# Preparation and Properties of Unsaturated Polyester Nanocomposites Based on Silylated Sepiolite Nanofibers

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**ABSTRACT:** The novel surface-modified sepiolite/unsaturated polyester (sepiolite/UP) nanocomposites were prepared by *in situ* polymerization. Sepiolite fibers were first organo-modified by grafting of vinyltriethoxysilane (VTS) containing a double bond onto the surfaces and used as nanofillers. The morphology of sepiolites and nanocomposites were characterized by X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FTIR), scanning electron microscope (SEM), and transmission electron microscope (TEM). Moreover, the thermal properties were determined by thermogravimetric analysis (TGA) and the thermal degradation mechanism was discussed. © 2010 Wiley Periodicals, Inc. J Appl Polym Sci 119: 3043–3050, 2011

**Key words:** sepiolite nanofibers; unsaturated polyester; nanocomposites; thermogravimetric analysis (TGA); transparency

## INTRODUCTION

Unsaturated polyester (UP) resins are one of the most commonly used thermosetting polymers, which are generally formed by a condensation reaction between a glycol and an unsaturated dibasic acid.[1] Owing to their easy processability, excellent mechanical properties, and low price, UP resins have been extensively used in a variety of applications, ranging from automobile and water pipes to packaging and building materials. However, pure unsaturated polyester cured resins have drawbacks of relatively low thermal stability and flame resistance, which limit their use in more fields. Recently, the reinforcement of the unsaturated polyester with nanofillers, such as layered double hydroxides,[2] nanometer-sized $Al_2O_3$,[3] $TiO_2$,[4] and MMT,[5] has been widely reported. Among them, polymer/clay nanocomposites exhibited better mechanical and thermal properties because of their lower filler loading and superior interfacial properties. As far as we know, no reports were found on the formation of sepiolite/UP nanocomposites.

Sepiolite is a natural hydrous magnesium silicate mineral fibers with $(Si_{12}Mg_8O_{30})(OH)_4(OH_2)_4 \cdot 8H_2O$ as the theoretical unit cell formula that exhibits microfibrous morphology with a particle length of 4–8 mm. Sepiolite belongs to the 2 : 1 layered structure composed of two tetrahedral silica sheets enclosing a central sheet of octahedral magnesia. Among them, tetrahedral silica sheets are a continuous layer with an inversion of the apical ends every 6 U,[6] while octahedral sheets are discontinuous, forming the nanostructured tunnels parallel to the fiber axis. These nanostructured tunnels measure ~ $1.06 \times 0.35$ nm$^2$ in cross section, which contain some exchangeable $Ca^{2+}$ and $Mg^{2+}$ cations and "zeolitic water."[7,8] Furthermore, a point worth emphasizing is that the large presence of silanol groups on sepiolite surface, caused by the discontinuities in the external silica sheet, are easily available for coupling reactions with both polymers and organic surfactants.[8] Consequently, it could improve the adhesion with polymers, increasing the mechanical and thermal properties of the final nanocomposites. According to these prominent advantages, sepiolite fibers are potentially suitable as one of fillers for the design of polymer-based nanocomposites. Nevertheless, sepiolite fibers are hydrophilic and lack adhesion with polymers. Thus, sepiolite fibers must be modified before mixing with the polymers. It is well known that organosilanes are the most widely used coupling agents for improvement of the interfacial adhesion in the preparation of composites. Thus, siloxane containing C=C bond was selected as coupling or sepiolite fiber modifying agent as to the chemical composition of polymer matrix.

In this study, the main aim is to enhance the performance of UP by preparing nanocomposites

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using the silylated sepiolite nanofibers. Vinyltri-ethoxysilane (VTS) is used as polymerizable silyl group for the modification of sepiolite fibers. The morphology and thermal properties of the resulting nanocomposites were evaluated.

## EXPERIMENTS

### Materials

The matrix material used in the study was unsaturated polyester (UP, 191#). Cyclohexanone peroxide (CPO) and cobalt naphthenate (CN) were used as UP's curing agent. Sepiolite fibers with the average length of 4–8 μm, obtained from Xixia, China, were chosen as the nanofibers. Sodium hexametaphosphate (SHP) was kindly supplied by Tianjin Kaitong Chemical Reagent. The silane coupling agent (VTS) was purchased from Belgium (USA). All the chemicals were used as received without further purification. Deionized water was used throughout.

### Modification of sepiolite

#### Sepiolite-SHP (sepiolite-s)

The microfibers of sepiolite stick together and form bundles in nature. The interaction force between fibers is very large and it is hard to disperse them by the general process. The most frequently used mechanical grinding process does destruction to crystal structure of fibers. Therefore chemical loosening method was employed to increase disagglomeration of the bundles of microfibers. The SHP acting as chemical loosening agent and the desired amount of sepiolite fibers were added into the flask with 200 mL of deionized water and then stirred continuously for about 30 min at room temperature until a homogeneous mixture was formed. The resultant mixture was filtered, washed with deionized water, and dried at 80°C. The obtained material was denoted as sepiolite-s.

