

# Sodium Alginate/Na<sup>+</sup>-Rectorite Composite Films: Preparation, Characterization, and Properties

Lianli Yang, Guozheng Liang, Zengping Zhang, Shaobo He, Jinhe Wang

Department of Applied Chemistry, School of Science, Northwestern Polytechnical University, Xi'an 710072, Shaanxi, People's Republic of China

Received 12 March 2008; accepted 15 October 2008

DOI 10.1002/app.30521

Published online 18 June 2009 in Wiley InterScience (www.interscience.wiley.com).

**ABSTRACT:** Rectorite (REC), one kind of layered silicates, has been applied to polymers to improve their properties. The sodium alginate (SA) layered silicate is a new option to modify the properties of polysaccharides. In this article, SA was modified by Na<sup>+</sup>-rectorite (Na<sup>+</sup>REC). The chemical structures and microstructures of Na<sup>+</sup>REC and Na<sup>+</sup>REC modified SA (SA/Na<sup>+</sup>REC) were analyzed by using Fourier transform infrared spectrometer and X-ray diffraction. The morphologies of SA/Na<sup>+</sup>REC composites were observed by using scanning electron microscopy and transmission electron microscopy. The mechanical and

anti-ultraviolet properties as well as thermal properties of SA/Na<sup>+</sup>REC composites were investigated. The results show that the properties of pure SA film can be improved by the addition of Na<sup>+</sup>REC, and SA/Na<sup>+</sup>REC composite containing 2 wt % Na<sup>+</sup>REC has the best intercalation effect and optimum comprehensive properties among the prepared composites in this article. © 2009 Wiley Periodicals, Inc. *J Appl Polym Sci* 114: 1235–1240, 2009

**Key words:** rectorite; sodium alginate; composite film; structure and morphology; properties

## INTRODUCTION

The synthesis of polymer/inorganic nanocomposites have attracted great interest from researchers in the world since the Toyota invented nylon/montmorillonite nanocomposites because this kind of novel nanocomposites already exhibits new and improved properties compared to their micron and macrocomposites due to the ultrafine phase dimensions and special phase structure involved.<sup>1–4</sup> Particularly, intercalation of polymer into inorganic layered host lattice is an effective way to construct polymer/inorganic nanocomposites. Intercalation actualizes a molecular level combination of two extremely different components, which is expected to produce materials with superior or novel properties.<sup>4,5</sup> The majority of previous studies have focused on synthetic polymers such as nylon, poly(methyl methacrylate), polypropylene, epoxy resin, polyimide, polystyrene, polyester, etc.<sup>6–10</sup> whereas few works on polysaccharides have been done. Recently, the biodegradable and biocompatible polysaccharides/layered silicate clay nanocomposites have been investigated because they exhibit markedly improved mechanical, optical, ther-

mal, physicochemical, decreased gas/vapor permeability, reduced flammability, and controlling release properties compared with pure polysaccharides.<sup>11–13</sup> For example, Avella et al.<sup>12</sup> prepared the starch/clay nanocomposite films and used them for food packaging instead of synthetic plastics. Wang et al.<sup>14</sup> obtained chitosan/organic rectorite nanocomposite films and investigated their water resistance, mechanical property, optical transmittance, anti-ultraviolet capacity, and bactericidal activity, and the results show that chitosan/organic rectorite nanocomposite films were good drug-controlled release carriers. The layered silicates such as montmorillonite, hectorite, and saponite belong to the structural family known as the 2 : 1 phyllosilicates with a hydrophilic surface in nature and possess good physical properties. They are commonly used in nanocomposites.<sup>13,15,16</sup> These phyllosilicates can be treated with various agents and the modified clay is very compatible with polymer or polysaccharides, so intercalated hybrids consisting of well-ordered multilayers or exfoliated hybrids consisting of individual nanometer-thick silicate layers suspended in polymer or polysaccharides matrix may be obtained under well-designed experimental conditions.<sup>12,14</sup>

Sodium alginate (SA) produced from renewable resources is composed mainly of (1–4)-linked β-D-mannuronic acid units and α-L-guluronic acid units.<sup>16</sup> SA is water-soluble and has good membrane-forming property. Because of its nontoxicity, biocompatibility, biodegradability, and reproducibility, SA has been used in many areas such as food, pharmaceutical additives, biology or enzyme carrier, and tissue

Correspondence to: G. Liang (lgzheng@nwpu.edu.cn).

