

Influence of Reaction Conditions on the Grafting Pattern of 3-Glycidoxypropyl trimethoxysilane on Montmorillonite

Wentao He, Yong Yao, Min He, Zhang Kai, Lijuan Long, Minmin Zhang, Shuhao Qin,* and Jie Yu*

National Engineering Research Center for Compounding and Modification of Polymeric Materials,
and College of Materials Science and Metallurgy Engineering, GuiZhou University, GuiYang 550003, China

*E-mail: yuji@gz@126.com

Received September 18, 2012, Accepted October 12, 2012

Surface modification of montmorillonite (MMT) with 3-glycidoxypropyl trimethoxysilane (3GTO) in mild methanol/water mixture has been investigated in detail. The influence of reaction conditions (including silane concentration in feed, reaction time and reaction temperature) on the grafting amount and yield of silane, and further on the grafting pattern of silanes was studied by thermogravimetric analysis, elemental analysis, X-ray diffraction (XRD) and BET. Higher silane concentration, longer reaction time and higher reaction temperature are all benefit to higher grafting amount. When the grafting reaction was performed with 3 mmol/g silane concentration, at 90 °C for 24 h, the grafted amount and yield of silane reached 1.4443 mmol/g and 30%, respectively. Based on the XRD and BET data analysis, a speculation that the grafting pattern of silanes was concentration dependence was proposed.

Key Words : Surface modification, Montmorillonite, 3-Glycidoxypropyl trimethoxysilane, Grafting pattern

Introduction

Since Toyota research reported a nylon-6/montmorillonite material,¹ where very small amount of inorganic loadings resulted in remarkable enhancements of thermal and mechanical properties, continuing research efforts have been emphasized on the layered silicate/polymer nanocomposites.^{2,3} It is well known that the interactions between the polymer matrix and the clay layers have a great effect on the dispersion level of the clay layers, and ultimately on the mechanical properties of the polymer/clay composites. Much effort has been made to improve the interaction between the polymer and clay including ion-exchange reaction with traditional cationic surfactant or various cationic polymers,^{4,5} intercalative copolymerization and so on.⁶ However, the thermal instability and inaccessibility to calculate the degree of organic coverage limit the application of the widely used cationic surfactants.^{7,8}

Surface modifications of clay minerals with silane coupling agents is also a widely used method to enhance the interfacial interaction.⁹⁻¹³ Configuration arrangement and grafting efficiency of the silane molecules in the clay depend on the nature of the clay minerals, silane coupling agents, dispersing medium, reaction temperature and so on. He *et al.* studied the grafting of fluoro-hectorite and montmorillonite with 3-aminopropyltriethyl silane.⁹ The result demonstrated interlamellar distance of the clay increased to 1.45 nm and 1.77 nm, and the silane molecular adopted monolayer arrangement for fluoro-hectorite and bilayer arrangement for montmorillonite. The grafting of laponite clay particles with monofunctional and trifunctional silane coupling agents was also reported.¹⁰ The monofunctional silane formed a monolayer coverage on the border of the clay plates while the

trifunctional silane formed a submonolayer coverage at low concentrations and a multilayer coating at higher concentrations. However, some research found that the interlamellar distance of montmorillonite or Laponite exhibited nearly no change after grafting with monoalkoxy silane according to the XRD analysis.^{14,15} To date there isn't a consistent conclusion about whether the silane molecular increases interlamellar distance or not. But relative studies all reveal that the grafting of silane coupling agents can increase the hydrophobicity and further enhance the interfacial compatibility between the clay and polymers, making the intercalation of hydrophobic molecules into clay materials easier. Therefore systematical investigation about the silane grafting of MMT is an important and useful work since MMT is used to improve the properties of polymer in many fields of applications. However, we find that researchers paid great attention to the grafting of silanes containing amino-group, and little attention was paid to the grafting of other kinds of silanes.¹⁶⁻¹⁸