#### Sepiolite-SHP-VTS (sepiolite-G)

About 10 g of sepiolite-s was placed in a flask and stirred continuously in 200 mL deionized water at room temperature for 20 min. Then a solution made of ethanol and VTS was added to the mixture above and stirred vigorously for about 3 h at 60°C. It was filtrated and washed several times with deionized water and placed on a glass-surface vessel and dried at 80°C for 48 h. The obtained material was denoted as sepiolite-G.

### Preparation of sepiolite-G/UP nanocomposites

Prior to mixing with polymers, the sepiolite-G was first dried at 60°C for 30 min to remove any mois-

ture present. Then the mixtures of unsaturated polyester and sepiolite-G with different weight ratios were stirred continuously in a glass beaker using a mechanical mixer for about 30 min at room temperature at a speed of 2000 rpm until a homogeneous mixture was formed. To eliminate the bubbles created during the mixing process, the mixture was completely degassed in a vacuum chamber for about 30 min. After degassing, appropriate amounts of CPO and CN were slowly added into the mixture of the nanofibers and the matrix, respectively. The mixtures were quickly mixed and finally poured into the preprepared molds for casting films. The pristine UP and sepiolite/UP nanocomposites were cured at 25°C for 24 h, and subsequently they were postcured at 60°C for ~ 2 h. Nanocomposites with 1, 3, and 5 wt % sepiolite-G (denoted as 1%sepiolite/UP, 3%sepiolite/UP, 5%sepiolite/UP, respectively) were prepared via this procedure. Composite with the 3 wt % pristine sepiolite was also prepared as to the process, and the composite was denoted as 3%nonsepiolite/UP.

### Characterizations and measurements

The X-ray diffraction (XRD) data were recorded by using an X-Ray diffractometer, Rigaku D/Max-Rc, equipped with a Cu Kα radiation ($\lambda = 0.154060$ nm) source generated at 40 kV and 40 mA and the diffraction spectra were obtained in the range 4°–26° at a scan rate of 2° min$^{-1}$ (step size = 0.02°).

The FTIR spectra were performed by a Nicolet 380 FTIR spectrometer using a resolution of 4 cm$^{-1}$. A scanning coverage was from 4000 to 400 cm$^{-1}$. KBr was used as a background material and disks of sample/KBr mixtures were prepared to obtain the FTIR spectra.

The transmission electron microscopy (TEM) images were obtained by using a Hitachi H-800 transmission electron microanalyzer with an accelerating voltage of 200 kV. The sepiolite sample was dispersed in the ethanol and collected on 300 hexagonal mesh copper grids.

The morphology of the samples was observed by using JSM-5800 scanning electron microscope (SEM). The fracture surfaces of the materials were coated by sputtering with gold before observation.

The thermal behavior of the materials was determined by using DTG-60A thermogravimetric analyzer under nitrogen or air atmosphere with flow rate of 50 mL min$^{-1}$. The samples were heated from room temperature to 600°C with a constant heating rate of 20°C min$^{-1}$.

Limiting oxygen index (LOI) tests of materials were performed according to Chinese National Standard GB 2406-1993. The shape of samples was 100 mm × 6.5 mm × 3 mm in size. Two specimens

were tested for each composition to get the average value. Three specimens with 125 mm × 13 mm × 3.2 mm in size were used for each composition in UL94 Horizontal Burning test. The result obtained were the average of three samples.

## RESULTS AND DISCUSSION

### Characterization of sepiolite-G

FTIR

The key to preparing the good compatibility nanocomposites lies in the organo-modified process of the fillers. So, the first step of this work is to select the optimal modified method. Grafting is one of the most useful methods of introducing functional groups onto the surfaces of inorganic fillers.[6,8–12] Comparing with the adsorption process, the chemical grafting process shows a better modification effect because of the formation of the covalent bonds between the modifier and the filler surface. Therefore, the chemical grafting process is employed to enhance the interfacial adhesion of the system.

