

## Effects of a Coupling Agent on the Mechanical and Thermal Properties of Ultrahigh Molecular Weight Polyethylene/Nano Silicon Carbide Composites

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**ABSTRACT:** Ultra-high-molecular-weight polyethylene (UHMWPE)/nano silicon carbide (nano-SiC) composites were prepared by compression molding. The effects of a coupling agent and the content of the filler on the filler dispersion and the mechanical and thermal properties of the composites were investigated. The results show that the mechanical properties of the composites first increased and then decreased with increasing SiC content. The macromolecular coupling agent exhibited a much better reinforcing effect than the small-molecule coupling agent. The tensile strength of the composites with 3-aminopropyltriethoxysilane (KH550),  $\gamma$ -methacryloxypropyltrimethoxysilane (KH570), and silicone powders reached its maximum value when the silicon carbide (SiC) content was 3%. We found that a web of the UHMWPE/SiC/coupling agent was formed and played a significant role in improving the heat resistance of the composites. In addition, appropriate amounts of SiC could increase the crystallinity of UHMWPE via a process of heterogeneous nucleation. The comprehensive performance of the KH550/silicone/SiC/UHMWPE composites was the best. © 2012 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* 129: 1218–1222, 2013

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### INTRODUCTION

Ultra-high-molecular-weight polyethylene (UHMWPE)<sup>1,2</sup> occupies the extreme end of the polyethylene performance spectrum. With a molecular weight ranging from 1 to 10 million g/mol, UHMWPE linear polymer chains are 10 times longer than those of conventional high-density polyethylene. This unique molecular structure gives UHMWPE exceptional properties, such as the greatest sliding wear resistance and notched impact strength. For these reasons, UHMWPE has been applied to fields such as textiles, paper, agriculture, food packaging, coal, and chemical machinery.<sup>3</sup> However, some weaknesses, such as a low surface hardness, poor creep resistance, and low heat distortion temperature, constrain the further application of UHMWPE; consequently, much attention has been focused on the modification of UHMWPE.<sup>4–6</sup>

Because of the strong antioxidant properties, good wear resistance, good thermal stability, low coefficient of thermal expansion, high thermal conductivity, high hardness, and excellent resistance to chemical corrosion of nano silicon carbide (nano-SiC),<sup>7–9</sup> nano-SiC is widely used as a filler in polymer-based composites. Nano-SiC possesses a unique small size effect and

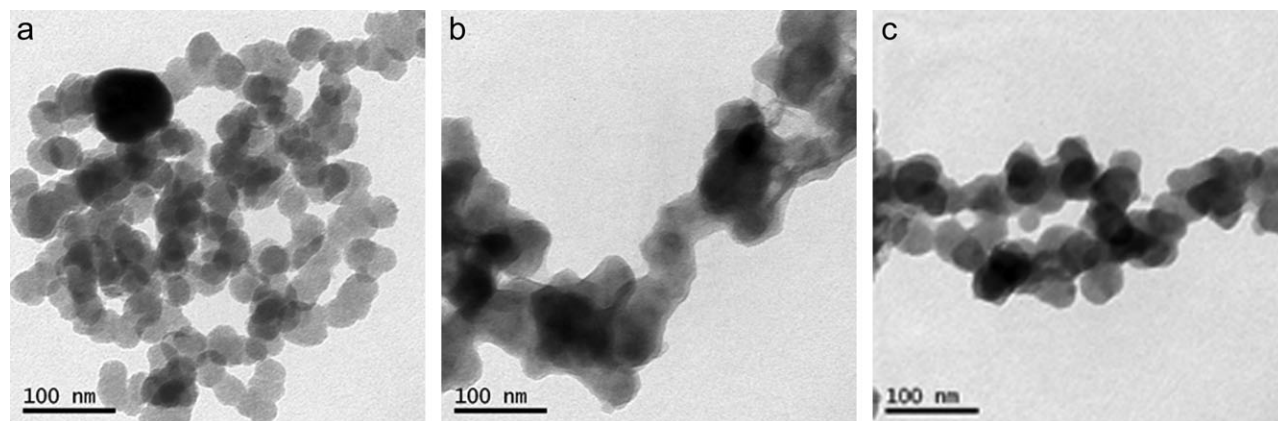
surface and interface effects; these advantages can effectively improve the mechanical properties and heat resistance of the resin matrix.

