in Table 1. The specific surface area and pore volume of M-NH_2 were concomitantly reduced.

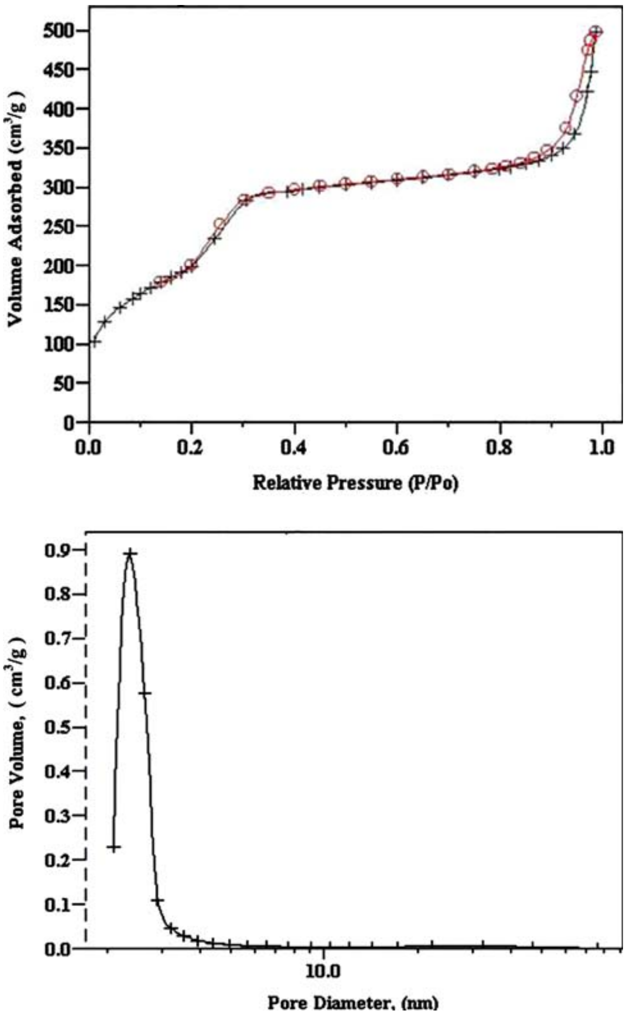


Fig. 2 Nitrogen adsorption and pore size distribution isotherms of the MCM-41

Table 1 Textural properties of the products

	S_{BET} (m^2/g)	D (nm)	Pore volume (cm^3/g)
MCM-41 (without template)	732.3	3.6	0.86
CM	564	6.3	0.28
M-NH_2	356	2.5	0.33

XRD patterns were recorded for all samples, visible in Fig. 3. An intense (100) diffraction peak at low reflection angles was found in the samples, which corresponded to the characteristics of hexagonal ordering [9]. However, various samples exhibited differences in their peak intensities. For CM and M (without template) samples, the peak intensity increased and the (100) peak position shifted from

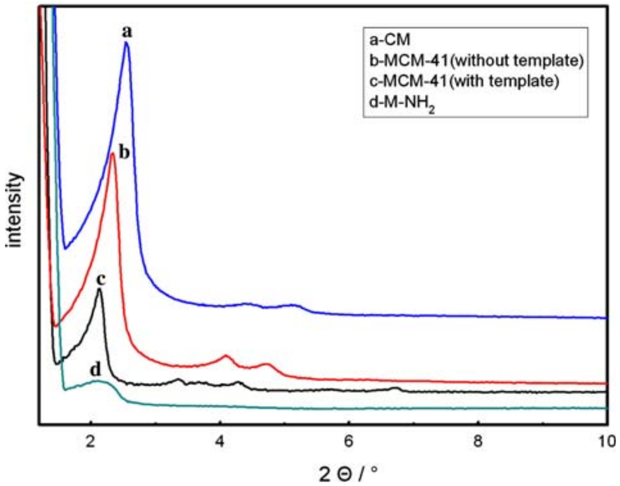


Fig. 3 X-ray diffraction patterns of all samples

low angle to high angle, which attributed to the results of condensing water between the two silanol groups after calcinations (Fig. 3a, b). The decrease of the peak intensity for M-NH$_2$ supported the fact that –NH$_2$ group was adsorbed inside the mesopores of MCM-41 without affecting its structure (Fig. 3a, b).