The FTIR spectra of sepiolite and sepiolite-G samples are shown in Figure 1. The band at 3695 cm$^{-1}$ is attributed to the presence of O—H groups in the octahedral sheet and the O—H stretching vibration in the external surface of sepiolite. Moreover, the sepiolite has a broad absorption band at around 3447 cm$^{-1}$ due to O—H stretching of zeolite water in the channels. The $\delta_{H—O—H}$ vibration of coordinated water appears at about 1636 and 1431 cm$^{-1}$. Besides these bands, the intensity of band at 1020 cm$^{-1}$ associated with the Si—O stretching vibration of Si—O—Si groups is clearly enhanced in sepiolite-G, indicating that the Si—O groups of the sepiolite surface were increased during the chemical grafting process. The absorption bands at 1408 and 760 cm$^{-1}$
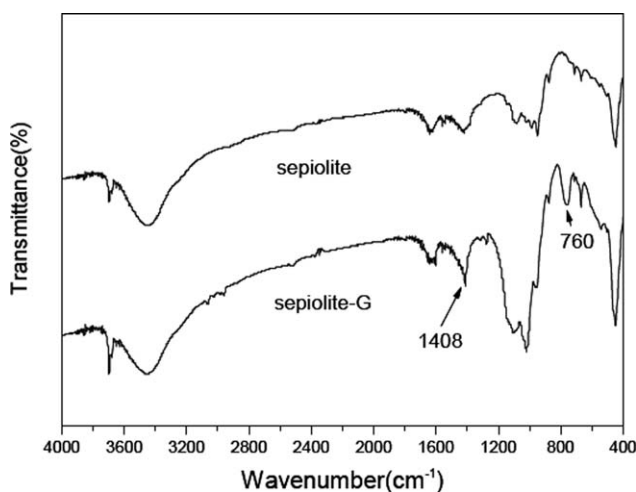


**Figure 1** FTIR spectra of sepiolite and sepiolite-G.
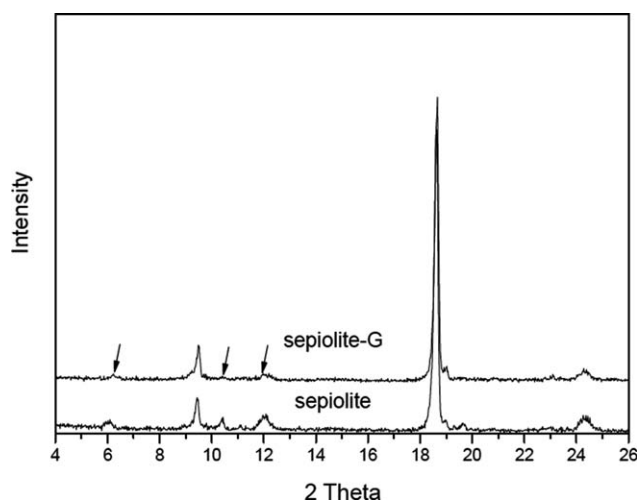


**Figure 2** XRD patterns of the sepiolite and the sepiolite-G.

associated with C=C stretching vibration reflect the presence of silane in sepiolite-G, as shown in Figure 1. These prove that vinyltriethoxysilane was successfully grafted by covalent bonding onto the sepiolite surface.

XRD

The XRD patterns in the range of $2\theta = 4°–26°$ for the sepiolite and the sepiolite-G are presented in Figure 2. The two characteristic diffraction peaks of the sepiolite-G at $2\theta = 9.50°$ ($d_{110} = 0.93$ nm), $2\theta = 18.62°$ ($d_{060} = 0.47$ nm) are similar to those of the sepiolite, which indicate that the $d$-spacing of the sepiolite-G does not change. One main reason is that the layers of sepiolite are linked by covalent bonds, which are different from the layers of montmorillonite by the faint Van der Waals force.[13] Another possible reason is that the silanol groups participating in the chemical grafting reaction are mainly presented on the whole external surface of sepiolite. So it can be observed that the $d$-spacing of the sepiolite-G is the same as that of sepiolite. Our results fully agree with previous studies.[6,10] Furthermore, the peaks of sepiolite-G at $2\theta = 6.21°$ ($d_{100} = 1.422$ nm), $2\theta = 10.44°$ ($d_{120} = 0.846$ nm), $2\theta = 12.05°$ ($d_{130} = 0.733$ nm) (the arrows in Fig. 2) are declined in the intensity compared to those of the sepiolite. This indicates that the aggregation of sepiolite-G is decreased, because as the volume fraction of fibers is lower, the diffraction peak is weaker.[10] So, although the structure of sepiolite fibers is not changed by organosilane, the loosening or dispersion of sepiolite fibers are affected by organosilane. So, a conclusion can be drawn that the functionalization with silane agents increase significantly the deagglomeration of the bundles of sepiolite fibers,
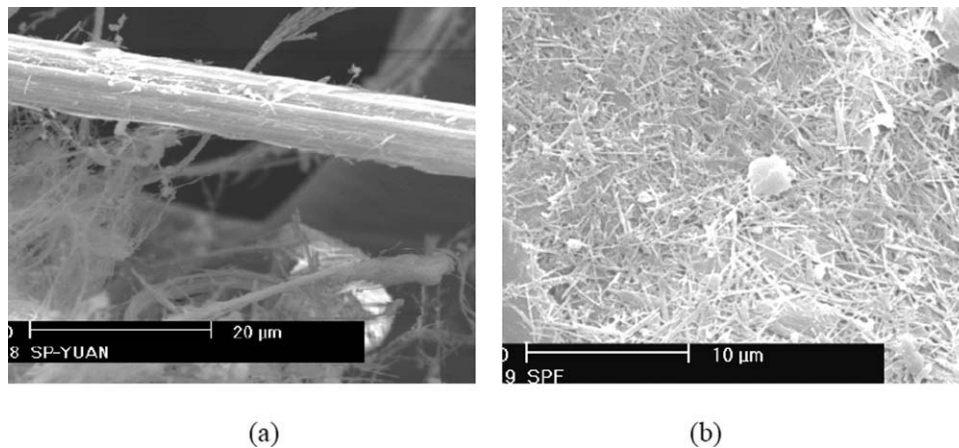
**Figure 3**   SEM images of nanofibers: (a) pristine sepiolite; (b) sepiolite-s.