The addition of a coupling agent is a commonly used method for improving the adhesion of the composites.<sup>10–12</sup> Because of the effect of the coupling agent on the size and distribution of nanoparticles, the mechanical and thermal properties of the nanocomposites are improved. In this study, KH550,  $\gamma$ -methacryloxypropyltrimethoxysilane (KH570), and silicone powders were used to treat the nano-SiC surface, and nano-SiC-filled UHMWPE composites were prepared by compression molding. The effects of the coupling agents and filler content on the mechanical and thermal properties of the composites were investigated.<sup>13–16</sup>

### EXPERIMENTAL

#### Materials

UHMWPE was obtained from Beijing Dongfang Petrochemical Co., Ltd., No. 2 Assistant Factory, Beijing, China. Nano-SiC, obtained from Shanghai ST-NANO Material Technology Co., Ltd. (Shanghai, China), was used as an additive. KH550 (3-



**Figure 1.** TEM photographs of the nano-SiC powders: (a) pure SiC, (b) KH550-g-SiC, and (c) KH570-g-SiC.

aminopropyltriethoxy silane) and KH570 were supplied from Nanjing Shuangguang Chemical Group (Nanjing, China). Silicone powders were provided by Hangzhou Jieyika Chemical Co., Ltd. (Hangzhou, China).

#### Treatment of Nano-SiC

**Small-Molecule Coupling Agents (KH550 and KH570).** The silane coupling agent [1 wt % silicon carbide (SiC)] was diluted with anhydrous ethanol (volume ratio = 10:1). The KH550/ethanol solution was alkaline, and the pH of the KH570/ethanol solution was adjusted to pH 4–5 by the addition of acetic acid. SiC powders and the coupling/ethanol solution were put into a three-necked flask (250 mL). After ultrasonic agitation for 30 min, the mixture was stirred for an additional 2 h at a temperature under 80°C. After washing and drying, the SiC was placed in a sealed container.

**Macromolecular Coupling Agent (Silicone).** Silicone powders (1 wt % formula) and a certain amount of SiC were mixed in the high-speed mixer. After mixing, SiC was placed in a sealed container.

#### Preparation of the UHMWPE Specimens

The UHMWPE powder and SiC were mixed in a mixer, and the mixture of UHMWPE and SiC was filled into a mold. The testing specimens were sintered under 15 MPa of pressure at 220°C for 15 min; this was followed by cooling under 15 MPa.

#### Characteristics

**Mechanical Properties.** The mechanical properties tests of the SiC/UHMWPE composites were performed with an electronic universal testing machine (CMT-4104, Sansi, Shenzhen, China). Five test specimens were subjected to tests of their mechanical properties. The speed of the tensile strength testing was 50 mm/min. The flexural strength was tested by three-point bending with a span of 60 mm and a test speed of 2 mm/min.

#### Heat Distortion Temperature.

The heat distortion temperature was tested by a Vicat tester (Vicat-RHV, Riger, Shenzhen, China) in accordance with GB/T1634.2-2004 (0.45 MPa, flat).

**Thermal Conductivity.** Steady-state measurement of thermal conductivity was performed with thermal conductivity equipment (TC-3A, Jingke, Hangzhou, China). When the heating pan

constant temperature was 60°C, the constant-temperature record of the cooling was recorded; then, we calculated the thermal conductivity of the test samples by formula.