In the present work, 3GTO is chosen due to its bi-functional properties. The three alkoxy groups enable covalent bonding to the hydroxyl group of MMT while the epoxide ring can further react with a nucleophile such as hydrophilic or hydrophobic moieties to satisfy various needs for intercalation in applications. However, in most studies the grafting of silane was performed in organic solvent, which would bring about environmental problems.^{10,15} Yoon JS *et al.* successfully obtained 3GTO-functionalized organoclay by reacting 3-glycidoxypropyl trimethoxysilane with Cloisite25A in mild ethanol/water mixture, but the detailed report about the parameters influencing grafting amount and grafting patterns was not described.¹⁹

The study described the effect of different parameters on the grafting degree of 3GTO in the case of pristine MMT in

detail, further on the grafting pattern in order to investigate the mechanism of action. For this purpose, the silane concentration in feed, reaction time and reaction temperature were changed to control the grafting amount. The amount and yield of grafted silane was assessed by TG, elemental analysis. XRD and BET were employed to characterize the final properties of 3GTO-functionalized montmorillonite.

Experimental

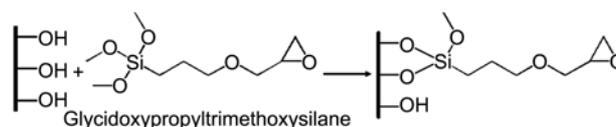
Materials. The unmodified montmorillonites used were provided by Nanocor, Inc. (Nanomer PGN), and were purified by dissolving in ethanol at 70 °C for 4 h in order to remove any contaminants. 3GTO was provided by Hubei Debang Chemical Co. Ltd (China). All other solvents and reagents were used as received without further purification.

Preparation of 3GTO-functionalized MMT. The preparation of 3GTO-functionalized MMT was performed according to the procedure reported previously with a minor modification.¹⁹ Briefly, after a calculated amount 3GTO was hydrolyzed at pH 4.0 for 4h in a solution of acetic acid in ethanol (90 wt %)/deionized water (10 wt %) mixture (200 mL), the MMT (10 g) was added and the mixture was then heated with reflux at 50-90 °C for different times. The product was diluted five times with ethanol to remove the soluble homocondensates. The resulting product was then filtered and repeatedly washed with ethanol at room temperature and dried in a vacuum oven at 90 °C for at least 48 h. The synthesized 3GTO-functionalized MMT is denoted as GMMT_{m/n/o}, where m represents the 3GTO concentration in feed, n represents the reaction time and o represents reaction temperature.

Characterization. Thermogravimetric analysis of the untreated and treated MMTs was performed on a TA Instruments Q50 to quantitatively determine the grafting degree and yield as well as the thermal stability. Samples were heated from 25 °C to 800 °C at the rate of 10 °C/min under a nitrogen flow (60 mL/min). An organic Elemental Analyser (Elementar, Germany) was used to determine the carbon and hydrogen content of the bare and the functionalized MMT. And the results are compared with that of TG analysis to survey the degree of measurement data reliability. The variation of the interlayer distance of the clays was studied by means of wide-angle X-ray scattering using a Rigaku DMAX 2200 (Rigaku, Japan). The Cu K α radiation source ($\lambda = 0.154$ nm) was operated at 40 kV and 40 mA. Patterns were recorded by monitoring diffractions appearing in the range from 2° to 10° with a scanning rate of 1° min⁻¹. The nitrogen adsorption analysis was performed on NOVA 1000e instrument from Quantachrome. Prior to the adsorption, all samples were degassed at 120 °C for 8 h in a vacuum. The Brunauer-Emmett-Teller (BET) method was used for determination of the surface areas.

Results and Discussion

3GTO is employed as an organic modifier and the alkoxy



Scheme 1. The grafting process of the silane molecules.

groups first hydrolyse in acid condition into hydroxyl, and then react with the silanol on the MMT. The reaction process is shown in Scheme 1. Repeated washing was performed to ensure complete removal of unreacted 3GTO. A series of samples were prepared by changing the mole ratio of reactants, reaction temperature and reaction time to systematically investigate the factors effecting grafting degree.