Contract grant sponsor: National Natural Science Foundation of China; contract grant number: 50573046.

Contract grant sponsor: Shaanxi Province Education Commission Foundation; contract grant number: 06JK161.

Contract grant sponsor: Xianyang Teacher's College Foundation; contract grant number: 08XSYK216.

TABLE I  
Sample Codes of Binary Composite Samples

Sample code	Composition	Content of Na <sup>+</sup> REC (wt % based on SA)	Content of glycerine (wt % based on SA)
SA	SA	0	10
SA/Na <sup>+</sup> REC1	Na <sup>+</sup> REC/SA	1	10
SA/Na <sup>+</sup> REC2	Na <sup>+</sup> REC/SA	2	10
SA/Na <sup>+</sup> REC5	Na <sup>+</sup> REC/SA	5	10
SA/Na <sup>+</sup> REC10	Na <sup>+</sup> REC/SA	10	10

engineering materials, etc.<sup>17,18</sup> Because the mechanical properties of SA might not be adequate for high load-bearing applications, many investigations have been also performed to enhance its mechanical properties to have the ability to compete with low-cost commodity polymers. Considerable progress has been made by blending SA with other biodegradable and nonbiodegradable polymers.<sup>19–21</sup>

Rectorite (REC) is a type of layered material, having similar structure with montmorillonite (MMT), and is easily available in China. In addition, REC exhibits good mechanical and thermal properties as well as high resistance to ultraviolet rays, etc.<sup>1,5</sup> The thickness of a single rectorite layer is about 2 nm, while the width and length of a single rectorite layer vary from 1 to several microns. The interlayer cations of rectorite layers can be exchanged easily by either organic or inorganic cations, which makes it possible to prepare polymer/REC nanocomposites by solution-mixing or melt-mixing processing technique. Research on organically modified rectorite (OREC) composites based on polyurethane elastomer, polypropylene, natural rubber, and chitosan have been carried out and results show that the addition of OREC can endow polymers with higher mechanical, thermal, and anti-ultraviolet properties, etc.<sup>1,5,6,14,18,22</sup>

In this study, we attempt to intercalate SA into the interlayers of the rectorite to prepare the SA/Na<sup>+</sup>-rectorite (Na<sup>+</sup>REC) nanocomposites by the operational and noncontaminative solution mixing process technique. The bivalent or trivalent cations such as Al<sup>3+</sup> for Ca<sup>2+</sup> in the tetrahedral lattice and octahedral sheet of REC can crosslink with SA to produce gel, which effects the intercalation, so REC was first treated by sodium pyrophosphate and then intercalated by SA. The structure, morphology, thermal, mechanical, and anti-ultraviolet properties of developed nanocomposites were investigated by Fourier transform infrared spectrometer (FTIR), X-ray diffraction (XRD), scanning electron microscopy (SEM), transmission electron microscopy (TEM), and thermogravimetry (TG), etc. This composite film could be used as a coating material for modifying drug release from tablets, food packaging, one-shot things, and composite superabsorbent polymer, etc.

## MATERIALS AND METHODS

### Materials

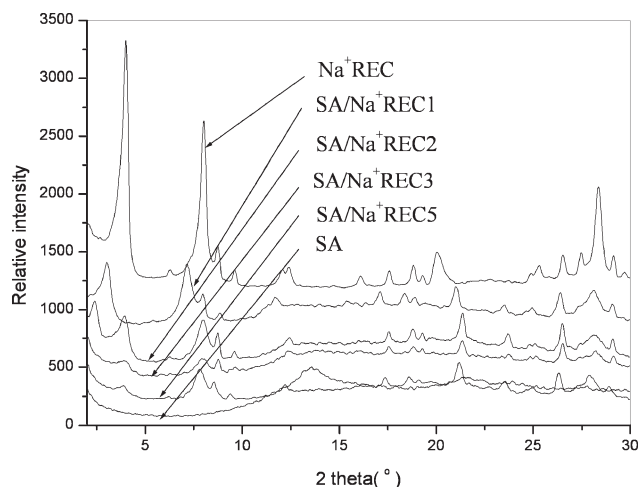
SA was obtained from Kemiou Chemical Co., Ltd., (Tianjing, China). REC was purchased from Hubei Zhongxiang Rectorite Mine (Wuhan, China). REC was analyzed in our lab according to the reported method,<sup>23</sup> and results show that its cationic exchange capacity (CEC) is 45 mequiv/100 g, and its *d*-space value is 2.1225 nm. Sodium pyrophosphate was purchased from Tianjin Boddy Chemical Co., Ltd. (Tianjing, China). Glycerine was obtained from Tianjin Daqiu-zhuang Froth Plastics Plant (Tianjing, China).