#### Transmission Electron Microscopy (TEM)

The coated morphology of the SiC particles was investigated on a JSM-2100 transmission electron microscope (JEOL, Tokyo, Japan) with an acceleration voltage of 120 kV.

#### Scanning Electron Microscopy (SEM)

The dispersion of the nano-SiC particles modified by nano-SiO<sub>2</sub> in the SiC/UHMWPE system nanocomposites and the wear surface of SiC/UHMWPE composites were investigated on a JSM-5610LV scanning electron microscope. For clear observation, the surfaces of the samples were coated with thin gold layers of about 100 Å.

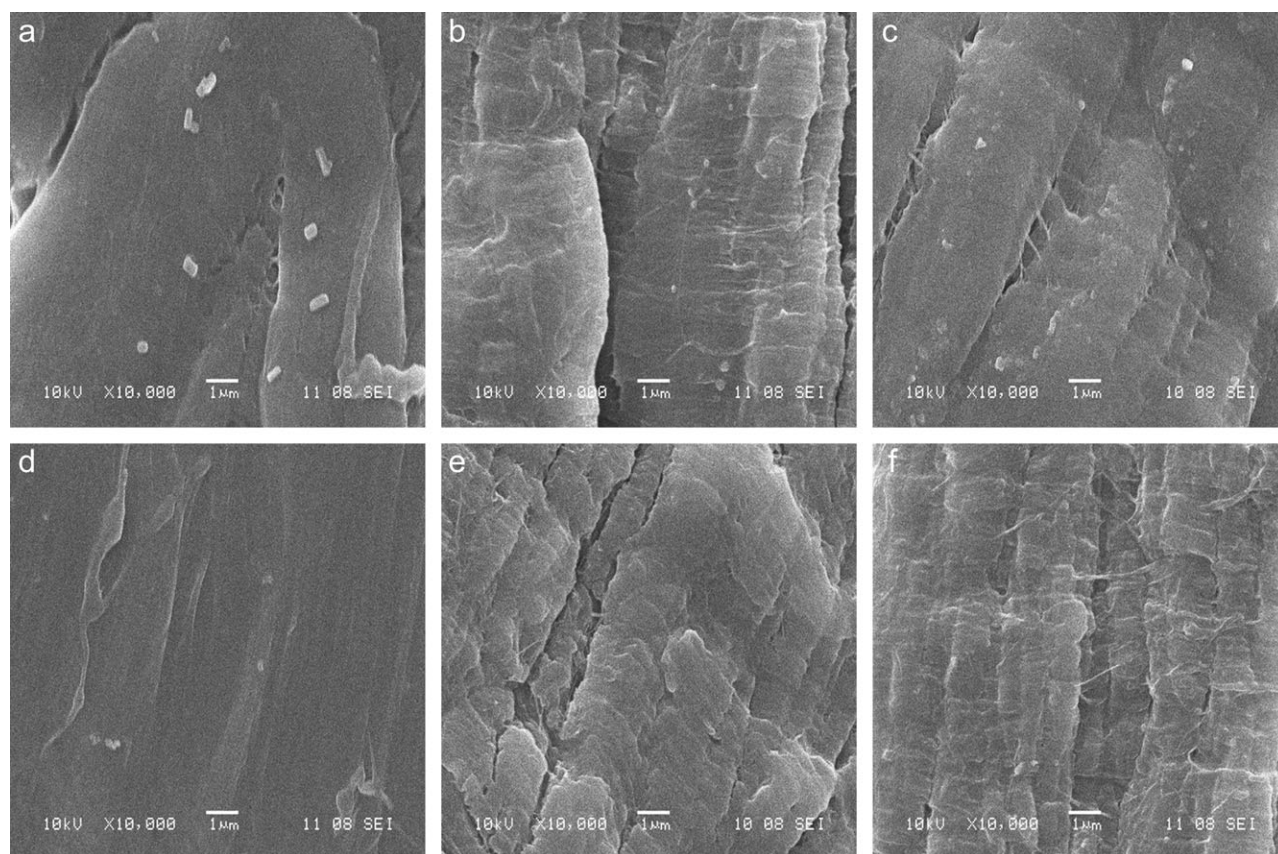
## RESULTS AND DISCUSSION

#### Morphology of the Nano-SiC Powders

Figure 1(a) shows the morphology of the uncoated SiC particles. The pure SiC particles were irregularly shaped and relatively homogeneous. The SiC powders coated with KH550 are displayed in Figure 1(b). It was obvious that a heterogeneous surface was obtained after the deposition of KH550. A relatively weak heterogeneous surface was also obtained after the deposition of KH570, as revealed in Figure 1(c). This phenomenon was due to the fact that the chemical bonding and physical adsorption that was formed between the hydrolysis groups of the silane coupling agent and SiC particle surface hydroxyls led to the formation of an organic adsorption layer.