leading to the formation of some weak diffraction peaks in sepiolite-G.

## SEM and TEM

The SEM micrographs of fibers used in the present study are displayed in Figure 3(a,b). From the SEM micrograph in Figure 3(a), the individual fibers of pristine sepiolite generally accumulate into bundles with a diameter of about 8 μm. The SEM photograph of sepiolite-s is illustrated in Figure 3(b). The image clearly reveals that sepiolite-s still remain the structure of long fibers, exhibiting the high aspect ratio and large surface area. Compared with the pristine sepiolite, the dimension of sepiolite-s is declined. The average diameter of sepiolite-s is around 300 nm and the length varies in the range from 8 to 12 μm. The results demonstrate that these dispersion procedures loosened the sepiolite bundles but did not enable fiber to be shorter or cause deformation, which was confirmed by the good crystal morphology of sepiolite in Figure 2. SHP is employed to only loose the pristine sepiolite bundles and has a smaller dimension. After organosilane grafts onto the surface of sepiolite-s, sepiolite-G is obtained and the dimension of the sepiolite-G shows a great change in comparison with sepiolite-s. It is evident from the TEM image (Fig. 4) that sepiolite-G has a length of 500 nm and width in the range 10–20 nm.

### Characterization of nanocomposites

#### FTIR

The FTIR spectra of UP, sepiolite-G and 3%sepiolite/UP nanocomposites are displayed in Figure 5. The UP spectrum shows the characteristic bands of UP (ascribed to the O—H stretching of the polyester chains 3450 cm$^{-1}$; ascribed to asymmetric and
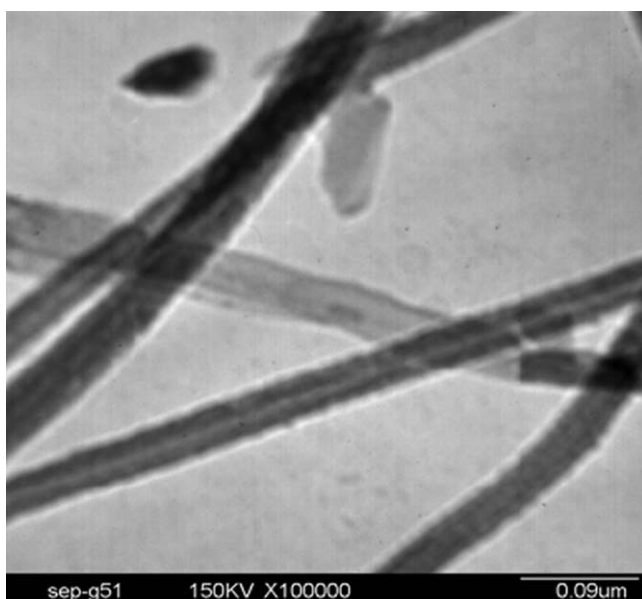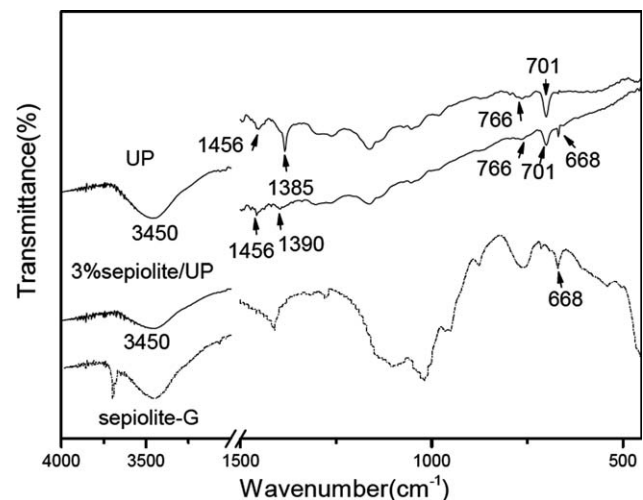


