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## Influence of Alumina Content and Thermal Treatment on the Thermal Conductivity of UPE/Al<sub>2</sub>O<sub>3</sub> Composite

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**ABSTRACT**: Ultra high molecular weight polyethylene/alumina (UPE/Al<sub>2</sub>O<sub>3</sub>) microcomposites with high loading micro alumina (Al<sub>2</sub>O<sub>3</sub>, 20 to 100 phr) were prepared by casting method. The composites were thermal treated (cooled slowly) and then the thermal properties were studied at temperatures from 25 to 125°C. Thermogravimetric analysis (TGA) and scanning electron microscopic (SEM) proves the homodispersion of Al<sub>2</sub>O<sub>3</sub> microparticles in UPE. TGA indicates that the temperature of 5% weight loss of UPE/Al<sub>2</sub>O<sub>3</sub> (100 phr) composite is 467.0°C, 10.5°C higher than that of pure UPE. Differential scanning calorimetry (DSC) shows that the melting point and the real degree of crystal ( $X_{rc}$ ) of treated UPE/Al<sub>2</sub>O<sub>3</sub> composite (100 phr) are 141.4°C and 65.7%, respectively, all higher than that of untreated composite, which can be described by crystal bridge mechanism. The density of the composite is also be enhanced because of crystal volume shrinkage induced by thermal treatment. The thermal conductivity of the treated UPE/Al<sub>2</sub>O<sub>3</sub> composite (100 phr) is 1.920 W (m K)<sup>-1</sup> at 25°C, 23.6% higher than that of the untreated composite. Crystal bridge thermal conductivity of UPE/Al<sub>2</sub>O<sub>3</sub> composite has some dependency on the increasing Al<sub>2</sub>O<sub>3</sub> content and also thermal treatment. These results can give some advice to design formulations for practical applications in pipe area and other wear area. © 2014 Wiley Periodicals, Inc. J. Appl. Polym. Sci. **2014**, *131*, 40528.

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#### INTRODUCTION

UPE is a linear and highly entangled polyethylene with an average molecular weight more than  $1.5 \times 10^6$  g mol<sup>-1</sup>. Excellent properties in terms of high resistance to chemicals, high physical abrasion, low fiction coefficient, and high impact strength have made UPE to be used in the areas of mechanism, transportation, colliery oil and natural gas field and medicine to replace metals.<sup>1–7</sup> Among them, the maximum using amount of UPE is in pipes such as oil pipe and natural pipe which need excellent abrasion resistance property, and a special and the most important application is the replacement of damaged articulating cartilages.<sup>8</sup> However, the structure of UPE also originates many problems, like weak creep and fatigue strength compared with metal and bone materials. In the material transfer process, a large amount of heat generates because of friction heat. If the friction heat cannot be derived from the pipeline, the accumulation heat will further aggravate the fatigue of UPE and the creep deformation. So the thermal conductivity of UPE material should be enhanced in order to transfer the friction heat to the outside of the pipeline, and then prolong the service

life of the product. If the UPE material service life becomes longer, the product will be more competitive for the downstream industry. There are two methods to enhance the thermal conductivity of UPE material, one method is increasing the intrinsic thermal conductivity of UPE, another is adding particle fillers with high thermal conductivity.<sup>9–16</sup>

Previous reports and our studies all show that the addition of inorganic filler (such as boron nitride,<sup>17</sup> Alumina,<sup>18</sup> Grphene and Nanodiamond,<sup>19</sup> aluminum nitride,<sup>20,21</sup> Boron Nitride Nanotube,<sup>22</sup> Graphene Nanoplatelets and Carbon Nanotubes<sup>23</sup> and so on) into polymer matrix with formation of polymer-inorganic composites has been proved to be an efficient way to enhance the thermal conductivity of polymer–inorganic filler composite. But the dispersion of the filling phase and the interfacial adhesion between various composite components plays important role in influencing the thermal conductivity property of the composite. But most of the filler should be surface treated and most of the surface treating methods needs organic solvents in the treating process. The solvents pollute the environment and the process is so complicated and also expensive

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that it is not suitable to be used in the practical applications now.

Now streching orientation method is often used to increase the intrinsic thermal conductivity of PE.<sup>24-27</sup> The thermal conductivity of PE after stretching can reach a very high level. If there are 20% of molecular orientating along the direction of the phonon conduction, the thermal conductivity of PE can reach a staggering 465 W (m K)<sup>-1</sup>, theoretical calculated by Choy,<sup>24</sup> higher than that of silver 417 W  $(m \ K)^{-1}$  and Cu 398 W (m K)<sup>-1</sup>, even high than that of aluminum nitride 300 W  $(m \text{ K})^{-1}$  and boron nitride 290 W  $(m \text{ K})^{-1}$  with the same thermal conduction theory-phonon conduction theory. In the research of Chen Gang,<sup>25</sup> PE is stretched into nanowires and the thermal conductivity of nanowire can reach 104 W  $(m K)^{-1}$ . When PE is highly oriented, lattice along the orientation direction are arranged, so the phonon can transfer along the orderly arrangement, and then the thermal conductivity will be enhanced along the orientation direction, can achieve even metal electronic conductivity level and inorganic crystal materials (such as aluminum nitride and boron nitride) phonon conductivity level.