#### Morphology of the Freeze-Fractured Surfaces of the Composites

Figure 2 shows the freeze-fractured surfaces of the 3% UHMWPE/SiC composites treated for 24 h with liquid nitrogen. As we all know, the better the fillers are dispersed, the better the material properties will be. As shown in Figure 2(a), there was a clear presence of agglomerated particles, which were SiC particles dispersed in the UHMWPE matrix. We observed that the decentralization of SiC was improved apparently by the addition of the coupling agent. As shown in Figure 2(d–f), it was hard to see any pits on the fracture surface. The nano-SiC modified by the coupling agent had the better bonding force with the matrix resin. Among them, silicone powder weakened



**Figure 2.** SEM photographs of the freeze-fractured surface under liquid nitrogen of the UHMWPE composites: (a) without the coupling agent, (b) with added KH550, (c) with added KH570, (d) with added silicone powders, (e) with added KH550/silicone, and (f) with added KH570/silicone.

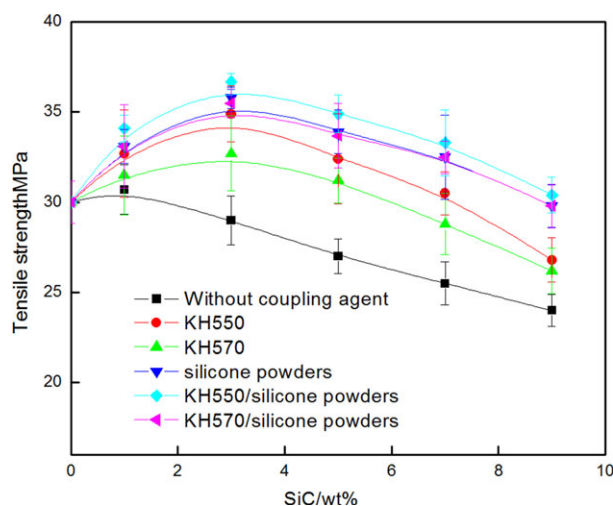
the cohesion of the UHMWPE resin and led to a reduction in the intermolecular forces in polymers. It not only improved the processing properties of the material but also was more conducive to the dispersion of SiC.