### Synthesis of Na<sup>+</sup>REC

REC was calcined in 850°C for 4 h to increase its white degree and improve its activity.<sup>24,25</sup> Then calcined REC was treated with sodium pyrophosphate to intensify insertion effect of SA. The Na<sup>+</sup>-modified REC (Na<sup>+</sup>REC) was prepared by cationic exchange between REC galleries and sodium pyrophosphate in an aqueous solution. The synthesis of Na<sup>+</sup>REC was performed as follows. First, 10.0 g REC was dissolved in deionized water to obtain 15 wt % suspending solution. Second, 0.3 g sodium pyrophosphate was added into the suspending solution with stirring and maintained at that condition for 0.5 h to obtain a mixture. Third, the mixture was slowly heated to 60°C and maintained at that temperature for 12 h. Fourth, the mixture was cooled to room temperature, and then it was filtered on a Buncher filter and dried. The product is coded as Na<sup>+</sup>REC.

### Preparation of SA/Na<sup>+</sup>REC composite films

Four SA/Na<sup>+</sup>REC composite films with different mass ratios (Table I) were prepared via a solution-mixing processing technique. The preparation was performed by the following steps. Na<sup>+</sup>REC was dissolved in deionized water to obtain 3 wt % suspending liquid through ultrasonic dispersion for 10 min. SA was dissolved in deionized water to form a homogeneous solution of 3 wt % polysaccharide. The SA solution was slowly mixed into the Na<sup>+</sup>REC suspending liquid using homogenizer for 5 min and



**Figure 1** X-ray diffraction patterns of Na<sup>+</sup>REC, SA, and SA/Na<sup>+</sup>REC composites.

then glycerin (10% w/w based on SA) as the plasticizer was dropped into the mixture.<sup>26</sup> The mixture was stirred with a high-speed shear mixer for 3 h and salivated on a dust-free glass plate with a uniform thickness for curing by a procedure of 50°C for 5 h. After curing, the dried membrane was peeled off from the glass plate. The resultant film is designed as SA/Na<sup>+</sup>REC composite film. The average thickness of the samples was 0.08 mm.

### Characterizations

The structures of SA/Na<sup>+</sup>REC composite films were investigated using DPmax23C X-ray diffraction (XRD) instrument (Rigaku, Osaka, Japan) with Cu K $\alpha$  ( $\lambda = 0.154$  nm) radiation source. The X-ray generator operated at 35 kV and 50 mA, the reflection angle  $2\theta$  was monitored from 2.0° to 30° at a scanning speed of 2°/min and a step size of 0.02°.

FTIR spectra of composites were recorded with KBr pellets on a Fourier transform infrared spectrometer (Model VECTOR-22, Shimadzu, Kyoto, Japan).

The dispersion of clay layers in nanocomposites was observed by using SEM (KYKY1000B) (Scientific Instrument Factory CAS, Beijing, China). Prior to observation, samples were arranged on metal grids by using double-sided adhesive tape; in addition, samples were coated with gold under vacuum.

The exfoliation and molecular dispersion of clay layers in nanocomposites were observed by using a

Hitachi H-800 TEM instrument (Hitachi, Tokyo, Japan) with an acceleration voltage of 150 kV, and the ultrathin samples with a thickness of less than 1  $\mu$ m were microtomed in liquid nitrogen by using a LKB Bromma 2088 cutter.

The tensile strength and the percentage of elongation at break for SA/Na<sup>+</sup>REC composite films were determined on a testing machine (Model PT-1036PC; Perfect Instrument Co., Ltd., Taiwan, China). The films were cut into 15 cm  $\times$  1 cm strips. The gauge length was 50 mm and the crosshead speed was 50 mm/min. At least five specimens for each SA/Na<sup>+</sup>REC composite were tested.

The ultraviolet aging was measured after the sample was radiated by short-wave untraviolet radiation (Model ZF-1; Jinpeng Analytical Instrument Co., Ltd., Shanghai, China) for 1 month; the radiated power was 6 W, and the distance between the sample and the light source was 0.1 m.