The amount of grafted 3GTO on MMT was estimated by TG. Typical TG spectrograms of unmodified and modified MMT are exhibited in Figure 1. Pristine MMT shows an initial mass loss up to 150 °C, due to the removal of adsorbed water. A small mass loss is observed over the region of 200-550 °C, due to the removal of interlayer water. A final mass loss occurs in the temperature region spanning from 550-800 °C mainly due to the dehydroxylation of aluminosilicate.²⁰ After grafting of the silane molecules, the mass loss in the region between 200 °C and 550 °C, which mainly contributed to the thermal decomposition of the organic molecules, increases obviously. Besides, the initial degrada-

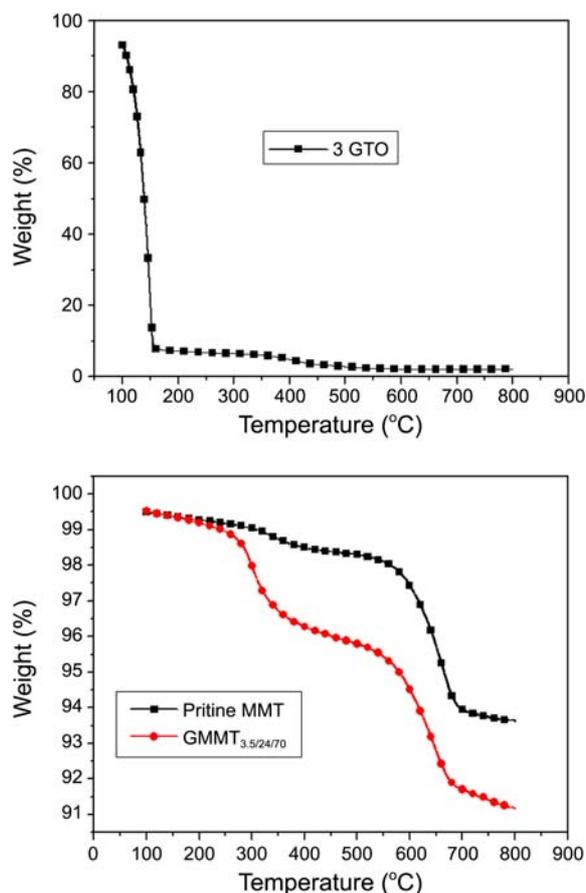


Figure 1. Typical TG spectrograms of 3GTO, unmodified and modified MMT.

tion temperature of silane molecular on the MMT increases compared to that of ungrafted silane molecular. The above results confirmed that silane molecular is chemically grafted on the MMT but not physically absorbed. The following equation is used to calculate the amount of grafted silane based on the weight loss between 200 °C and 550 °C, $W_{200-550}$, taking into account the interlayer water loss of pristine MMT that occurs in same temperature range, where M (g/mol) is the molecular weight of the grafted silane molecules.

$$\text{Grafted amount (mequiv/g)} = \frac{10^3 W_{200-550}}{(100 - W_{200-550})M} \quad (1)$$

To determine the grafted yield, corresponding to the percentage of silane molecules successfully grafted, the following equation is employed, where [silane concentration] (mequiv/g) is the silane concentration in feed.

$$\text{Grafted yield (\%)} = \frac{\text{Grafted amount}}{[\text{silane concentration}]} \times 100\% \quad (2)$$

The thermogravimetric data of different reaction time of samples are shown in Table 1. The data clearly show that the grafting reaction is time-dependent. The mass loss in the 200-550 °C region increases continuously with the reaction time. At 24 h, the grafted amount is 0.233 mmol/g and the grafted yield reaches 15.7%. Longer reaction time is beneficial for silane molecular and MMT contacting each other and increases the interaction probability. But too long time is not benefit for practical applications, therefore the reaction time is set to 24 h in the following experiments.