#### Effects of the Couplings on the Mechanical Properties of the SiC/UHMWPE Composites

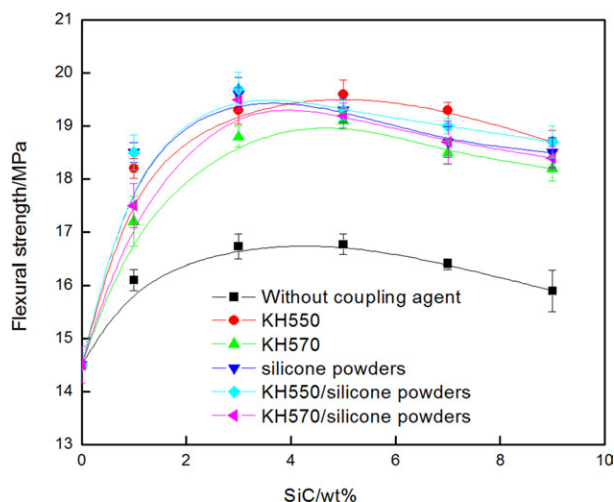
The tensile strength of the UHMWPE/SiC composites with coupling agents is shown in Figure 3. The tensile strength decreased markedly when the untreated SiC content was greater than 1%. Curves of the tensile strength of the composites with coupling agent showed a similar trend with increasing SiC content. The tensile strengths of the composites with coupling agent reached a maximum when the SiC content was 3%. The effects of the SiC content on the flexural strength of the SiC/UHMWPE composites are shown in Figure 4. The flexural strength of the composites reached 16.7 MPa when the pure SiC content was 5%. Upon the addition of different small-molecule coupling agents, KH550 and KH570, the flexural strengths of the composites with a 5% SiC content reached 19.6 and 19.1 MPa, respectively. The bending strengths of the composites with macromolecular coupling agent (silicone powders, KH550/silicone, and KH570/silicone) reached their maximum values when the SiC content was 3%. These values were 19.6, 19.7, and 19.5 MPa, respectively.

Figures 3 and 4 show that the mechanical properties of the SiC/UHMWPE composites increased initially with increasing SiC

content, and then, they decreased. This was mainly attributed to the observation that a small amount of SiC was dispersed well in the matrix, and this made the interface between the SiC and UHMWPE stronger. Because of this, the deformation ability and the antishear deformation ability of the systems increased,



**Figure 3.** Effects of the coupling agent on the tensile strength of the UHMWPE/SiC composites. [Color figure can be viewed in the online issue, which is available at [www.interscience.wiley.com](http://www.interscience.wiley.com).]



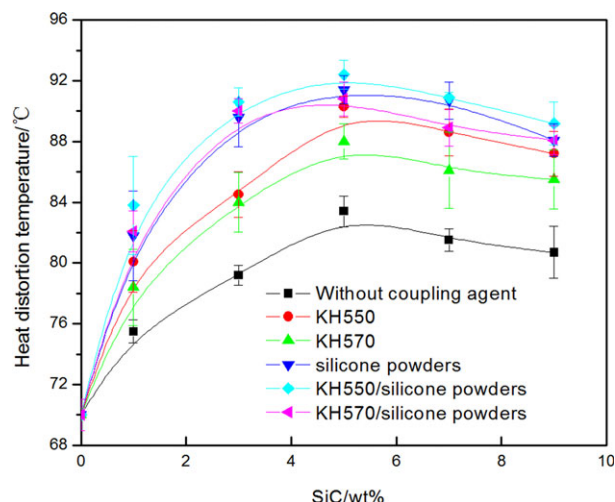
**Figure 4.** Effects of the coupling agent on the flexural strength of the UHMWPE/SiC composites. [Color figure can be viewed in the online issue, which is available at [www.interscience.wiley.com](http://www.interscience.wiley.com).]

so the strength and toughness of the UHMWPE/SiC composites were significantly improved. However, with increasing SiC content, the agglomeration phenomenon of nano-SiC became more serious in the matrix, and this led to an increase in the defects and the stress concentration. Therefore, the mechanical properties of the composites deteriorated.

After the addition of the coupling agent, the mechanical properties of the UHMWPE/SiC composites improved significantly when the content of SiC was less than 5%. The phenomenon was related to the fact that the coupling agent caused an increase in the SiC repulsion, which could have inhibited the agglomeration to promote the uniform dispersion of particles. The reinforcing effect of macromolecular coupling on the SiC/UHMWPE composites was better than that of small-molecule coupling. As a non-polar resin, a physical combination between the small-molecule coupling and the UHMWPE resin was only formed from the interdiffusion of the molecular chains. As the molecular chains of small-molecule coupling were very short, the physical combination was weak. There were two advantages of adding the macromolecular coupling agent. On the one hand, it achieved a stronger physical combination between the inorganic filler and the matrix. On the other hand, changes in the molecular weight and molecular structure of macromolecular coupling could control and optimize the interface combination.