The thermal stability of composites was evaluated by using a Perkin-Elmer thermogravimetric analyzer (SDT 2960 DTA-TGA; NETZSCH, Selb, Germany) over the temperature range 25–500°C at a heating rate of 10°C/min in a nitrogen atmosphere.

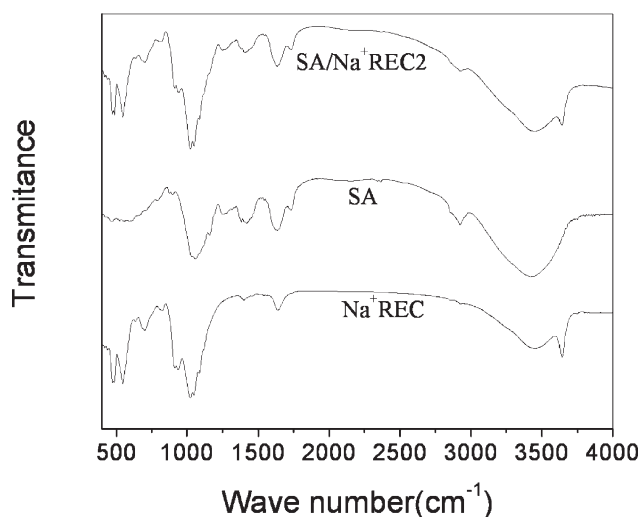
## RESULTS AND DISCUSSION

### Characterization of Na<sup>+</sup>REC/SA composites

Figure 1 shows XRD patterns of Na<sup>+</sup>REC, SA, and SA/Na<sup>+</sup>REC composite films. Pure SA film presents a broad peak at 13.8° ( $2\theta$ ), indicating that SA has an amorphous morphology. The XRD pattern of the Na<sup>+</sup>REC shows a reflection peak at about  $2\theta = 4.0$ , corresponding to a basal spacing ( $d_{001}$ ) of 2.2073 nm. It can be observed from Figure 1 that all the (001) plane diffraction peaks of SA/Na<sup>+</sup>REC composites are shifted to low angle and have weaker (001) plane reflection peaks than Na<sup>+</sup>REC. According to Bragg's law, the  $d_{001}$  values of SA/Na<sup>+</sup>REC composites are larger than Na<sup>+</sup>REC, indicating that intercalation is formed between Na<sup>+</sup>REC and SA. It also can be observed from Table II that the angle of 001 plane reflection peaks of SA/Na<sup>+</sup>REC2 composite is the smallest and that of SA/Na<sup>+</sup>REC5 is the biggest, whereas the  $d$ -spacing value of SA/Na<sup>+</sup>REC2 is the biggest and that of Na<sup>+</sup>REC5/SA is the smallest, indicating that SA/Na<sup>+</sup>REC2 has the highest intercalation degree and SA/Na<sup>+</sup>REC5 has the lowest intercalation degree. The data of Table II suggested that

**TABLE II**  
The Crystallinity Values of Composites with Different Na<sup>+</sup>REC Contents

Name	SA/Na <sup>+</sup> REC1	SA/Na <sup>+</sup> REC2	SA/Na <sup>+</sup> REC3	SA/Na <sup>+</sup> REC5
Plane of 001 peaks ( $2\theta$ , °)	2.8	2.40	3.0	3.84
$d_{001}$ (nm)	3.15158	3.6774	2.9415	2.29687



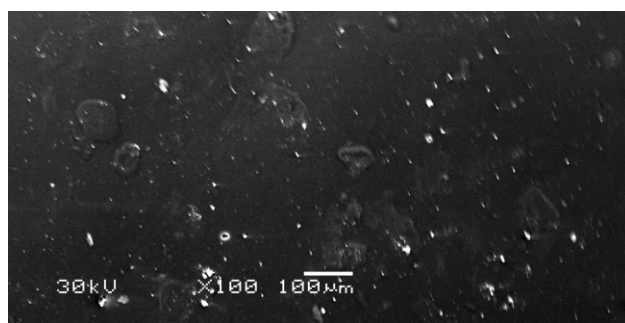
**Figure 2** FTIR spectra of Na<sup>+</sup>REC, SA, and SA/Na<sup>+</sup>REC2 composite.

for the composite with a low concentration of Na<sup>+</sup>REC, SA can be intercalated into layers of Na<sup>+</sup>REC, but in the case of the composite with a high concentration of Na<sup>+</sup>REC, SA is almost not intercalated into layers of Na<sup>+</sup>REC.