The weight loss below 200 °C was due to the water adsorptions, and above 500 °C the water loss caused the weight loss also, as a result of the condensation of the silanol groups. Therefore, the weight loss between 200 and 500 °C was assigned to the decomposition of the organic compounds for the –NH$_2$ group. The TGA measurements revealed that the total content of mixture template was 68 wt.% and the content of –NH$_2$ organic group was 18 wt.% (Fig. 4b, c).

Figure 5 showed the IR spectra between 4,000 and 400 cm^{-1} of all samples. The as-synthesized samples exhibited the absorption bands around 2,921, 2,850, and 1,490 cm^{-1}, respectively, which corresponded to n–C–H and d–C–H vibrations of the surfactant molecules. The broad bands at 3,500 cm^{-1} may be attributed to the surface silanols and adsorbed water molecules. The adsorption bands at 1,620–1,640 cm^{-1} were caused by the deformation vibrations of adsorbed water molecules [9]. The absorption bands at 1,050 and 1,221 cm^{-1} were due to the asymmetric stretching vibrations of Si–O–Si bridges [9] (Fig. 5a). The bands corresponding to the organic surfactant molecules disappeared after calcinations (Fig. 5b). The modification of –(CH$_2$)$_3$NH$_2$ was evident by the wavenumber part of the spectra, where the transmission bands at 2,925 and 1,480 cm^{-1} formed the asymmetric and bend vibrations of CH$_2$ units (Fig. 5c). The band at 960 cm^{-1} (Fig. 5a), one characteristic of the stretch vibration of Si–OH, disappeared and the intensity of the bands at 3,500 cm^{-1} decreased in Fig. 5c, which indicated most of the Si–OH reacted with coupling agent forming Si–O–Si (CH$_2$)$_3$–NH$_2$.