#### Effects of the Couplings on the Thermal Properties of the UHMWPE/SiC Composites

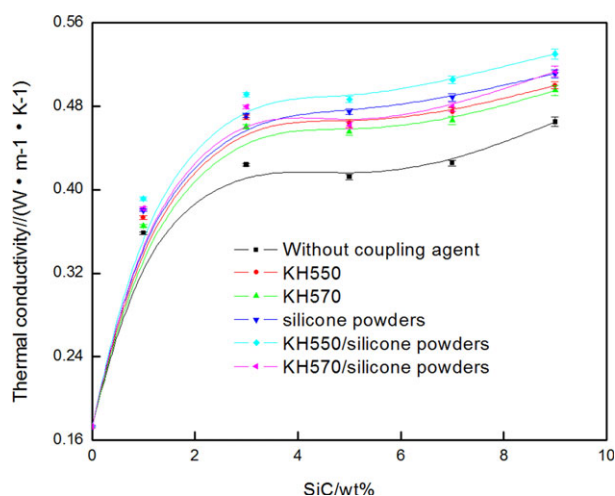
The effects of the couplings on the heat distortion temperature of the UHMWPE/SiC composites are given in Figure 5. We observed that the heat distortion temperature of the composites exhibited first an upward trend and then a downward one. The maximum heat distortion temperature was observed in the 5% SiC content. These corresponding temperature values were 83.4°C (without coupling), 90.3°C (KH550), 88.0°C (KH570), 92.4°C (KH550/silicone), and 90.8°C (KH570/silicone). The results show the heat resistance of the composites improved significantly. The role of the macromolecular coupling agent was better than that of the



**Figure 5.** Effects of the coupling agent on the heat distortion temperature of the SiC/UHMWPE composites. [Color figure can be viewed in the online issue, which is available at [www.interscience.wiley.com](http://www.interscience.wiley.com).]

small-molecule coupling agent, and the effect of compound coupling was the best. The main reasons were as follows:

1. It is known that SiC fillers remove a lot of heat and make the heat of the composites evenly; thereby, they increased the heat distortion temperature of the UHMWPE/SiC composites.
2. A web of the UHMWPE/SiC/coupling agent played a significant role in improving the heat resistance of the composites.<sup>17,18</sup> Macromolecular coupling improved the interfacial adhesion and filler dispersion, so its effect of radiating was better than that of small-molecule coupling, and the compound coupling was best.
3. When the SiC content is in excess, the SiC and UHMWPE adhesive became weakened. A large number of SiC easily generated agglomeration. As agglomerated SiC formed a lot of weak points and brought many defects, the heat distortion temperature of UHMWPE/SiC became lower.



**Figure 6.** Effects of the coupling agent on the thermal conductivity of the SiC/UHMWPE composites. [Color figure can be viewed in the online issue, which is available at [www.interscience.wiley.com](http://www.interscience.wiley.com).]

As shown in Figure 6, the thermal conductivity of the UHMWPE/SiC composites increased with increasing loading of SiC. The curves showed a similar trend. When the SiC content was less than 3%, the effects of different coupling agents essentially showed similar results. With increasing nano-SiC content, the thermal conductivity of the UHMWPE/SiC composites increased but slightly declined in the range SiC from 3 to 5 wt %. The silicone played an optimal role in the thermal conductivity, and the thermal conductivity, which when KH550/silicone was added, increased from 0.1728 to 0.5132  $\text{W}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$  when the SiC concentration was increased from 0 to 9.0 wt %. The results were related to the effective heat network of SiC. At low filler content, it was not enough to form effective heat paths, and the effect of the coupling agent on the thermal performance was small. Increasing the amount of SiC increased the dispersion of the individual SiC particles, and the ability to form thermal paths was improved. At this time, the obvious effect of coupling was imposed on the thermal conductivity. When SiC reached a certain amount, the reunion particles reduced the particle volume and the ability to form a thermal network. When the level of SiC was higher, the particle size distribution covered a wide range, and the formation of thermal pathways was greatly improved, so the thermal conductivity of the composite materials increased rapidly.

