

EFFECT OF SILANE COUPLING AGENT ON THE MECHANICAL, THERMAL PROPERTIES AND MORPHOLOGY OF TREMOLITE/PA1010 COMPOSITES

Xiao-li Liu^a, Ye Han^{a, b}, Ge Gao^a, Zhi-ying Li^a and Feng-qi Liu^{a*}

^a College of Chemistry and MacDiarmid Laboratory, Jilin University, Changchun 130012, China

^b Changchun University of Technology, Changchun 130023, China

Abstract Tremolite, a kind of inorganic filler, was modified with a silane coupling agent γ -methacryloxypropyl trimethoxy silane (MPS) in ethanol/ammonia solution. The graft of MPS on tremolite was confirmed by X-ray photoelectron spectroscopy (XPS), IR and thermogravimetric analysis (TGA) measurements. In addition, contact angle analysis showed that particle surface property was changed from hydrophilicity to hydrophobicity after the modification. Modified tremolite and pure tremolite were blended respectively with PA1010 (polydecamethylene esbacamide) and the mechanical properties of the composites were studied. Results revealed that MPS had a remarkable influence on the mechanical properties of the composites due to the improvement of interfacial adhesion between filler and matrix. Tensile strength and notched Izod impact strength of MPS-modified tremolite composites were improved simultaneously compared to those with pure tremolite. Composites with MPS modified tremolite exhibited a much higher thermal stability than the samples with pure tremolite confirmed by TGA. The morphologies of the composites were also investigated using scanning electron microscopy (SEM). Results showed that better dispersion of MPS modified tremolite in matrix was obtained.

Keywords: Tremolite; MPS; Composite materials; Mechanical properties.

INTRODUCTION

Incorporating inorganic mineral fillers into polymers is usually used to improve various physical properties of the materials, such as mechanical properties and heat deflection temperature *etc.* Also, the costs for the polymer products can be lowered by substitute the expensive resins with cheap fillers. Thus the field of particle-filled polymer composites has gained considerable attention^[1–7]. Polyamides are one of the most widely used engineering thermoplastics especially in machine, automotive, and electrical industries because of their excellent mechanical properties. However, the lower heat deflection temperature, higher water absorption, and dimensional instability of the pure nylon have prevented their applications as structural components. Numerous efforts have been made to utilize nylon as the matrix resin for composites by adding glass fibers or other inorganic fillers such as clay^[8, 9], montmorillonite^[10], MoS₂^[11], Kaolin^[12], Al₂O₃^[13], carbon^[14], mica^[5], tremolite^[15] and so on.

In a general way, the mechanical properties of particulate-filled polymer composites are dependent strongly upon dispersion of the filler in the matrix and adhesion at the filler/matrix interface^[6, 12, 16]. Because of the hydrophilic nature, the filler does not wet or interact with hydrophobic polymer due to the difference in surface energies. It is necessary to treat the filler with a coupling agent in order to improve the compatibility between filler and matrix. A widely used coupling agent is organic silanes, which formula can be simply written as RSiX₃, where R is a non-hydrolyzable organic group which can be combined with polymers, and X is a hydrolyzable group, for instance, an alkoxy group such as —OC₂H₅, —OCH₃ *etc.* A coupling agent is just like a molecular bridge in the interface of inorganic filler and organic polymer matrix^[17–19]. The incorporation of

* Corresponding author: Feng-qi Liu (刘凤岐), E-mail: liufengqi@jlu.edu.cn

Received March 19, 2007 ; Revised April 25, 2007; Accepted April 26, 2007

coupling agent can also reduce the water sensitivity of the composites.

Although much work on the composites combining polymer with inorganic fillers has been performed, MPS modified tremolite/PA1010 composite has not been studied. In this paper, tremolite ($\text{Ca}_2\text{Mg}_5[(\text{OH})\text{Si}_4\text{O}_{11}]_2$)^[20], a naturally occurring, cheap nonmetallic mineral was chosen as a filler to reinforce PA1010. For the C=C bond in methacryloxypropyl group of MPS may polymerize initiated by heat in extruder, the effect of MPS was better than other general coupling agents^[21]. MPS was chosen to modify the tremolite particles. The mechanical and morphologies of the composites were studied for various levels of filler. And, the thermal property and crystallization behavior were investigated.