From analysis above, the tensile orientation can improve the thermal conductivity of PE, but the thermal conductivity increases only in the tensile direction and the studies on the improvement of the thermal conductivity perpendicular to the PE fiber direction are rarely involved, so the thermal conductivity ity enhancement is only anisotropic. For many application occasions, thermal conductivity needs to be improved in all directions, it is not enough to enhance the thermal conductivity in one direction, so the research of enhancing the thermal conductivity of polymer materials and isotropic research in this area are very necessary, but very little research is found in this area, this article will study on this aspect.

In this article, Al<sub>2</sub>O<sub>3</sub> was chosen as fillers because of its high electrical resistivity (>10<sup>14</sup>  $\Omega$  cm  $^{-1}$  ), low cost and proper thermal conductivity (30.0 W (m K)<sup>-1</sup>).<sup>28–30</sup> UPE/Al<sub>2</sub>O<sub>3</sub> microcomposites with high loading micro alumina (Al<sub>2</sub>O<sub>3</sub>, 20 to 100 phr) were prepared by casting method. Then the composites were thermal treated to enhance the thermal conductivity in all directions. The intrinsic thermal conductivity of UPE is improved by controlling the cooling process (thermal treatment). SEM, TGA, DSC, specific gravity bottle, thermal conductivity tester, POM were used to find the influence of alumina content and thermal treatment on the thermal conductivity of UPE/Al<sub>2</sub>O<sub>3</sub> composite. The thermal properties of UPE/Al<sub>2</sub>O<sub>3</sub> microcomposites were tested at various temperatures from 25 to 125°C to simulate the environment of the practical application. These data can give some advice to design formulations for practical applications in pipeline area and so on.

#### **EXPERIMENTAL**

#### Materials

UPE (SLL-500,  $M_c = 5,000,000$ , China) was supplied by Shanghai Lianle Industry Science and Technology. Lamellar Al<sub>2</sub>O<sub>3</sub> microparticles (RF-2, 3.9 g cm<sup>-3</sup>, about 10  $\mu$ m, China) was



Figure 1. Schematic diagram of powder mixing of UPE and  $Al_2O_3$  microparticles and hot press process. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

provided by Zhengzhou Research Institute of Aluminum Corporation of China.

#### Preparation of UPE/Al<sub>2</sub>O<sub>3</sub> Microcomposites

The preparation of UPE/Al<sub>2</sub>O<sub>3</sub> samples could be described in Figure 1. Figure 1 shows Schematic diagram of powder mixing of UPE and Al<sub>2</sub>O<sub>3</sub> microparticles and hot press process. First, Al<sub>2</sub>O<sub>3</sub> microparticles (0, 20, 40, 60, 80, or 100 phr) were added to UPE powders (100 phr) with some acetone (50 mL) at 50°C, stirred for 10 min (1000 phr min<sup>-1</sup>), and then the mixture was sonicated for 30 min to ensure good homogeneity and degassed at 50°C for 2 h to remove the acetone entirely. Second, the above mixture was compression-molded into plates with dimensions of 100 mm × 100 mm × 1 mm under a pressure of 20 MPa at 200°C for 60 min. In the press process, the mixture should be deflated once every 10 min. Then the specimens were transformed to the cooling press machine (20 MPa with water cooling) and cooled for 10 min. UPE/Al<sub>2</sub>O<sub>3</sub> composites could be obtained after demolding.

#### Thermal Treatment of UPE/Al<sub>2</sub>O<sub>3</sub> Composites

The process of thermal treatment of UPE/Al<sub>2</sub>O<sub>3</sub> composites can be described in the following process. UPE/Al<sub>2</sub>O<sub>3</sub> composites obtained above in the mold were put in a hot press machine  $(200^{\circ}C, 20 \text{ MPa})$  for 1 h, then turn off the power and cooled slowly to the room temperature (about 3 h) with the cooling of the press machine. Then the thermal treated UPE/Al<sub>2</sub>O<sub>3</sub> composites could be obtained after demolding.

### Microstructure Analyses by Scanning Electron Microscopic (SEM)

SEM analyses for the morphology of UPE/Al<sub>2</sub>O<sub>3</sub> composites were made using a field emission scanning electron microscopy (FE-SEM, JEOL JEM-7401. Japan). The samples, gold-coated to avoid accumulation of charge, were analyzed at an accelerating voltage of 20 kV.