**Figure 4**   TEM image of sepiolite-G.

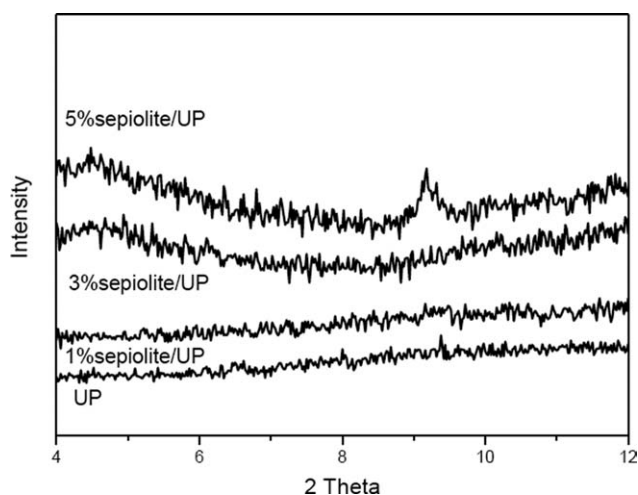**Figure 5**   FTIR spectra of UP, sepiolite-G and 3%sepiolite/UP nanocomposites.

**Figure 6** XRD patterns of the UP and the sepiolite/UP nanocomposites.

symmetric $-CH_2$ bending vibration $\sim$ 1456 and 1385 cm$^{-1}$; ascribed to $\gamma(C-H)$ in the aromatic ring $\sim$ 766 and 701 cm$^{-1}$). Apparently the FTIR spectrum of the 3%sepiolite/UP nanocomposites shows the combination of UP and sepiolite-G. The presence of peak at 668 cm$^{-1}$ in the 3%sepiolite/UP nanocomposites confirms the existence of sepiolite-G in the nanocomposites. Additionally, the broad band of the 3%sepiolite/UP nanocomposites at 3450 cm$^{-1}$ is different from that of UP. This is due to the result of the overlap of the O$-$H stretching of the polyester chains with the O$-$H stretching of coordinated water of sepiolite-G. These FTIR assignments give positive evidence that the sepiolite fibers have been dispersed in the UP matrix and thus form the sepiolite/UP nanocomposites.

### XRD

The diffraction patterns of the pure UP and the sepiolite/UP nanocomposites with different sepiolite-G contents in the angle range of $2\theta = 2.5°-12°$ are recorded in Figure 6. The characteristic peaks of sepiolite around $2\theta = 9.50°$ are found in 5%sepiolite/UP nanocomposites, whereas 1%sepiolite/UP and 3%sepiolite/UP nanocomposites have a homogeneous distribution. It indicates that some fiber bundles still remain in 5%sepiolite/UP composites. Indeed, the XRD analysis doesn't give positive evidence of the dispersion of the sepiolite fibers in the UP matrix. Therefore, the SEM analysis is necessary to investigate and prove the structure of nanocomposites.

### SEM

Figure 7 exhibits the SEM fracture surface morphology of the sepiolite/UP nanocomposites containing 3 wt % sepiolite-G. The gray regions represent the UP matrix and the white spots in the figure correspond to sepiolite fibers. It is observed from this micrograph that the sepiolite nanofibers deagglomerate and are relatively uniformity-dispersed in the UP matrix. Furthermore, the sepiolite fibers were perpendicular to the fracture surface of nanocomposites. To sum up, the image demonstrates that the functionalized sepiolite fibers are evenly dispersed into the UP matrix.

Although the XRD curves do not give more detail information about the dispersion extent of sepiolites in the UP matrix, the SEM image provides strong evidence that the most of the sepiolite-G nanofibers are relatively uniformly dispersed into the UP matrix. This is probably due to the C=C polymerization occurring on the sepiolite surface, improving essentially the dispersion extent of nanofibers and leading to a decrease in the degree of fibers agglomeration, as observed previously in other system.[14]

### Thermal stability

The TGA curves and the derivative thermogravimetric (DTG) curves of weight loss as a function of temperature for UP and the sepiolite/UP nanocomposites with different sepiolite contents in nitrogen and air are illustrated in Figures 8 and 9, respectively. All nanocomposites exhibit thermal degradation and mass loss at an elevated temperature. The summary of the important characteristic temperature obtained from TGA and DTG are listed in Tables I and II.