Table 1. Thermogravimetric data of pristine and 3GTO-grafted MMT

	Weight loss (%) ^a	Corrected weight loss (%) ^b	Grafted amount (mequiv/g) ^c	Grafted yield (%) ^d
Pritine MMT	1.169			
GMMT1.5/3/70	2.693	1.524	0.136	9.2
GMMT1.5/5/70	3.004	1.835	0.164	11.1
GMMT1.5/12/70	3.114	1.945	0.174	11.8
GMMT1.5/24/70	3.754	2.585	0.233	15.7
GMMT3/24/70	5.428	4.259	0.390	13.2
GMMT6/24/70	5.644	4.475	0.411	6.9
GMMT3/24/50	2.860	1.691	0.151	10.2
GMMT3/24/90	5.987	4.818	0.444	30.0

^aWeight loss between 200 °C and 550 °C. ^bWeight loss minus water loss of pristine MMT between 200 °C and 550 °C. ^cDetermined using Eq. (1). ^dDetermined using Eq. (2).

Table 2. Elemental analysis after different washing times

Code	C (W%)	H (W%)
GMMT1.5/24/70- _{X(3)} ^a	2.24/2.29	1.51/1.49
GMMT1.5/24/70- _{X(8)} ^b	2.25/2.33	1.50/1.49
Pristine MMT	0.75/0.76	1.16/1.16

^aAfter washing three times. ^bAfter washings eight times.

In order to verify the complete elimination of physically absorbed silane molecular, the elemental analysis after repeated washing eight times was compared with that after washing three times (Table 2). The carbon and hydrogen contents after washing eight times are almost the same as that after washing three times, indicating that washing three times is enough to remove ungrafted silane molecular.

The silane concentration in feed was varied and the reaction time was maintained at 24 h (Table 1). The data in Figure 2(a) show that the grafted amount first increases sharply and then smoothly with increasing the silane concentration in feed. This smoother increase is mainly due to the steric hindrance of already grafted silane molecular. Consequently, the grafted yield decreases continuously. Considering the above factor, the temperature change was performed while the silane concentration in feed was kept in 3 mmol/g.

The polygonal lines in Figure 2(b) reveal that the grafted amount and grafted yield increase simultaneously with increasing the reaction temperature. At 90 °C, the grafted amount is 0.444 mmol/g which is higher than that reported previously,¹⁸ obviously higher than that at 50 °C (0.151

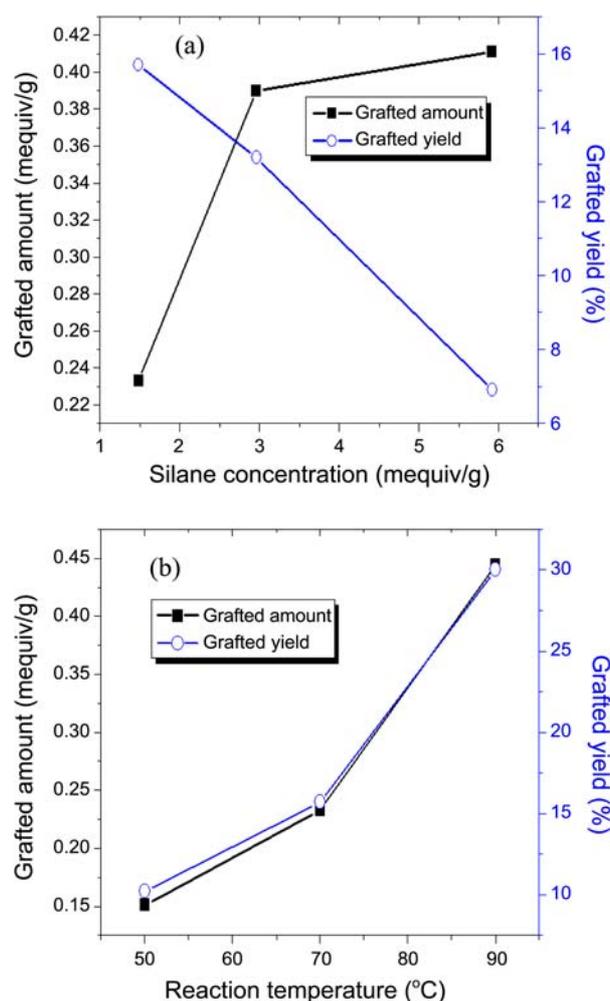


Figure 2. Effect of silane concentration (a) and reaction temperature (b) on the grafted amount and grafted yield.

mmol/g). The high grafted amount is contributed to improved reactivity of silane molecular at high temperature. Too high temperature costs energy and is not considered in the experiments.