EXPERIMENTAL

Materials

PA1010 resin used was commercially available and was provided by the Jilin Nylon Co., Ltd. The silane coupling agent MPS was purchased from Alfa Aesar. Tremolite (1250-mash) was a gift from Changchun DeChang Compound New Material Co., Ltd.

Modification of Tremolite

The modification of tremolite was carried out in a three-necked flask at 40°C. 250 g of tremolite was dispersed in 600 mL of anhydrous ethanol, and 10 mL of ammonia (25%) was added to the above mixture under rapidly stirring. Then a solution of 10 mL of MPS in 40 mL of ethanol was dropped into the flask with adding time of 2 h and the reaction was maintained for another 24 h. Rotary vacuum evaporator was used to promote that modification reaction and to distill the solvent and NH_3 . Excessive MPS was removed by suction filtration with plenty of anhydrous ethanol.

Preparation of Composites

Modified or pure tremolite was mixed with PA1010 resin at ratios of 5, 10, 20, 30, 40 wt% with respect to PA1010. Then the mixture extruded on a twin-screw extruder (SJSH-30, Nanjing Rubber and plastics machinery plant) with a screw diameter of 30 mm and a ratio of length to diameter of 25. The barrel temperature ranged from 190°C to 215°C with a screw speed of 30 r/min. The extrudate coming out in the form of a filament strand was water-cooled and granulated. Extruded samples were dried in vacuum at 90°C for 72 h and then injection-molded on a screw injection-molding machine (EAST-1000, Nanjing Rubber and plastics machinery plant) to prepare standard test specimens. The injection pressure was maintained at 50 MPa.

Characterization

X-ray photoelectron spectroscopy (VG ESCA LAB MKII) was used to determine the main elements and their valences in the composites. Thermogravimetry measurements were carried out by using a DTG-60H Simultaneous TDA-TG apparatus (Shimadzu) at a heating rate of 10 K/min under air atmosphere. Contact angle measurement was carried out by a FTA200 (USA) contact angle analyzer as following the procedure: 50 mg of tremolite powder dispersed in 0.3 mL of anhydrous ethanol under ultrasonic was spread on a clean glass sheet (20 mm× 20 mm) and dried under room temperature for 4 days. A bead of 5 μL was adopted in measurement. Infrared spectra were recorded using a Bruker Vector 22 spectrometer by using powder-pressed KBr pellets. Tensile property was measured with a Shimadzu AGS-H tensile testing machine at a crosshead speed of 50 mm/min. Tests were conducted in accordance with ASTM D638. The impact properties were obtained according to ASTM 256 on a XJU-22 tester (Chengde Tester Plant) using a pendulum of 11 J at a striking velocity of 3.5 m/s. The values reported were the average values from five samples. SSX-550 Superscan electron microscope (Shimadzu) at an accelerating voltage of 15 kV was used to characterize the morphology of the fractured surface of composites. The SEM specimens were sputter-coated with gold to increase surface conductivity using a compact coater CC50 (Shimadzu). The crystallization behavior of the composites was investigated by means of a Mettler Toledo Differential Scanning Calorimeter (DSC821e). Indium was used as the reference for the calibration of temperature and energy scales.

RESULTS AND DISCUSSION

Modification of Tremolite with MPS

In order to eliminate the interference coming from the free MPS or oligomers remained, MPS modified tremolite powder was extracted on a soxhlet with toluene for 12 h before measurement. Figure 1 shows a photograph of water contact angle for MPS-modified tremolite powder. The contact angle is 114.98 degree. Contact angle data for pure tremolite wasn't obtained because the water bead penetrated through the tremolite and disappeared too soon for us to take a picture. Those results showed that the surface character of tremolite was changed from hydrophilicity to hydrophobicity. That is owing to the existence of MPS grafted on the surface of tremolite. Referring to the papers on clay^[22, 23] and silca^[24] modified by coupling agents, the grafting process of MPS on tremolite is as follows: (1) The methoxy groups of MPS hydrolyzed under the influence of ammonia and water, and silanols were formed. (2) The silanols associated and formed oligomers, and the oligomers adsorbed on the particle surface by hydrogen bonding and condensed with surface hydroxyls to form siloxane linkages during the evaporation of solvent. That is to say chemical bonds have formed between MPS and tremolite surface.