In nitrogen, the 5% weight loss temperature ($T_{5\%}$) and the maximum decomposition temperature ($T_{max}$) of pure UP are 290 and 434°C, respectively, [Figs. 8(n) and 9(n)]. When the 5% weight loss
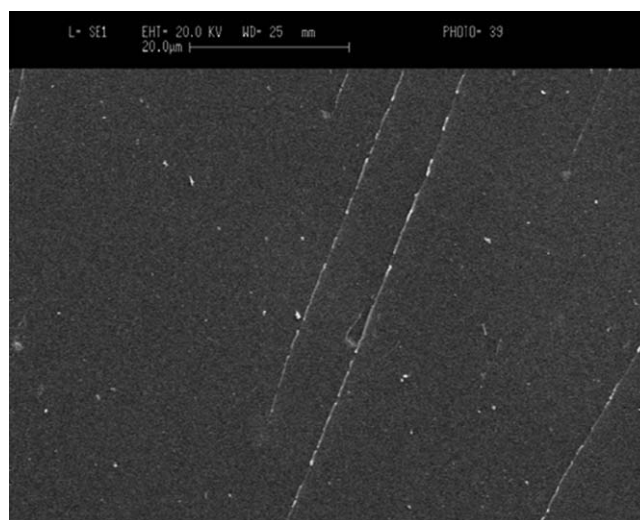


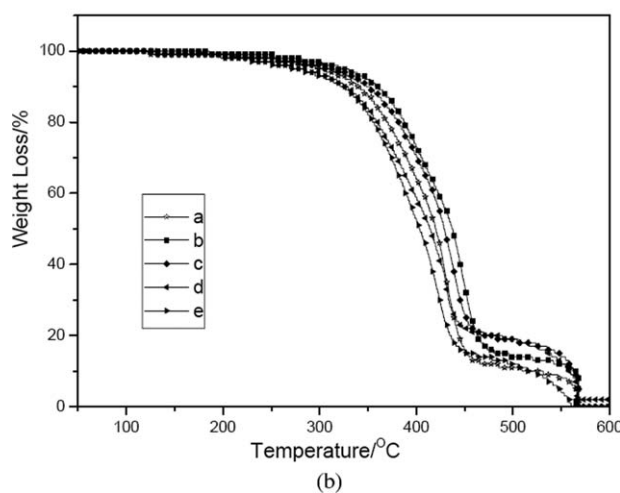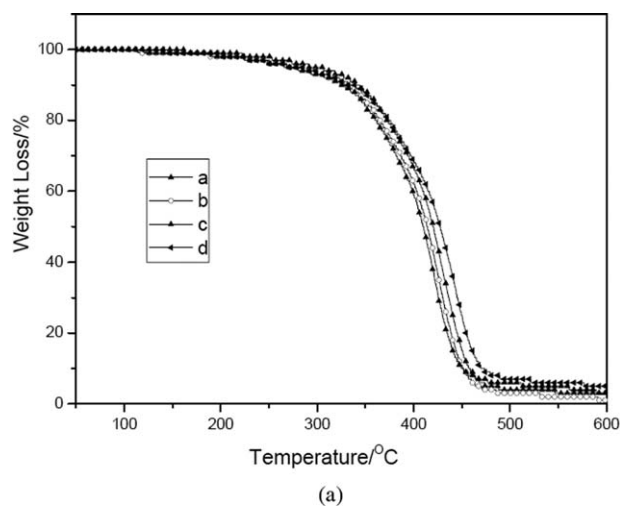**Figure 7** SEM image of the 3%sepiolite/UP nanocomposites.

**Figure 8** TGA weight loss curves for the UP nanocomposites having sepiolite contents of (a)0 wt %, (b) 1 wt %, (c) 3 wt %, (d) 5 wt %, and (e) 3% nonsepiolite/UP composites under nitrogen (n) and air (m).



**Figure 9** DTG curves for the UP nanocomposites having sepiolite contents of (a) 0 wt %, (b) 1 wt %, (c) 3 wt %, (d) 5 wt %, and (e) 3% nonsepiolite/UP composites under nitrogen (n) and air (m).

temperature is selected as a point of comparison, the decomposition temperatures of 1%sepiolite/UP, 3%sepiolite/UP, and 5%sepiolite/UP nanocomposites are 286, 280, and 286°C, respectively. It can be seen from the Figure 8(n) that the presence of the sepiolite-G leads to a decrease in the thermal stability of UP in nitrogen. A 20°C decrease in the temperatures of maximum rate of weight loss ($T_{max}$) is recognized for all nanocomposites as shown in Table I. The main reason for these results is that the sepiolite catalyze UP degradation.