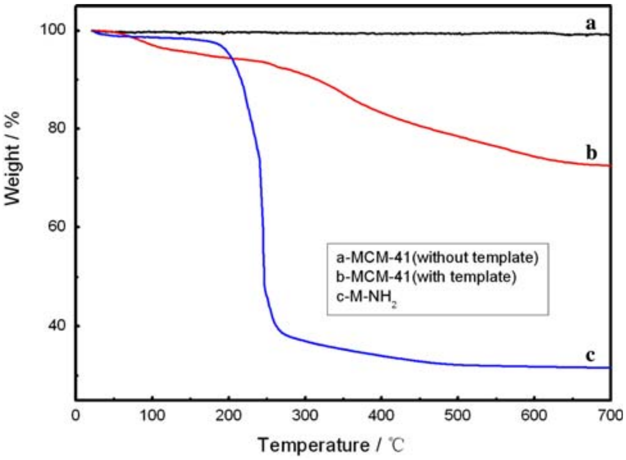


Fig. 4 The weight loss of samples analyzed by TGA

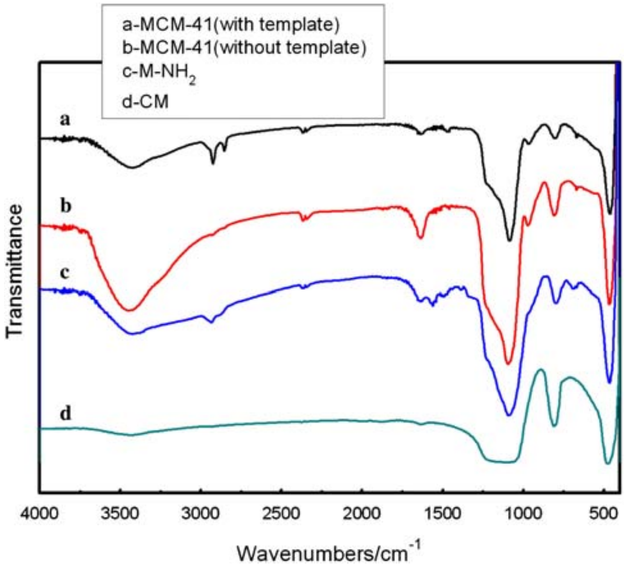


Fig. 5 The FTIR spectra of all samples

The band near 3,500 cm^{-1} (Fig. 5c) became broader due to –NH$_2$ vibrations of the coupling agent. The bands at 3,500 and 960 cm^{-1} disappeared in CM sample after recalcinations at higher temperature (Fig. 5d). However, it kept the highest intensity in M (without template) sample (Fig. 5b). MCM-41 (without template) was indeed modified by the –NH$_2$ group based on the analysis above.

Tensile properties of the composites

Table 2 showed the tensile properties for the composites investigated. The values of elongation at break (ε_b) and the area under stress–strain plots (U_k) were an indication of toughness properties [10]. It was worth noting that the

Table 2 Mechanical properties of epoxy resin filled with different functionalized nano-sized MCM-41 particles

	Tensile strength (MPa)	Elongation at break (%)	Tensile modulus (MPa)	U_K (mJ)
Epoxy resin	7.58	18	266	206.5
Epoxy/MCM-41(without template)-5%	14.2	17	595	273.7
Epoxy /MCM-41(with template)-5%	7.32	25	259	211.1
Epoxy resin/CM-5%	13.4	11	547	227.7
Epoxy resin/M-NH_2-5%	12.3	23	500	353.2

different enhancement of the tensile properties was observed between the composites filled with M (without template), M (with template), CM, and M-NH_2. The intrinsic properties of each component, such as the shape of fillers, the nature of the interface, and so forth, largely affected the properties of the composites.

The M-NH_2 filler showed the improvement of the epoxy resin matrix by both the reinforcing and toughening effects on the polymer, which was different from the M (without template) and CM particulate filled composites. The epoxy resin/CM composites exhibited the improvement in tensile strength (δ_y) and Young's modulus (E), but it led to a drop in elongation at break (ε_b) among the resulting composites which was much worse than that of the matrix. This may be attributed to the different interface adhesion property between the filler and the matrix. Coupling modification has important effects on increasing the compatibility between epoxy resin and the filler. –NH_2 group in the M-NH_2 channels was beneficial for incorporating epoxy group into the one-dimensional channels of M-NH_2. The epoxy group in the nano-sized pores, which extended along the channels to the openings, could enhance the interaction through the entanglement and interdiffusion between the matrix and the particulate on one hand. On the other hand, –NH_2 group on the outer surface of the particle was prone to react with epoxy group, which would be good for the matrix/filler miscibility. Much more interfacial surfaces could be generated between the polymers and M-NH_2 nanoparticles, which assisted in absorbing the stress. For M (with template), the organic template mixture of CTAB and F_{127} in the nano-sized pores or on the surface of the nanoparticles had a low molecular weight, which was helpful for the improvement of toughness and detrimental to the improvement of strength. Eight to twenty-seven percent –OH group was still in the pore channels or on the surface of the M (without template) nanoparticles, which was much more than that of CM nanoparticle. –OH group increased the miscibility between the epoxy matrix and M (without template) nanofiller. As a result, M (without template), CM, M (with template), and M-NH_2 nanoparticle showed different effects on the tensile properties of epoxy resin.

Currently, the thermal properties and other mechanical properties are being studied. Further experiments are underway to show the influence of the polymers within the pore channels and on the pore openings on the bulk matrix properties.

Conclusions

The tensile properties of epoxy/nano-sized MCM-41 composites are strongly influenced by the interfacial strength between the matrix and the fillers. Functional silane treatment of nano-sized MCM-41 could simultaneously improve the strength and toughness of the composites, as the mechanical tests indicated. The main reason is shown in the introduction of a flexible layer in the interface and the mesopore channels. The –NH_2 group in the M-NH_2 channels is beneficial for the incorporation of epoxy group into one-dimensional channels of M-NH_2. The epoxy group in the nano-sized pores, which extends along the channels to the openings, may enhance the interaction between the matrix and the particulate by the entanglement and interdiffusion that increase the miscibility.

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