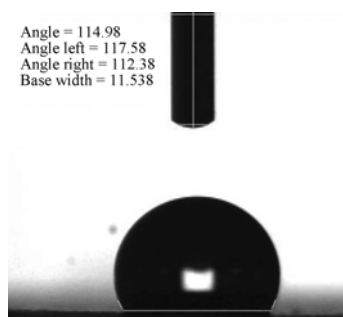


Fig. 1 Contact angle of MPS-tremolite (the volume of bead is 5 μ L)

Figure 2 displays the IR spectra of tremolite before and after modification with MPS. Owing to the strong absorbability of tremolite, differences between the two spectra are not distinct except the band at 1720 cm^{-1} , which can be attributed to the vibration of C=O bonds coming from MPS^[25]. Another more convictive proof for the graft of MPS was provided by X-ray photoelectron spectroscopy and the correlative data are listed in Table 1.

An evident change is that organic C (284.99 and 289.624 eV) appears which can not be found in the sample without modification. We can draw the conclusion that MPS has been grafted onto the surface of tremolite. Besides Si and O elements in the MPS modified tremolite having the same binding energies as these in pure tremolite, there are new bond states for O (bound with C) on the surface of MPS modified tremolite. The molar ratio of Si to O calculated on the base of the relative composition in Table 1 is 0.718 for tremolite and 0.637 for MPS modified tremolite. However the ratio should be 0.2 approximately for the latter based on the molecular formula of MPS. The greater difference between experiment and calculation shows that the grafting layer of MPS is not very thick. The thermogravimetric analysis of MPS-modified tremolite shows a weight loss of 0.771% between 200–400°C, which should be attributed to the decomposition of MPS oligomers. Though the amount of MPS grafted on tremolite is not too much, it is enough to influence the properties of tremolite/PA1010 composites.

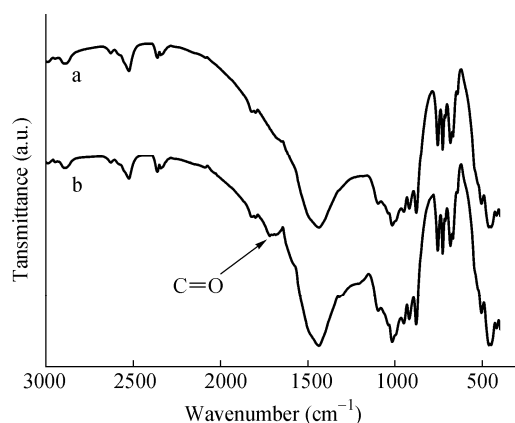


Fig. 2. IR spectra of (a) pure tremolite and (b) MPS modified tremolite

Table 1. Data of XPS for tremolite and MPS modified tremolite

Sample	Atom	Binding energy (eV)	State of binding	Relative mole composition ^b (%)
Tremolite ^a	Si	102.7	Si2p (Si—O)	41.8
	O	532.9	O1s (O—Si)	58.2
	Si	102.4	Si2p (Si—O)	25.8
	O	532.782	O1s (O—Si)	40.5
MPS-tremolite		534.419	O1s (O—C)	
	C	284.99	C1s (C—H)	33.7
		289.624	C1s (C—O, C=O)	

^a A little C polluted was also detected, but not listed in table; ^b The relative mole composition of atoms are calculated

according to the formula $c_i = \frac{A_i/S_i}{\sum A_j/S_j}$, where c_i expresses relative composites; A_i is peak area; S_i is sensitivity coefficient

and 0.27, 0.66, 0.75 are adopted for Si, O and C respectively.