The nanocomposites all show the two main degradation steps in nitrogen [Fig. 9(n)]. The first step of degradation of UP, overlapped by the main peak, is not clearly observed in these samples. The step is assigned to decarboxylation of ester. The main degradation step is due to the breaking of ester linkages. Additionally, the data of Table I displays that the residue of sepiolite/UP (3 and 5 wt %) are larger than that of pure UP at 550°C. However, the residue
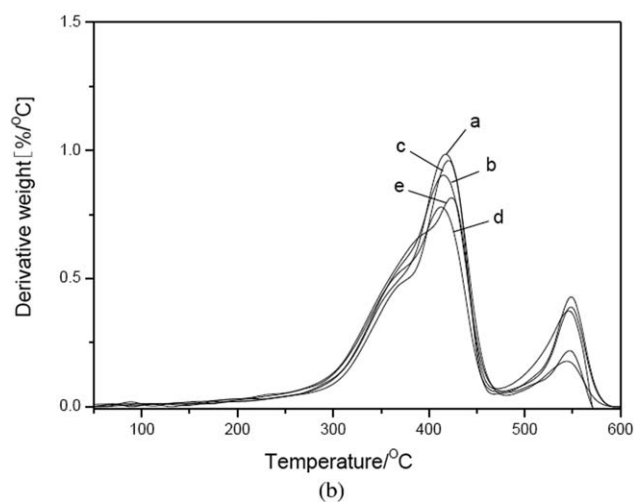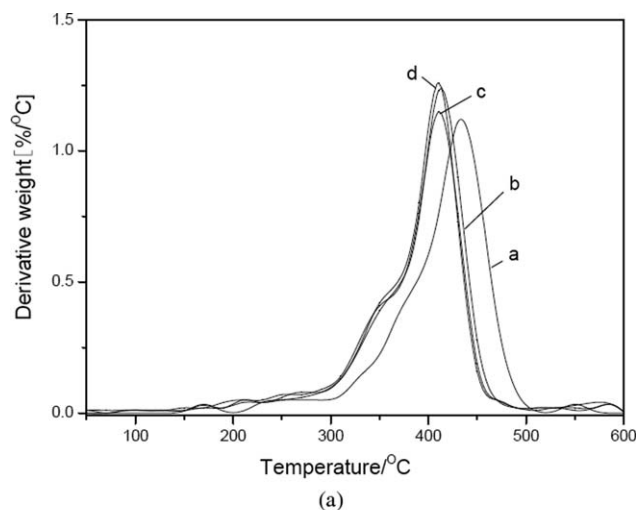
of sepiolite/UP (1 wt %) are lower than that of pure UP. The phenomenon is surprising. The probable reason for the result is that the sepiolites catalyze the degradation of the residue, resulting in the formation of the lower residue of 1%sepiolite/UP.

The thermal degradation behavior appears to be completely different when the pure UP and the corresponding nanocomposites are in air environment. The thermal degradation of these nanocomposites in

**TABLE I**
**TGA Weight Loss Data for UP and UP Nanocomposites Under Nitrogen**

| Samples | $T_{5\%}$ (°C) | $T_{max}$ (°C) | Residue mass at 550°C (%) |
|---|---|---|---|
| UP | 290 | 434 | 3.3 |
| 1%sepiolite/UP | 286 | 412 | 2.1 |
| 3%sepiolite/UP | 280 | 410 | 4.8 |
| 5%sepiolite/UP | 286 | 408 | 5.7 |

**TABLE II**
**TGA Weight Loss Data for UP and UP Nanocomposites Under Air**

| Samples | $T_{5\%}$ (°C) | $T_{max}$ (°C) | Residue mass at 550°C (%) |
|---|---|---|---|
| UP | 292 | 418 | 5.5 |
| 1%sepiolite/UP | 327 | 414 | 6.4 |
| 3%sepiolite/UP | 311 | 420 | 12.7 |
| 5%sepiolite/UP | 272 | 411 | 12.3 |
| 3%non-sepiolite/UP | 268 | 423 | 4.8 |

air shows three degradation stages [Fig. 9(m)]. The degradation of the first two steps is similar to those of samples in nitrogen. The different step is the third step at 550°C, which is assigned to the degradation of the residue.