The grafted amount (expressed in mequiv of grafted silane per g of bare MMT clay as mentioned above) is also calculated from the Eq. (3) based on the difference ΔC (wt %) of carbon content after and before grafting, where N_c and M (g/mol) designate the number of carbon atoms and the molecular weight of the grafted silane molecule ($N_c = 6$ and GPTMS = 236):

$$\text{Grafted amount (mequiv/g)} = \frac{10^3 \Delta C}{[1200N_c - \Delta C(M-1)]} \quad (3)$$

As seen in Table 3, the grafted amount determined by elemental analysis is in good agreement with that determined by TG (Table 1). The result confirms the accuracy of TG analysis method.

The XRD patterns of pristine MMT and 3GTO-modified MMT are shown in Figure 3. According to the Bragg's equation ($n\lambda = 2d\sin\theta$), the basal spacing of $n = 1$ was calculated on the basis of the observed $n = 2, 3$ and so on.²¹ Unmodified

Table 3. Elemental analysis of pristine and 3GTO-modified MMT

	Carbon content (wt %)	ΔC (%)	Grafted amount (mequiv/g)	Grafted yield (%)
Pristine MMT	0.75			
GMMT1.5/24/70	2.29	1.54	0.225	15.2

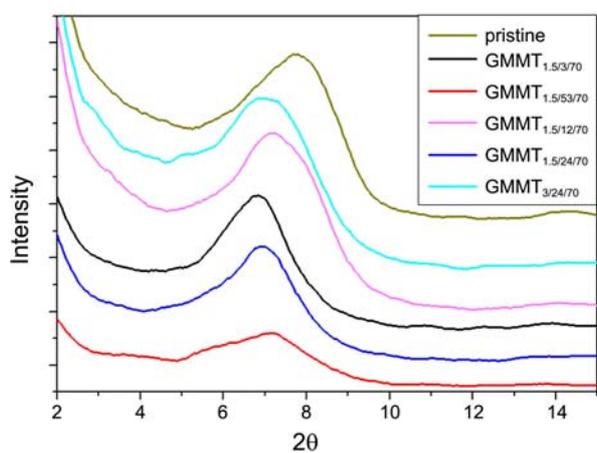
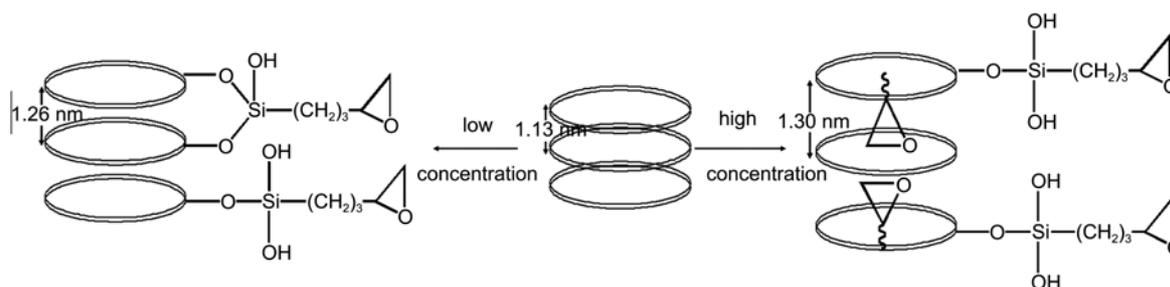


Figure 3. XRD patterns of pristine and 3GTO-modified MMT.