Effect of MPS Modification on Mechanical Properties of Composites

The addition of filler brings about evident change in PA1010's mechanical properties. The variation of tensile strength with the content of filler is shown in Fig. 3. In case of composites with the loading of MPS modified tremolite, the tensile strength is much higher than that of pure PA1010 matrix in the range of filler content of test.

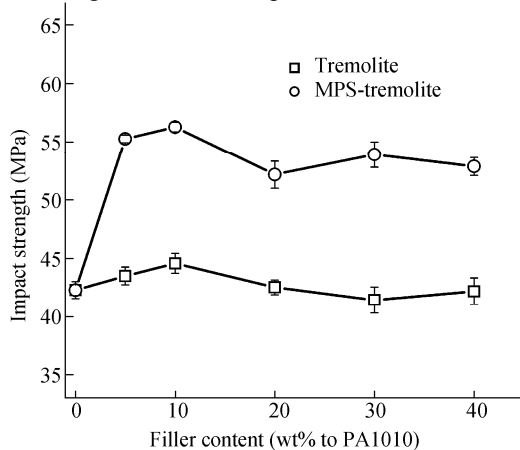


Fig. 3 Tensile strength of the composites with different filler content (wt% to PA1010)

Furthermore, a maximum is achieved at filler content of 10%, which increases 33.1% compare to PA1010 matrix. When the content is above 10%, the tensile strength has a little decrease and changes slowly, but it is still higher than that of pure matrix. As pure tremolite is concerned, the improvement in tensile strength is very limited.

Figure 4 depicts the variation of the notched Izod impact strength of the composites with filler content. The impact strength decreases with increasing filler content in the case of non-modified tremolite composites. This result is owing to the agglomeration of inorganic particles in organic PA1010 especially with high filler content. The aggregation spots act as stress concentration points, for the cohesion between particles in the spot is poor and accelerate the weakening of the composites. Whereas the modified composites are concerned, the strength is greater than that of non-modified ones, and a 22.6% increase compared to pure PA1010 at filler content of 10%.

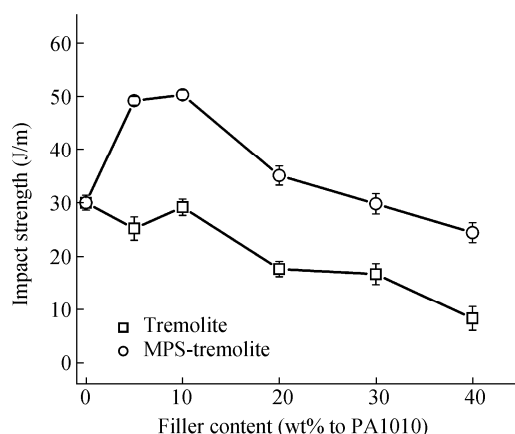


Fig. 4 Notched Izod impact strength of the composites with different filler content (wt% to PA1010)

From the results above, a conclusion can be drawn that the incorporation of MPS into tremolite has a remarkable effect on tensile strength and notched Izod impact strength simultaneously. When organic MPS is incorporated onto the surface of tremolite, good wetting of the particle by the PA1010 is achieved. This is owing to the group of $\text{CH}_2=\text{CHCOO}-$ on MPS molecule, which is similar to structure of PA100 molecule. Furthermore, the $\text{C}=\text{C}$ bonds may polymerize initiated by heat during blend in extruder. A thin polymer layer may appear which is much firmer to prevent the MPS from peeling off^[26]. Hence, improvement in two aspects can be found: one is that better dispersion of particle in matrix can be obtained as aggregation has been avoided, and the other is that interfacial adhesion of the filler to matrix is strengthened so that it can play an important role in transferring stress from matrix to fillers^[12, 27]. Further evidence will come from SEM photographs of fractured surface of composites.

