Study on Sepiolite-Reinforced Polymeric Nanocomposites

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ABSTRACT: Epoxy nanocomposites reinforced by nano-sized sepiolite are investigated. Sepiolite particles and the nanocomposites were characterized by SEM, TEM, XRD, and IR. The level of reinforcement is assessed from impact strength and flexural strength. It is shown that significant improvement in mechanical property is obtained for all reinforced nanocomposites and the addition of 1% sepiolite appears to be an optimum blend ratio. © 2005 Wiley Periodicals, Inc. J Appl Polym Sci 99: 2163–2166, 2006

Key words: sepiolite; epoxy resin; nanocomposites; impact strength; flexural strength

INTRODUCTION

Nanomaterials are a relative new class of materials, which exhibit ultrafine phase dimensions, typically in the range 1–100 nm. Because of the nanometer-sized dispersion, nanocomposites display markedly improved properties when compared with pure polymers or conventional composites.[1] Nano-sized layered silicates are frequently used as the fillers. The surface of layer silicates is often hydrophilic. Ion exchange reactions with cationic surfactants, preferably R—NH$_3^+$ group can make the hydrophilic silicate surface organophilic. The organic cations lower the surface energy of the silicate surface and make the intercalation of many engineering polymers possible because of the improvement in the wetting characteristics with the polymer matrix. Montmorillonite (MMT) belongs to the general family of 2 : 1 layered silicates. Extensive work has been done on MMT nanocomposites,[1–3] while little is documented on sepiolite nanocomposites.

Sepiolite is a fibrous magnesio-silicate formed of staggered talc sheets, ideal formula [Si$_{12}$Mg$_8$O$_{30}$(OH)$_4$](H$_2$O)$_4$ · 8H$_2$O], whose structure is composed of two bands of silica tetrahedrons linked by magnesium ions in octahedral coordination. The discontinuous octahedral layer provides for infinite channels along the fiber axis with a cross section of about 1×0.4 nm^2. The surface properties of sepiolite cannot be modified by cation exchange, but have been achieved by partial isomorphic replacement of the octahedral magnesium. The measured cation-exchange capacity on naturally pure minerals is in the order of 0.07 mequiv/g.[4]

In this work, nanometer-sized sepiolite particles are used as a reinforcement filler to prepare for epoxy nanocomposites. The physical properties of the nanocomposites are carefully examined and the role of nanofiller particles during the deformation processes is also studied.

EXPERIMENTAL

Materials

The CYD-128 purchased from Yue Yang Chemical Co. is a diglycidyl ether of bisphenol, a resin with an average molecular weight of 385 g/mol. Aromatic hardener (JHB-590) with an acid value of 660–685 mg KOH/g was received from Dalian–Jinshi Chemical Industry Ltd. Nanometer-sized sepiolite particles were obtained from Shaanxi Institute of Mining. Acetone and coupling agent KH-570 were obtained form Nanjing Shuguang Chemical Co.

Preparation of nanocomposites

Sepiolite particles were washed using a dilute HCl solution and then distilled water. The clean samples were dried in an oven. When cooled down to room temperature, these sepiolite particles were stored in a desiccator. Blending was carried out in a Haake mixer followed by an hour of ultrasonic treatment to gain uniform dispersion of sepiolite fillers. The mixing temperature was 130°C. Hardener (epoxy:hardener = 1: 0.875) was then added to the mixture as its temperature was lowered. After degasification, the mixture was quickly poured into a preheated steel mold coated with the mold release agent to prepare for specimens.