Apparently, the presence of the sepiolite-G improves UP thermal stability in air. The temperature at 5% weight loss of 1%sepiolite/UP and 3%sepiolite/UP nanocomposites are about 35 and 19°C higher than that of pristine UP, respectively, as shown in Figure 8(m) and Table II. The increase of the thermal stability is attributed to the formation on the surface of the nanocomposites of an interconnected clay network, left behind by polymer thermal ablation, which plays the shielding role.[8] Thus the thermo-oxidative process is slowed and thermal decomposition shifts to higher temperatures. However, the $T_{5\%}$ value drop down to 274°C, with the content of sepiolite up to 5 wt %. It may be due to that the C=C groups on the sepiolite-G surface can be polymerized preferentially and sepiolites have the trend to be agglomerated into bundles, resulting in the poor dispersion of sepiolite fibers in the polymer matrix and worse diffusion of the resin between fibers. Indeed, the $T_{5\%}$ value of the nanocomposites is decreasing with the contents of sepiolite increasing. This is because the increase of the organic modifying agent (VTS) of low $T_d$ into the sepiolite fibers decreases the thermal stability of the UP. It is obvious that 3%nonsepiolite/UP composites exhibit a worse thermal stability because of the poor compatibility of the system comparing with the sepiolite/UP nanocomposites. Moreover, the temperature of the main decomposition step of UP nanocomposites seems not to be influenced in the presence of

sepiolite-G in air as shown by Figure 9(m) and Table II. In addition, it can be seen in Table II that the higher residues of nanocomposites are left at 550°C compared with that of pure UP in air and nanocomposites in nitrogen.

## Flame retardant properties

The results of the limiting oxygen index (LOI) and UL94 Horizontal Burning test of the UP nanocomposites are listed in Table III. The introduction of sepiolites improves the flame retardant properties of the UP matrix. A larger increase in the LOI is obtained in the sepiolite/UP nanocomposites in comparison with the 3%nonsepiolite/UP composites. Furthermore, the 1%sepiolite/UP and 3%sepiolite/UP nanocomposites attain V-0 from the UL94 results, while 3%nonsepiolite/UP composites only achieve V-1. This makes out that the grafting modification of sepiolite greatly enhanced the flame retardant properties of the UP matrix. The reason for it is that the strong chemical bonding generated in the interface between the inorganic and organic phases has advantage over the formation of the dense charring layer during burning.

## Optical properties

The digital photograph of Figure 10 shows the optical properties of the sepiolite/UP nanocomposites with different contents of the sepiolite fibers. It is apparent that the sepiolite/UP nanocomposites with 1 and 3 wt % sepiolite contents exhibit a good transparency. This may be the result of the good
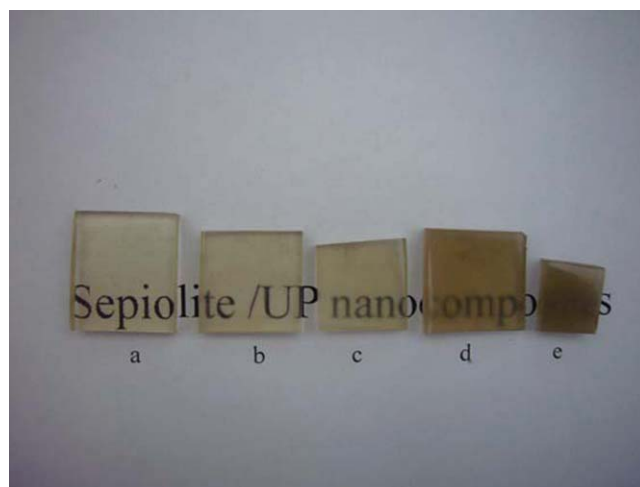


**Figure 10** Optical images of the sepiolite/UP nanocomposites with various sepiolite contents: (a) 0 wt %, (b) 1 wt %, (c) 3 wt %, (d) 5 wt %, and (e) 3%nonsepiolite/UP composites. The thickness of each sample is about 4 mm. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

**TABLE III**
**Combustion Results of UP and UP Nanocomposites**

| Samples | LOI | UL94 |
|---|---|---|
| UP | 20.8 | Burning |
| 1%sepiolite/UP | 24.1 | V-0 |
| 3%sepiolite/UP | 23.6 | V-0 |
| 5%sepiolite/UP | 23.8 | V-1 |
| 3%non-sepiolite/UP | 22.1 | V-1 |

dispersion of the sepiolite-G in the matrix. In addition, the sepiolite/UP nanocomposites are slightly translucent at 5 wt % suggesting the presence of some fiber bundles in the materials. In contrast, 3%nonsepiolite/UP composites display opacity because of the poor dispersion of sepiolite fibers in the UP matrix.

## CONCLUSIONS

The preparation and characterization of sepiolite/unsaturated polyester (sepiolite/UP) nanocomposites were performed. The chemical grafting modification renders the sepiolite fibers reactive and hydrophobic, enhancing the compatibility of the sepiolite/UP system. More importantly, the reaction between the sepiolite-G nanofibers and UP chains increases the crosslinking density of polymer, thus improving the interfacial interaction of the system. According to the experimental datum, the thermal and flame retardant properties of these nanocomposites were hence enhanced. The nanocomposites with low sepiolite-G content showed excellent transparence.

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