## CONCLUSIONS

1. The UHMWPE/SiC composites with a high strength and heat resistance were prepared by the addition of coupling agents. The addition of coupling agents also significantly improved the dispersion of SiC particles.
2. The modification effect of the couplings, from strong to weak, was silicone/KH550, silicone/KH570, silicone, KH550, and KH570, respectively.
3. The composites of SiC-filled modified UHMWPE, which exhibited good mechanical properties and heat resistance, were a superior performance material. The optimum formula consisted of KH550 (1 wt % SiC), silicone powders (1 wt % formula), and SiC (3–5%).

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## REFERENCES

1. Mark, H. F.; Bikales, N. M.; Overberger, C. G.; Menges, G. *Encyclopedia of Polymer Science and Technology*; Wiley-Interscience: New York, **1986**; p 490.
2. Juran, R. *Modern Plastics Encyclopedia*; McGraw-Hill: New York, **1991**; p 66.
3. Buice, E. S.; Yang, H.; Smith, S. T.; Robert, J. H.; Richard, M. S. *J. Precision Eng.* **2006**, *30*, 185.
4. Chand, N.; Dwivedi, U. K.; Sharma, M. K. *J. Wear* **2007**, *262*, 184.
5. Jana, S.; Hinderliter, B. E.; Zhong, W. H. *J. Mater. Sci.* **2008**, *43*, 4236.
6. Xiong, D. S.; Ge, S. R. *J. Wear* **2001**, *250*, 242.
7. Huang, L.; Sun, Z. B.; Zhang, J. S. *J. Acta Mater. Compos. Sinica (in Chinese)* **2001**, *18*, 1.
8. Rong, M. Z.; Zhang, M. Q.; Zheng, Y. X. *J. Polymer* **2001**, *42*, 167.
9. Ji, Q. L.; Rong, M. Z.; Zhang, M. Q. *J. Polym. Polym. Compos.* **2002**, *10*, 531.
10. Chen, H. X.; Zeng, D. L.; Xiao, X. Q.; Zheng, M. S.; Ke, C. M.; Li, Y. J. *J. Mater. Sci. Eng. A.* **2011**, *528*, 1656.
11. Jia, Q. X.; Wu, Y. P.; Wang, Y. Q.; Lu, M.; Zhang, L. Q. *J. Compos. Sci. Technol.* **2008**, *68*, 1050.
12. Jiang, M. J.; Dang, Z. M.; Xu, H. P. *J. Eur. Polym. J.* **2007**, *43*, 4924.
13. Urkac, E. S.; Oztarhan, A.; Tihminlioglu, F. *J. Nucl. Instrum. Methods Phys. Res. B.* **2007**, *261*, 699.
14. Peltzer, M.; Wagner, J. R.; Jiménez, A. J. *J. Therm. Anal. Calorim.* **2007**, *87*, 493.
15. Rudnik, E.; Dobkowski, Z. J. *J. Therm. Anal.* **1997**, *49*, 471.
16. Adrian, M.; Zaharescu, T.; Jipa, S.; Andrade, L. J. *J. Optoelectron. Adv. Mater.* **2008**, *10*, 826.
17. Zhang, Q. H.; Lippits, D. R.; Rastogi, S. *J. Macromolecules* **2006**, *39*, 658.
18. Chen, Q. Y.; Bin, Y. Z.; Matsuo, M. *J. Macromolecules* **2006**, *39*, 6528.