Figure 2 shows FTIR spectra of Na<sup>+</sup>REC, SA and SA/Na<sup>+</sup>REC2 composite. For Na<sup>+</sup>REC, 3431 cm<sup>-1</sup> is attributed to the bending vibration of hydrogen band of interlaminal water in Na<sup>+</sup>REC, 3632 cm<sup>-1</sup> is attributed to the hydroxyl stretching of SiOH, 1639 cm<sup>-1</sup> represent hydroxyl bending of H<sub>2</sub>O, 1050 cm<sup>-1</sup> is associated with the anisomerous stretching vibration of Si—O—Si, 450–550 cm<sup>-1</sup> is attributed to the bending vibration of Si—O.<sup>22,25,27</sup> The stretching vibration of P—O is 927 cm<sup>-1</sup>.

The infrared spectrum of alginate showed absorption bands at 3430 cm<sup>-1</sup> (OH stretching), 1618 cm<sup>-1</sup> (COO<sup>-</sup> asymmetric stretching), and 1421 cm<sup>-1</sup> (COO<sup>-</sup> symmetric stretching). For SA/Na<sup>+</sup>REC2, the absorption band at 3430 cm<sup>-1</sup> concerned with OH stretching and 1618 cm<sup>-1</sup> assigned to the asymmetric stretching vibration of COO<sup>-</sup> for pure alginate shifted to a low wave number. Also, compared with pure SA, it was obvious the peak at 1042 cm<sup>-1</sup> assigned to the anisomerous stretching vibration of Si—O—Si and 550 cm<sup>-1</sup> assigned to the bending vibration of Si—O were presented in SA/Na<sup>+</sup>REC2 nanocomposites,<sup>27,28</sup> while the vibration bands at 3632 cm<sup>-1</sup> corresponding to the hydroxyl stretching of SiOH and the peaks at 927 cm<sup>-1</sup> corresponding to the vibration of P—O appeared. These results confirmed that a certain degree of intermolecular interactions between alginate and Na<sup>+</sup>REC existed due to the intercalation.<sup>21,29</sup>

Figures 3–5 give SEM pictures of SA/Na<sup>+</sup>REC1, SA/Na<sup>+</sup>REC2, and SA/Na<sup>+</sup>REC5 composite film, respectively. They show the disperse degree of



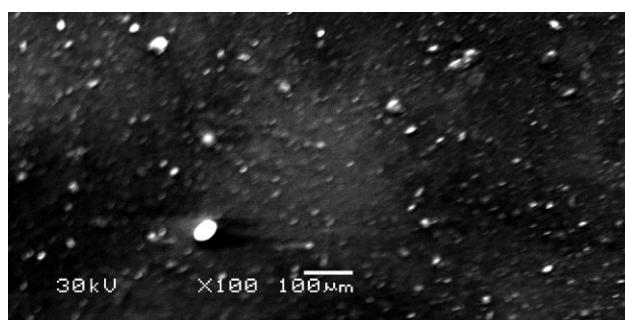
**Figure 3** SEM photograph of SA/Na<sup>+</sup>REC1 composite film.

Na<sup>+</sup>REC in composites with different contents of Na<sup>+</sup>REC. Na<sup>+</sup>REC is well dispersed in the SA matrix of both SA/Na<sup>+</sup>REC1 and SA/Na<sup>+</sup>REC2 composite films, but it has poor dispersion in SA/Na<sup>+</sup>REC5 composite film because of the aggregation of Na<sup>+</sup>REC clusters.

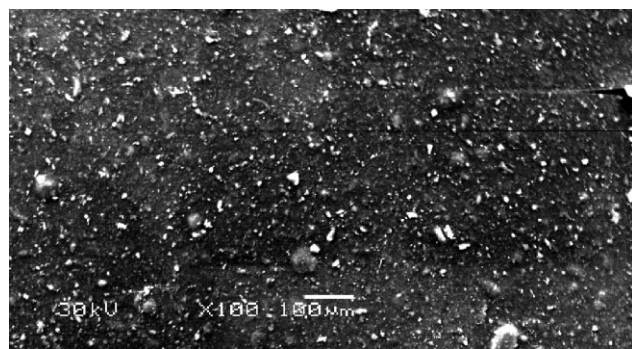
TEM was also used to visually evaluate the degree of intercalation and the amount of aggregation of clay clusters. Figure 6 shows TEM micrographs of SA/Na<sup>+</sup>REC2 nanocomposite, in which the gray areas represent the silicate layers in the SA matrix (bright). It can be seen that the layered silicate is separated in the SA matrix, indicating that the swellable silicate layers are exfoliated into SA matrix. Figure 6 also shows that a mixture of intercalated and unintercalated clay species coexists in SA matrix; the intercalation effect is not quite ideal, just showing partial intercalation.