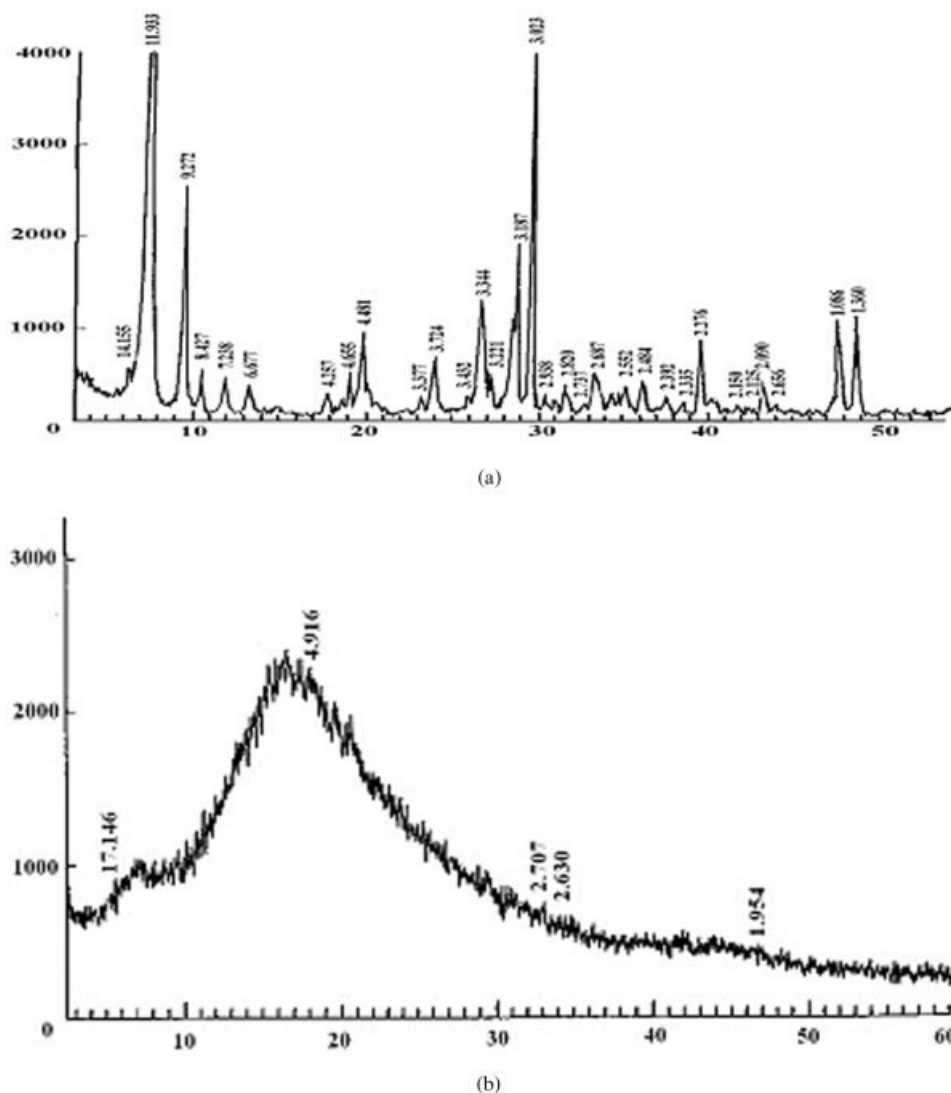*Correspondence to:* Y. Zheng (yzheng@unb.ca).

Figure 1 XRD patterns for (a) sepiolite nanofillers; (b) epoxy nanocomposite with 1 wt % sepiolite.

Mechanical and morphological properties

The impact and flexural strength tests followed ASTM-D256 and ASTM-D790, respectively. Ten specimens for each test were examined. The mean values and their standard deviations were calculated.

T_g was determined using a differential scanning calorimetry (DSC) (TAM 2910) at a heating rate of 20°C/min in nitrogen atmosphere. The morphology of the fracture surface of the specimens was examined by a scanning electron microscope (AMRAY 1000-B model). Transmission electron microscope (TEM) examination of an ultrathin film was conducted on a Joel H-600. XRD analysis was carried out using a D/MRX-RA equipped with a Cu anticathode. It has an acceleration voltage of 45 kV and a current of 80 mA.

RESULTS AND DISCUSSION

Structurally, sepiolite is composed of two tetrahedral silica sheets sandwiching a central sheet of magne-sium oxide–hydroxide. This unique structure imparts sepiolite a fibrous matrix with channels oriented in the longitudinal direction of the fibers. The fibrous structure of sepiolite induces sorptive, colloidal/rheological, and catalytic properties.[5] The XRD patterns for the crystalline structure of sepiolite and the epoxy nanocomposites with 1 wt % addition of sepiolite are shown in Figure 1(a,b), respectively. The crystalline structure of sepiolite disappears in the sepiolite-reinforced nanocomposites. The texture change in the sepiolite can be attributed to the fact that sepiolite has completely intercalated with polymeric matrix during the formation of the nanocomposites.