Thermal Analysis and Crystallization Behavior

Figure 5 illustrates the variation of decomposition temperature at 10% weight loss under different filler content. The data come from TGA curves of the composites filled with modified and non-modified tremolite respectively. It is obvious that the addition of tremolite into the PA1010 causes the decomposition temperature to shift to higher temperature compared with the pure PA1010. Also, whether modified or non-modified is used, the decomposition temperature of composites doesn't increase when the filler content is more than 30%, which is perhaps the result of particle aggregate in matrix. Furthermore, the increasing degree of thermal stability of composites with modified tremolite is larger than that of non-modified ones. This suggests a strong interaction between the matrix and filler, which is consistent with that of mechanical analysis.

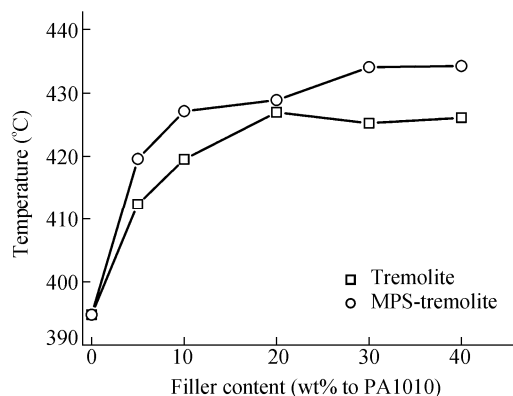


Fig. 5 Decomposition temperature at 10% weight loss under different filler content

The crystallization behavior of PA1010 and its composites was investigated. Isothermal crystallization from the melt was carried out by heating the samples to 230°C at the rate of 10 K/min, held there for 5 min to eliminate residual crystals, then cooling it quickly (−100 K/min) to the predetermined crystallization temperature, and isothermally crystallizing it for 40 min in a temperature range of 176–192°C. Figure 6 shows the isothermal crystallization DSC curves for PA1010 and its composites filled with MPS modified tremolite. It can be found that the crystallization exothermic peak shifted to shorter time with the incorporation of filler. The crystallization rate of PA1010 is enhanced. The Avrami equation^[28] was adopted to describe the crystallization kinetics. Results showed that the incorporation of tremolite displayed a high propensity to nucleate PA1010 crystallization. The crystallization rate of PA1010 was enhanced and the Avrami exponent n was decreased slightly with the increase of tremolite. The detailed results will be reported elsewhere^[29].

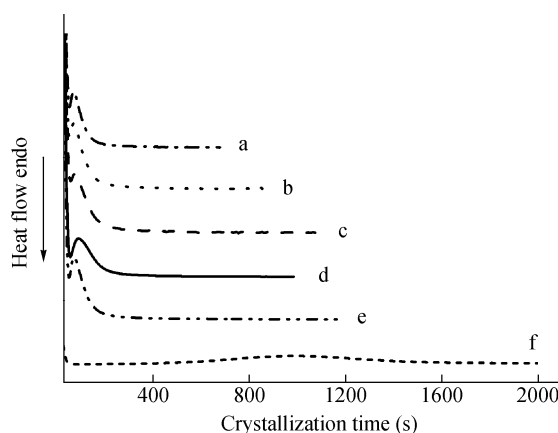


Fig. 6 DSC curves of isothermal crystallization for MPS modified tremolite/PA1010 composites at 186°C
Filler content: a) 40%; b) 30%; c) 20%; d) 10%; e) 5%; f) 0% in wt% to PA1010

Morphology

In order to illustrate the dispersion state of filler in PA1010 matrix, both modified and non-modified tremolite/PA1010 composite samples were refrigerated in liquid nitrogen for 5 h so that they could be brittle-fractured under impact. SEM micrographs of the fractured surface with a filler content of 10% are shown in Fig. 7. There is no aggregate in MPS-modified composites as the filler content is lower than 20% shown in Fig. 7(a), whereas the sample with pure tremolite, particle congeries are evident as shown in Fig. 7(b). It is clear that a good dispersion has been obtained with the help of MPS modification.