#### Mechanical properties of SA/Na<sup>+</sup>REC composite films

The mechanical properties of SA/Na<sup>+</sup>REC composite films are summarized in Figure 7. For the SA/Na<sup>+</sup>REC composites with Na<sup>+</sup>REC content under 2 wt %, the tensile strength and elongation values slightly increase with the increase of Na<sup>+</sup>REC content. The tensile strength and elongation values of SA/Na<sup>+</sup>REC2 composite film increase by 91.7%, 100% compared with pure SA film, respectively. As the loading of Na<sup>+</sup>REC goes beyond 2 wt %, the

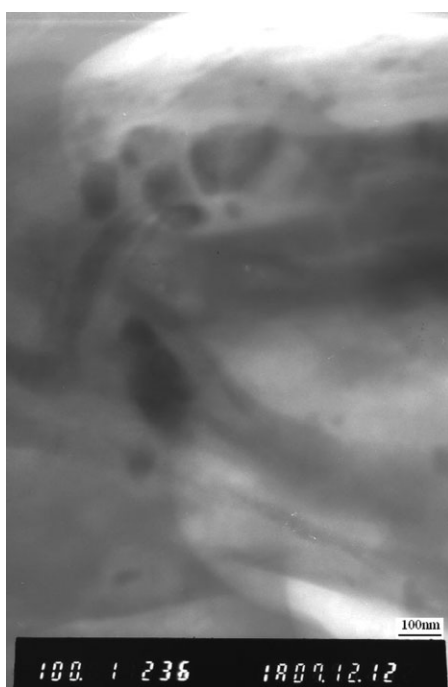


**Figure 4** SEM photograph of SA/Na<sup>+</sup>REC2 composite film.

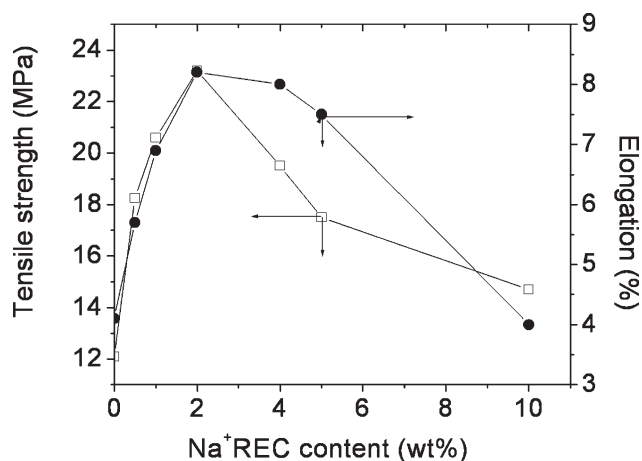


**Figure 5** SEM photograph of SA/Na<sup>+</sup>REC5 composite film.

system shows a decrease in tensile strength and elongation values. The improvement of tensile strength and elongation values of SA/Na<sup>+</sup>REC composite film may be explained by three main reasons. First, when the content of Na<sup>+</sup>REC is low, Na<sup>+</sup>REC in SA can be dispersed readily, leading to the formation of intercalated structure and thus preventing the extending of cracks. In addition, the existence of the laminates induces yielding of the matrix, and absorbing a lot of energy owing to the tight binding between the laminates and the matrix. Third, the addition of Na<sup>+</sup>REC can reduce the volume shrinkage of SA during the coagulating course possibly due to the immobilization of SA at the silicate-matrix interface.<sup>30,31</sup> However the aggregation of Na<sup>+</sup>REC at higher Na<sup>+</sup>REC content, the tensile strength, and elongation values of composites decrease.