Scheme 2. A schematic diagram describing the grafting patterns.

Table 4. The interlayer distance of pristine and 3GTO-modified MMT

	2θ (°)	d-value (nm) ^a
Pristine MMT	7.8	1.13
GMMT1.5/3/70	6.9	1.28
GMMT1.5/5/70	7.0	1.26
GMMT1.5/12/70	7.1	1.24
GMMT1.5/24/70	7.0	1.26
GMMT3/24/70	6.8	1.30

^aThe basal spacing of pristine and 3GTO-modified MMT.

MMT shows a peak at $2\theta = 7.8^\circ$ corresponding to an interlayer spacing of 1.13 nm (Table 4). After modifications with 3GTO, the interlayer spacing exhibits a little increase (about 1.26 nm) when the silane concentration in feed is 1.5 mmol/g regardless of the reaction time. As the silane concentration increases to 3 mmol/g with the reaction time of 24 h, the interlayer spacing increases to 1.30 nm. The difference in XRD spectrum is probably due to interlayer grafting occurring for GMMT3/24/70, while the silane molecules only graft on the edge of clay platelets when the silane concentration in feed is 1.5 mmol/g. These results indicate that hydroxyl groups on the edge of clay platelets are more accessible to silane molecules and the grafting pattern is silane concentration dependence. When the silane concentration in feed is in a relatively low range, grafting reaction mainly occurs on the edge of clay platelets even if the reaction time changes

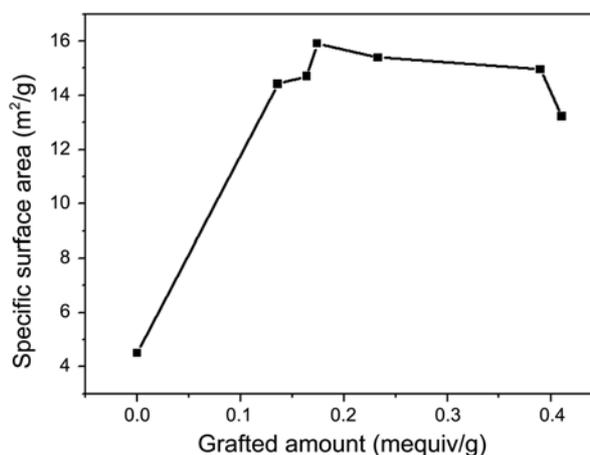


Figure 4. Specific surface area of pristine MMT and 3GTO-modified MMT.

from 3 h to 24 h. While the silane concentration in feed reaches 3 mmol/g, grafting reaction occurs not only on the edge but also the interlayer surface. A schematic diagram describing the grafting patterns is shown in Scheme 2.

Figure 4 shows the specific surface area of pristine MMT and 3GTO-modified MMT. The specific surface area of 3GTO-modified MMT has an obvious increase compared with the unmodified clay, which is similar to related research reported previously.²² With the increase of grafted amount, the surface area data remain in the range of 13 to 16 m²/g. The increased surface roughness of MMT attributed to 3GTO grafting on the edge and limited access to the internal porosity may explain the above phenomenon that the specific surface area didn't change with the grafted silane amount.¹⁰ These results are accordance with our speculations about the grafting process as described in Scheme 2.

Conclusion

MMT was surface modified with 3GTO in mild reaction conditions. TG and elemental analysis after repeated washing verified successful grafting of the silane molecule on MMT. The grafted amount increased but the grafted yield decreased with increasing the silane concentration. Extending the reaction time and raising the reaction temperature are also effective methods to increase the grafted amount and yield. The interlayer spacing exhibits a little increase when the silane concentration in feed is 1.5 mmol/g regardless of the reaction time, and the interlayer spacing further increases to 1.30 nm as the silane concentration increases to 3 mmol/g. Based on the results, a speculation about the concentration dependence of grafting pattern is proposed, which argued that the silane molecules only graft on the edge of clay platelets at low silane concentration and interlayer grafting occurs simultaneously at high silane concentration. The specific surface area data are accordance with our speculations.