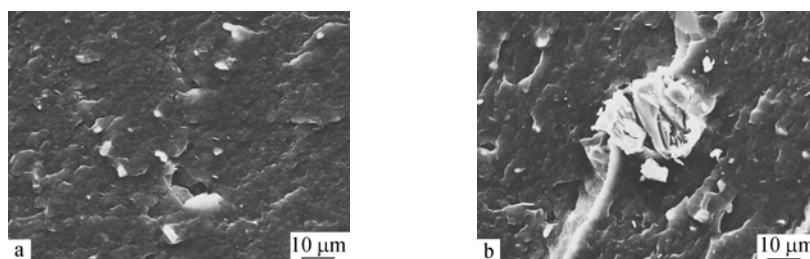


Fig. 7 SEM micrographs of the brittle-fractured surface of composites at a filler content of 10%
a) MPS-tremolite/PA1010; b) Tremolite/PA1010

SEM micrographs of the tensile fracture surface of composites are expressed in Fig. 8. In composites with non-modified tremolite, it can be seen the particles are embedded fully in matrix or exposed wholly without any PA1010 remnants on the surface. Furthermore, the wall of cavities is regular and smooth which indicates easy pulling out of filler due to weak interaction between matrix and filler as Figs. 8(b, d). On the contrary, in composites with MPS-modified tremolite, the particles are embedded partly in matrix. In addition, the particle surface is not smooth, there being filiiform PA1010 remained on it. The matrix around the particles or wall of the cavities is irregular, as if the PA1010 was torn up layer by layer, meaning strong adhesion between matrix and filler^[5, 12] as Figs. 8(a, c). It can be deduced that during the tensile course, the external stress is transferred to the particle efficiently until the stress exceeds the strength of interfacial cohesion, and then, the matrix is stripped away from the surface of particle. This process will absorb certain energy, so the PA1010 is reinforced markedly.

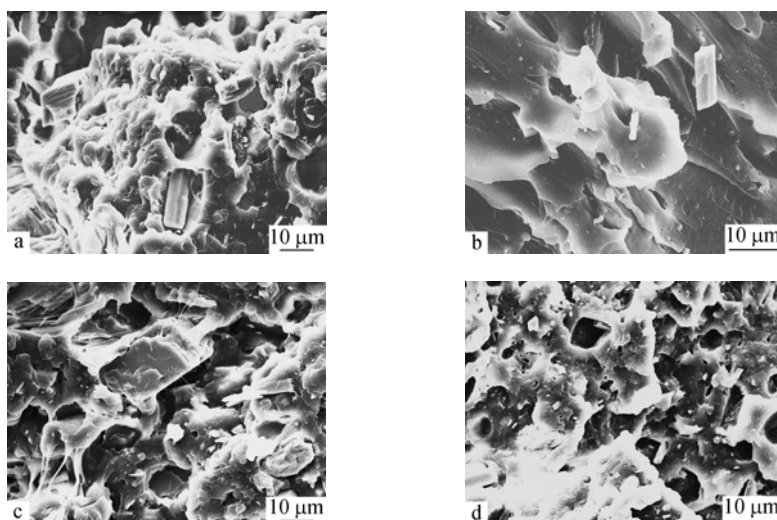


Fig. 8 SEM micrographs of the tensile fracture surface of composites with MPS-modified tremolite
(a, c) and pure tremolite (b, d)
Filler content: a), b) 5%; c), d) 20%

CONCLUSIONS

Tremolite is modified with an organic silane coupling agent, MPS in ethanol/ammonium hydroxide. The contact angle analysis shows that particle surface nature has changed from hydrophilicity to hydrophobicity by that modification. Studies on mechanical properties reveal that Young's modulus, tensile strength and notched Izod impact strength have been enhanced due to MPS modification. Moreover, the optimum concentration of filler is 10%. TGA analysis shows that higher thermal stability is also obtained. SEM micrographs of the brittle-fractured surface and tensile fractured surface illustrate a good dispersion of filler in matrix and interface adhesion between filler and matrix has been improved by that MPS modification.