**Figure 6** TEM photograph of SA/Na<sup>+</sup>REC2 composite.

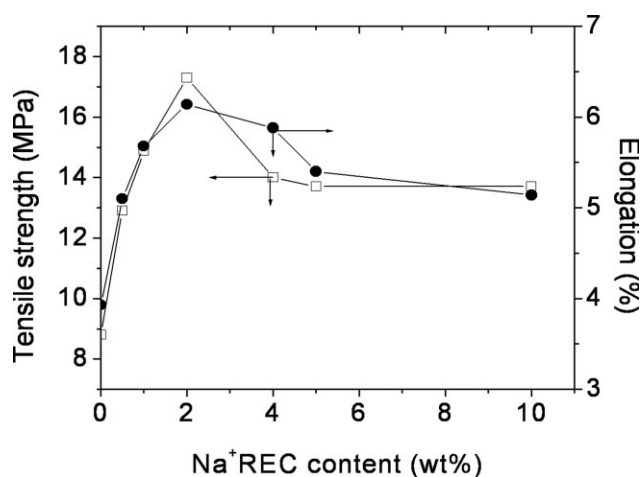


**Figure 7** Tensile properties of SA/Na<sup>+</sup>REC composite films.

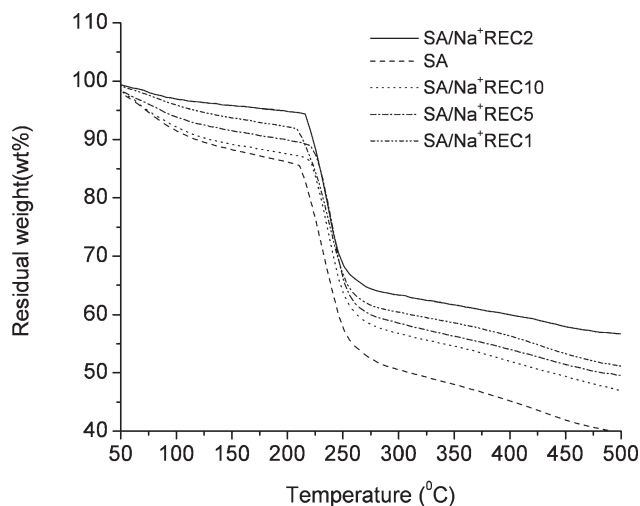
Figure 8 summarizes the ultraviolet aging properties of SA/Na<sup>+</sup>REC composites. It can be observed that the decreasing degrees of tensile strength and elongation break of SA/Na<sup>+</sup>REC composite films are smaller than that of pure SA film, indicating that the addition of Na<sup>+</sup>REC can improve the resistance to ultraviolet ray because of good absorbance of Na<sup>+</sup>REC to ultraviolet ray.

#### Thermal properties of SA/Na<sup>+</sup>REC composites

TG curves of pure SA film and the SA/Na<sup>+</sup>REC composite films are shown in Figure 9. The TG temperature of 10% weight loss of pure SA, SA/Na<sup>+</sup>REC1, SA/Na<sup>+</sup>REC2, SA/Na<sup>+</sup>REC5, and SA/Na<sup>+</sup>REC10 is 125, 223, 230, 225, and 220°C, respectively. The TG temperatures of 40% weight loss of the above materials are 240, 365, 425, 325, and 275°C, respectively. The results clearly show that the decomposition temperature of the composites are



**Figure 8** The ultraviolet aging properties of the SA/Na<sup>+</sup>REC composite films.



**Figure 9** TG curves of SA and SA/Na<sup>+</sup>REC composites.

higher than that of pure SA, suggesting that the addition of Na<sup>+</sup>REC would endow the SA/Na<sup>+</sup>REC composites with higher thermal stability. The decomposition temperature of SA/Na<sup>+</sup>REC2 composite is the highest and that of SA/Na<sup>+</sup>REC10 composite is the lowest among these composites. Moreover, the decomposition temperature of the composites show a trend of increasing in low concentration of Na<sup>+</sup>REC and then decreasing in high concentration. Reasons lie in two main aspects. First, rectorite has high heat resistance. Second, rectorite should be equably dispersed in SA matrix.

## CONCLUSIONS

Rectorite, a kind of natural silicate clay similar to MMT, is a good nanometer modifier for modifying SA. First, natural REC must be calcinated and modified by sodium pyrophosphate through cationic-exchange reaction, and the modified REC (Na<sup>+</sup>REC) can be used to prepare SA/Na<sup>+</sup>REC nanocomposites by water solution processing at lower clay loading. Mechanical properties and the capability of resistance to ultraviolet ray of the SA/Na<sup>+</sup>REC nanocomposites can be substantially enhanced, and the maximum tensile strength and elongation values can be obtained at 2 wt % Na<sup>+</sup>REC loading. The decomposition temperature of SA/Na<sup>+</sup>REC systems is higher than that of pure SA, indicating that the binary systems have higher thermal stability.