Curing of a resin system is the critical and productivity controlling step in fabrication of thermoset composites. As resin cures, the crosslinked density, viscosity, and modulus of the resin system increase. Figure 2 shows gel time of the sepiolite/epoxy nanocomposites with different addition of sepiolite fillers under five different temperatures. As expected, the gel time of
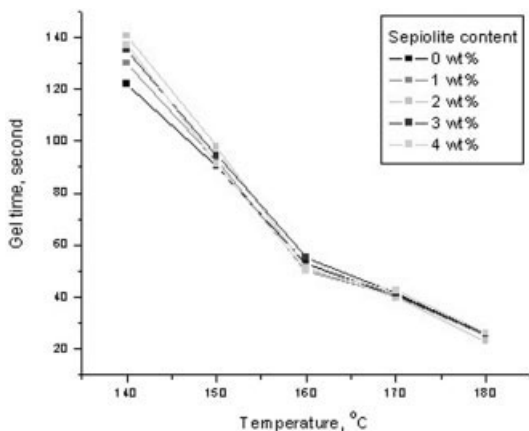
Figure 2 The effect of sepiolite nanofillers on the gel time of epoxy nanocomposites.

nanocomposites reduces with increasing temperature. It is noted that the addition of sepiolite fillers has no significant impact on gel time, that is, there is no variation expected to occur in the production process of the sepiolite-reinforced epoxy nanocomposites.

Figure 3 shows the IR spectrum of epoxy composites with and without the addition of sepiolite. The absorption peak at 909 cm^{-1} is a characteristic peak for epoxy group, which disappears for all samples and indicates that all epoxy groups has participated the curing reaction. It confirms that the nanocomposites have cured completely and sepiolite has no negative effect on the curing process of epoxy nanocomposites.

A TEM image of sepiolite-reinforced epoxy nanocomposite is shown in Figure 4. Sepiolite nanofiller appears to be in tree-branched shape. The interaction between sepiolite fillers and epoxy resin makes the crystal structure of sepiolite fillers broken and the tree-branched network is formed within the nanocomposites. The glass transition temperatures of the epoxy composites with and without sepiolite nanofillers are shown in Table I. Addition of sepiolite nanofillers results in 50°C increase in the glass transition temper-
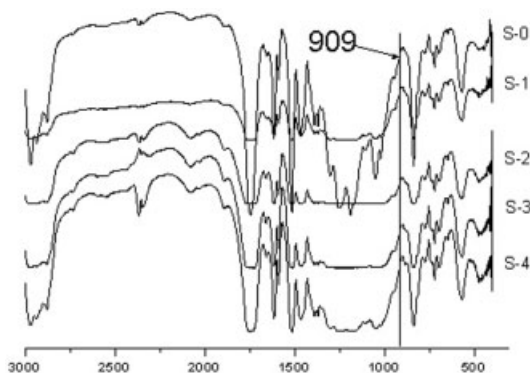

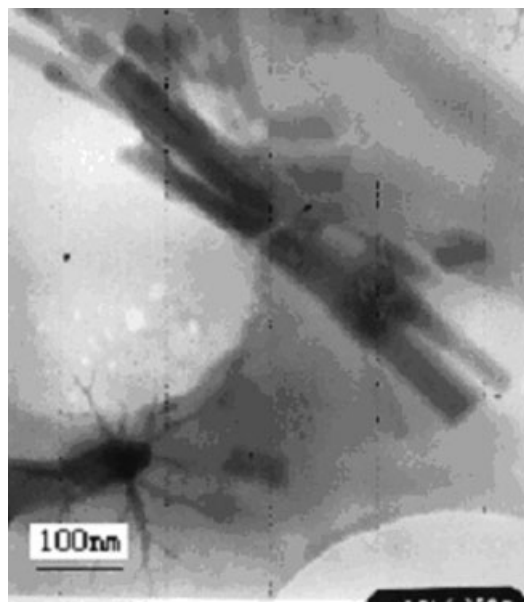**Figure 3** FTIR spectrum of sepiolite-reinforced epoxy nanocomposites.

Figure 4 TEM image of epoxy nanocomposite with 1 wt % addition of sepiolite.

atures, while the quantity of nanofillers added has no influence on the glass transition temperature.

The flexural strength and impact strength of epoxy nanocomposites with various addition ratios of sepiolite are listed in Table II. For comparison, the mechanical properties of the composite without sepiolite fillers are also listed in Table II. It is seen that the addition of sepiolite fillers can significantly improve both the impact strength and the flexural strength of nanocomposites. The best results are obtained at the filler content of 1 wt %. A fourfold improvement is observed in its impact strength while the flexural strength is doubled. Further increase in the content of sepiolite fillers, those mechanical properties of the nanocomposites decrease but are still much higher than those of epoxy composite without sepiolite reinforcement. The improved mechanical properties should be resulted from the large interfacial area and the strong interaction between the polymer and the nanofillers.