Acknowledgments. The work was financially supported by National Natural Science Foundation of China (20964001, 51263003), Guizhou Province Excellent Young Technological

Talents Training Objects Special Fund (Grant No. 2009 12), Governor Special Funds for Excellent Talents in Scientific and Technological Education in Guizhou (2011[5]) and the Science Foundation of Guizhou Province ([2011]2020).

References

1. Usuki, A.; Kawasumi, M.; Kojima, Y.; Okada, A.; Kurauchi, T.; Kamigaito, O. *J. Mater. Res.* **1993**, *8*, 1174.
2. Manias, E.; Touny, A.; Wu, L.; Strawhecker, K.; Lu, B.; Chung, T. *Chem. Mater.* **2001**, *13*, 3516.
3. Leu, C. M.; Wu, Z. W.; Wei, K. H. *Chem. Mater.* **2002**, *14*, 3016.
4. Juang, T. Y.; Chen, Y. C.; Tsai, C. C.; Dai, S. A.; Wu, T. M.; Jeng, R. *J. Appl. Clay Sci.* **2010**, *48*, 103.
5. Brnardić, I.; Huskić, M.; Žigon, M.; Ivanković, M. *J. Non-cryst. Solids.* **2008**, *354*, 1986.
6. Rzaev, Z. M. O.; Şenol, B.; Soylemez, E. A. *Eng.* **2011**, *3*, 1446.
7. Xie, W.; Gao, Z.; Pan, W. P.; Hunter, D.; Singh, A.; Vaia, R. *Chem. Mater.* **2001**, *13*, 2979.
8. Krishna, S. V.; Pugazhenthii, G. *Int. J. Polym. Mater.* **2010**, *60*, 144.
9. He, H.; Duchet, J.; Galy, J.; Gerard, J. F. *J. Colloid Interface Sci.* **2005**, *288*, 171.
10. Herrera, N. N.; Letoffe, J. M.; Reymond, J. P.; Bourgeat-Lami, E. *J. Mater. Chem.* **2005**, *15*, 863.
11. Wang, L.; Wang, K.; Chen, L.; He, C.; Zhang, Y. *Polym. Eng. Sci.* **2006**, *46*, 215.
12. Shanmugaraj, A.; Rhee, K. Y.; Ryu, S. H. *J. Colloid Interface Sci.* **2006**, *298*, 854.
13. Yang, S.; Yuan, P.; He, H.; Qin, Z.; Zhou, Q.; Zhu, J.; Liu, D. *Appl. Clay Sci.* **2012**, *62*, 8.
14. Park, M.; Shim, I. K.; Jung, E. Y.; Choy, J. H. *J. Phys. Chem. Solids* **2004**, *65*, 499.
15. Frost, R. L.; Daniel, L. M.; Zhu, H. Y. *J. Colloid Interface Sci.* **2008**, *321*, 302.
16. Park, K. W.; Kwon, O. Y. *Bull. Korean Chem. Soc.* **2004**, *25*, 965.
17. Shen, W.; He, H.; Zhu, J.; Yuan, P.; Frost, R. L. *J. Colloid Interface Sci.* **2007**, *313*, 268.
18. Piscitelli, F.; Posocco, P.; Toth, R.; Fermeglia, M.; Pricl, S.; Mensitieri, G.; Lavorgna, M. *J. Colloid Interface Sci.* **2010**, *351*, 108.
19. Chen, G. X.; Kim, H. S.; Shim, J. H.; Yoon, J.-S. *Macromol.* **2005**, *38*, 3738.
20. Xie, W.; Xie, R.; Pan, W. P.; Hunter, D.; Koene, B.; Tan, L. S.; Vaia, R. *Chem. Mater.* **2002**, *14*, 4837.
21. Lin, J. J.; Hsu, Y. C.; Wei, K. L. *Macromol.* **2007**, *40*, 1579.
22. Dai, J. C.; Huang, J. T. *Appl. Clay Sci.* **1999**, *15*, 51.