## References

- Wang, Y. Q.; Zhang, H. F.; Wu, Y. P.; Yang, Y.; Zhang, L. Q. *Eur Polym J* 2005, 41, 2776.
- Wu, T. M.; Wu, C. Y. *Polym Degrad Stab* 2006, 45, 2198.
- Kokabi, M.; Sirousazar, M.; Hassan, Z. M. *Eur Polym J* 2007, 43, 773.
- Jia, X.; Li, Y. F.; Zhang, B.; Cheng, Q.; Zhang, S. J. *Mater Res Bull* 2007, 43, 611.
- Ma, X. Y.; Lu, H. J.; Liang, G. Z.; Zhao, J. C.; Lu, T. L. *J Appl Polym Sci* 2005, 96, 1165.
- Ma, X. Y.; Lu, H. J.; Liang, G. Z.; Yan, H. X. *J Appl Polym Sci* 2004, 93, 608.
- Alsina, O. L. S.; Carvalho, L. H.; Ramos Filho, F. G.; D'almeida, J. R. M. *Polym Test* 2005, 24, 81.
- Morgan, A. B.; Harris, J. D. *Polymer* 2004, 45, 8695.
- Haque, A.; Shamsuzzoha, M.; Hussain, F.; Dean, D. *J Compos Mater* 2003, 37, 821.
- Vlasveld, D. P. N.; Parlevliet, P. P.; Bersee, H. E. N.; Picken, S. J. *J Compos A* 2005, 36, 1.
- Dong, Y. C.; Feng, S. S. *Biomaterials* 2005, 26, 6068.
- Avella, M.; De Vlieger, J. J.; Errico, M. E.; Fischer, S.; Vacca, P.; Volpe, M. G. *Food Chem* 2005, 93, 467.
- Ray, S. S.; Bousmina, M. *Prog Mater Sci* 2005, 50, 962.
- Wang, X. Y.; Du, Y. M.; Luo, J. W.; Lin, B. F.; John, F. K. *Carbohydr Polym* 2007, 69, 41.
- Darder, M.; Colilla, M.; Hitzky, E. R. *Chem Mater* 2003, 15, 3774.
- Sara Poncea, B.; Orivea, G.; Ndeza, R. H.; Alicia, R. G.; Pedraza, J. L.; Bart, J. H.; Marijke, M. F.; Mathieuc, H. J.; De Vos, P. *Biomaterials* 2006, 27, 4831.
- Smitha, B.; Sridha, S. R.; Khan, A. A. *Eur Polym J* 2005, 41, 1859.
- Boontheekula, T.; Kongc, H.-J.; David, J. M. *Biomaterials* 2005, 26, 455.
- Guilhermea, M. R.; de Mouraa, M. R.; Radovanovica, E.; Geuskensb, G.; Rubiraa, A. F.; Muniz, E. C. *Polymer* 2007, 46, 2668.
- Teli, S. B.; Gokavi, G. S.; Aminabhavi, T. M. *Sep Purif Technol* 2007, 54, 178.
- Tuncer, C.; Demircia, S.; Mehmet, S. E.; Guvensuh, O. *Polymer* 2005, 46, 10750.
- Ma, X. Y.; Lu, H. J.; Lü, M. L. *China Plast* 2002, 16, 37.
- Lin, F. H.; Lee, Y. H.; Jian, C. H.; Wong, J. M.; Shieh, M. J.; Wang, C. Y. *Biomaterials* 2002, 23, 1981.
- Castelein, O.; Soulestin, B.; Bonnet, J. P. *Ceram Int* 2001, 27, 517.
- Li, Z. H.; Jiang, W. T.; Hong, H. L. *Spectrochim Acta Part A: Mol Biomol Spectrosc*, to appear.
- Pongjanyakul, T.; Puttipatkhachorn, S. *Int J Pharm* 2007, 333, 34.
- Changa, J. H.; Ana, Y. U.; Choa, D. W.; Emmanuel, P. G. *Polymer* 2003, 44, 3715.
- Dean, K.; Yu, L.; Wu, D. Y. *Compos Sci Technol* 2007, 67, 413.
- Ferreira, P. A.; Almeida, A. J. *J Controlled Release* 2004, 97, 431.
- Abdullah, A. K.; Maisa, E. G.; Abdelsamie, M. *J Appl Polym Sci* 2005, 98, 767.
- Jacobs, P. M.; Jones, F. R. *Polymer* 1993, 34, 2122.