REFERENCES

- 1 Liu, Z.H., Kwak, K.W., Li, R.K.Y. and Choy, C.L., *Polymer*, 2002, 43: 2501
- 2 Liao, M.Y., Zhang, W.Q., Zhu, J.D., Li, T. and Xu, H.D., *Atca Polymeric Sinica (in Chinese)*, 2006, (1): 37
- 3 Sheng, N., Boyce, M.C., Parks, D.M., Rutledge, G.C., Abes, J.I. and Cohen, R.E., *Polymer*, 2004, 45: 487
- 4 Zheng, Y.P., Chen, Q.H., Chen, L.X., Di, Y. and Ning, R.C., *Atca Polymeric Sinica (in Chinese)*, 2005, (6): 933
- 5 Bose, S., Raghu, H. and Mahanwar, P.A., *J. Appl. Polym. Sci.*, 2006, 100: 4074
- 6 Zhao, S., Zhang, J.Z., Zhao, S.Q., Li, W.Z. and Li, H.D., *Compos. Sci. Technol.*, 2003, 63: 1009
- 7 Wu, S.S., Cheng, A.M., Luo, Y.C., Ran, Q.P. and Shen, T., *Atca Polymeric Sinica (in Chinese)*, 2005, (5): 796
- 8 Shen, L., Phang, I.Y., Chen, L., Liu, T.X. and Zeng, K.Y., *Polymer*, 2004, 45: 3341
- 9 Liu, T.X., Lim, K.P., Tjiu, W.C., Pramoda, K.P. and Chen, Z.K., *Polymer*, 2003, 44: 3529
- 10 Liu, Z.J., Zhou, P.L. and Yan, D.Y., *J. Appl. Polym. Sci.*, 2004, 91: 1834
- 11 Wang, J.X., Gu, M.Y., Bai S.H. and Ge, S.R., *Wear*, 2003, 255: 774
- 12 Buggy, M., Bradley, G. and Sullivan, A., *Composites: Part A*, 2005, 36: 437
- 13 Jia, X. and Ling, X.M., *Wear*, 2005, 258: 1342
- 14 Konell, J.P., King, J.A. and Miskioglu, I., *Polym. Compos.*, 2005, 25: 172
- 15 Zhang, G.Q., Gui, Y., Yang, Y.M., Li, B.Y. and Zhang, J.X., *J. Appl. Polym. Sci.*, 1998, 69: 589
- 16 Xei, T.X., Liu, H.Z., Ou, Y.C. and Yang, G.S., *Atca Polymeric Sinica (in Chinese)*, 2006, (1): 53
- 17 Laura, D.M., Keskkula, H., Barlow, J.W. and Paul, D.R., *Polymer*, 2002, 43: 4673
- 18 Bose, S. and Mahanwar, P.A., *Polym. Eng. Sci.*, 2005, 45: 1479
- 19 Yang, R., Liu, Y.J., Wang, K.H. and Yu, J., *J. Anal. Appl. Pyrolysis.*, 2003, 70: 413
- 20 Johnson, N.M. and Fegley, B., *Icarus*, 2003, 164: 317
- 21 Gao, G., Qin, S.H., Ma, R.T. and Chen, G.F., *Polym. Mater. Sci. Eng.*, 1998, 14(4): 114
- 22 Dai, J.C. and Huang, J.T., *Appl. Clay. Sci.*, 1999, 15: 51
- 23 Philipse, A.P. and Vrij, A., *J. Colloid. Interf. Sci.*, 1998, 128: 121
- 24 Lami, E.B., Espiard, P. and Guyot, A., *Polymer*, 1995, 36: 4385
- 25 Herrera, N.N., Letoffe, J.M., Putaux, J.L., David, L. and Lami, E.B., *Langmuir*, 2004, 20: 1564
- 26 Kyu, T., Zhou, Z.L., Zhu, G.C., Tajuddin, Y. and Qutubuddin, S., *J. Polym. Sci. Part B: Polym. Phys.*, 1996, 34: 1761
- 27 Gao, X.L., Qu, C., Zhang, Q., Du, R.N. and Fu, Q., *Chinese J. Polym. Sci.*, 2005, 23(5): 531
- 28 Avrami, M., *J. Chem. Phys.*, 1940, 8(2): 212
- 29 Liu, X.L., Fang, J.Y., Jiang, M., Li, Z.Y. and Liu, F.Q., *Journal of Jilin University (Engineering and Technology Edition)*, 2008, 38(2): 298