Figure 5 compares the SEM images of the fracture surfaces of the epoxy composite with and without sepiolite reinforcement. For the epoxy composite with-

TABLE I
The Effects of Sepiolite Content on the T_g of Nanocomposites

Sepiolite content (wt %)	Glass transition temperature (°C)
0	90.47
1	141.02
2	141.73
3	139.96
4	140.32

out sepiolite (Fig. 5(a)), small crazes and clear river lines with smooth surface can be seen on the fracture surface. Introduction of sepiolite results in massive new surfaces on the fracture surfaces, as shown in Figures 5(b)–5(d). These new surfaces can consume much more impact energy, which is an evidence of the significantly increased impact strength of the nanocomposite. Comparing Figures 5(b)–5(d), one may note that the fracture surface of the nanocomposite with 1 wt % sepiolite addition appears to have more new surfaces and cavities than the other two sepiolite addition ratios. This microscopic observation may provide evidence that the deformation is dominated by cavitation-induced energy-dissipating event. More than 1 wt % sepiolite may result in aggregation of fillers, which can act as stress concentrators leading to a reduction in the impact strength.

CONCLUSIONS

The structural and mechanical properties of epoxy nanocomposites with sepiolite nanofillers were investigated. The crystal structure of sepiolite was deformed when reacted with the epoxy groups of the matrix. An improvement in impact and flexural strength was observed for the nanocomposites when added sepiolite. 1 wt % sepiolite appears to be the optimum results for T_g of the nanocomposite, which

(a) 0% sepiolite

(b) 1% sepiolite

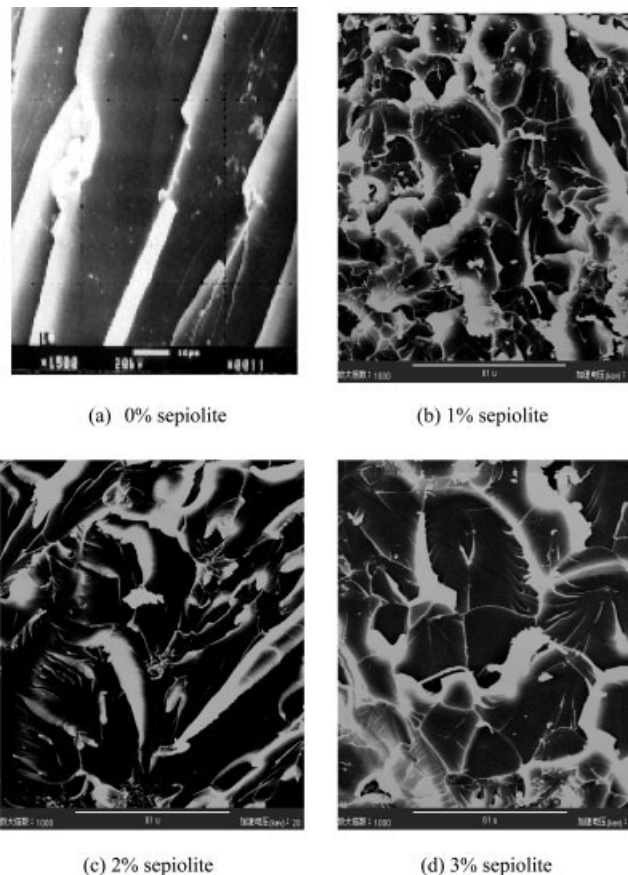(c) 2% sepiolite

(d) 3% sepiolite

Figure 5 SEM images of the fracture surfaces of the composites with different sepiolite additions.

increases by 50°C, but is not associated with the amount of fillers.

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TABLE II
Mechanical Properties of the Sepiolite/Epoxy Nanocomposites

Sepiolite content (wt %)	Flexural strength (MPa)	Flexural strength, enhanced ratio (%)	Impact strength (kJ/m^2)	Impact strength, enhanced ratio (%)
0	63.57		4.1	
1	125.71	98	20.92	410
2	116.22	83	11.74	186
3	114.1	79	12.81	212
4	108.89	71	13.63	232