#### Thermogravimetric Analysis (TGA)

The TGA data were obtained in nitrogen atmosphere at a heating rate of 10°C min<sup>-1</sup> with a Netzsch TG-209 F3 thermo gravimetric analyzer (NETZSCH. Germany). In each case, a 5– 10 mg sample was examined under the gas flow rate of 20 mL min<sup>-1</sup> at the temperatures ranging from 50 to 700°C to evaluate the thermal stabilities of UPE/Al<sub>2</sub>O<sub>3</sub> composites.

#### Differential Scanning Calorimetry (DSC)

The DSC data (200 F3, NETZSCH. Germany) were gained by a NETZSCH 200 F3 DSC. The temperature of the specimen firstly increased from 20 to 200°C to test the melting point and melting heat of UPE/Al<sub>2</sub>O<sub>3</sub> composites. The heating rate above was  $10^{\circ}$ C min<sup>-1</sup> under a nitrogen atmosphere (20 mL min<sup>-1</sup>).



The real degree of crystallinity of UPE in UPE/Al<sub>2</sub>O<sub>3</sub> composite  $(X_{rc}, \%)$  can be calculated by formula (1).

$$X_{rc} = \frac{\Delta H}{\Delta H_{100} \times x_{UPE}} \tag{1}$$

where  $\Delta H$  (J g<sup>-1</sup>) is the heat of fusion of the UPE/Al<sub>2</sub>O<sub>3</sub> composite, and  $\Delta H_{100}$  (J g<sup>-1</sup>) is the heat of fusion for a 100% crystalline UPE taken as 289.3 J g<sup>-1</sup> according to the literature,<sup>31</sup>  $x_{\rm UPE}$  (%) is the mass fraction of UPE in the UPE/Al<sub>2</sub>O<sub>3</sub> composite. Because there almost is no heat of fusion changes for the inorganic filler Al<sub>2</sub>O<sub>3</sub>, so the heat of fusion of Al<sub>2</sub>O<sub>3</sub> in the UPE/Al<sub>2</sub>O<sub>3</sub> composite is ignored here, it can be considered to be zero.

#### Densities of UPE/Al<sub>2</sub>O<sub>3</sub> Composites

The densities of UPE/Al<sub>2</sub>O<sub>3</sub> composites can be tested by specific gravity bottle method according to formula (2).

$$\rho_{t} = \frac{m_{1}\rho_{x}}{m_{1} + m_{2} - m_{3}} \tag{2}$$

Because the density of pure UPE is about 0.93 g cm<sup>-3</sup>, lower than the density of pure water (about 1.0 g cm<sup>-3</sup> at 25°C), and the density of ethanol ( $\rho_x$ , g cm<sup>-3</sup>) is 0.7893 g cm<sup>-3</sup> at 25°C, so ethanol (AR) is used as solvent here.  $\rho_t$  (g cm<sup>-3</sup>) is the density of the UPE/Al<sub>2</sub>O<sub>3</sub> composite.  $m_1$  (g) is the mass of the UPE/ Al<sub>2</sub>O<sub>3</sub> composite.  $m_2$  (g) is the mass of specific gravity bottle and ethanol solvent in the bottle.  $m_3$  (g) is the mass of specific gravity bottle, ethanol solvent and the UPE/Al<sub>2</sub>O<sub>3</sub> composite.

#### Thermal Conductivities of UPE/Al<sub>2</sub>O<sub>3</sub> Composites

Thermal conductivities of UPE/Al<sub>2</sub>O<sub>3</sub> composites were measured with LFA 447 Nanoflash (NETZSCH. Germany) according to ASTM E1461, using the measured specific heat and thermal diffusivity, with separately entered density data. Samples were prepared in cylindrical shape of 12.6 mm in diameter and 1.0–2.0 mm in thickness. The sample was places in a chamber, the front of the sample was heated by a laser beam and the temperature on the rear was recorded by an infrared recorder. Thermal diffusivity can be calculated using the equation:  $C = \alpha^* t_{50}/d$ , where *C* is the dimensionless constant,  $\alpha$  is the thermal diffusivity,  $t_{50}$  is the time to get one half of the maximum temperature on the rear, and *d* denotes sample thickness. Once thermal diffusivity was obtained, thermal conductivity can be calculated based on the eq. (3)

$$\lambda = \alpha \times Cp \times \rho \tag{3}$$

where  $\lambda$ ,  $\rho$ ,  $C_p$  represent thermal conductivity, bulk density, and specific heat of the composites, respectively.

#### Polarizing Optical Microscope (POM)

The crystal process of pure UPE was observed by POM (Linkam TH960, Linkam Scientific Instruments, UK). UPE sheet sample (the thickness is about 0.1 mm) was placed on the sample table, firstly heated to 200°C ( $10^{\circ}$ C min<sup>-1</sup>), then cooled to  $25^{\circ}$ C ( $1^{\circ}$ C min<sup>-1</sup>). POM images were taken on UPE sheet at different temperature point during the cooling process.

#### **RESULTS AND DISCUSSION**

#### Morphology and Dispersion of Al<sub>2</sub>O<sub>3</sub> Microparticles in UPE Matrix

In the inorganic filler–UPE composites, the homodispersion of the particles into the UPE matrix, which influences the proper-



Figure 2. SEM images of UPE/Al<sub>2</sub>O<sub>3</sub> composites (40 phr).

ties of the composite, plays a crucial role in the practical use. In the low loading, we can use surface treatment methods to modify the surface of inorganic filler in order to enhance the interface bonding strength between the fillers and UPE matrix. The surface treatment methods really have some effect, but the surface treatment usually use organic solvent or surface treating agent to treat the surface of the fillers. The organic solvent and the surface treating agent usually pollute the environment and they are not suitable to be used in the industry area at the present stage. In the high loading, the surface treatment of the fillers will block the particles to form network access between the particles and then influence the properties of the composites. In addition, Melt index of UPE is zero, UPE is difficult to melt in the high temperature. So Al<sub>2</sub>O<sub>3</sub> microparticles were not treated in this article, UPE powders and Al2O3 microparticles were mixed directly.

SEM can be used to observe the homodispersion of Al<sub>2</sub>O<sub>3</sub> in the UPE matrix intuitively. Figure 2 shows SEM images of UPE/ Al<sub>2</sub>O<sub>3</sub> composites (40 phr). UPE/Al<sub>2</sub>O<sub>3</sub> composites fail in brittle manner due to a crack deflection mechanism caused by the Al<sub>2</sub>O<sub>3</sub> microparticles. This crack deflection will increase the roughness of the fracture surfaces due to the tilting and twisting of the crack front. There are almost no obvious inorganic clusters present in the composites in Figure 2, suggesting the lamellar Al<sub>2</sub>O<sub>3</sub> microparticles are almost dispersed uniformly in the UPE matrix. So Al<sub>2</sub>O<sub>3</sub> microparticles don't need to be surface treated by various surface treating methods. In comparison to our previous study, Al<sub>2</sub>O<sub>3</sub> nanoparticles have to be surface treated, if not, Al<sub>2</sub>O<sub>3</sub> nanoparticles will easily aggregate. The aggregation of the fillers will influence almost all the properties of the composites. So Al<sub>2</sub>O<sub>3</sub> microparticles are convenient to be used in the practical application.

#### Thermal Stability of UPE/Al<sub>2</sub>O<sub>3</sub> Composites

TGA is often used to test the thermal stability, and also used to examine the residual mass of the composite at high temperature. In the present study, the whole process of the weight loss





Figure 3. TG curves of UPE/ $Al_2O_3$  composites with different  $Al_2O_3$  contents. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

of UPE/Al<sub>2</sub>O<sub>3</sub> composites has been investigated by TGA by using a heating rate of 10°C min<sup>-1</sup>. Figure 3 shows TG curves of UPE/Al<sub>2</sub>O<sub>3</sub> composites with different Al<sub>2</sub>O<sub>3</sub> contents. Seen from Figure 3, the residual mass increases with the increasing Al<sub>2</sub>O<sub>3</sub> content. After 700°C treatment, UPE matrix almost all decompose, the residuals are almost Al<sub>2</sub>O<sub>3</sub> microparticles. So the residual mass at high temperature can be used to calculate the weight of Al<sub>2</sub>O<sub>3</sub> in the UPE matrix, and also shows the homodispersion of Al<sub>2</sub>O<sub>3</sub> in the UPE matrix. Figure 4 shows comparison curves of the theoretical value and the actual value of Al<sub>2</sub>O<sub>3</sub> in UPE matrix are almost coincided with each other in Figure 4, illustrating that Al<sub>2</sub>O<sub>3</sub> microparticles disperse homogeneously in UPE/Al<sub>2</sub>O<sub>3</sub> composites.

Thermal stability is very important for polymeric materials. In the present study, the thermal stability of the UPE/Al<sub>2</sub>O<sub>3</sub> composite has been investigated by TGA by using heat ingrate of



**Figure 4.** Comparison curves of the theoretical value and the actual value of  $Al_2O_3$  in UPE matrix. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]



**Figure 5.** TGA curves with 5% weight loss of UPE/Al<sub>2</sub>O<sub>3</sub> composites. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

10°C min<sup>-1</sup>. Figure 5 shows the TG curves with 5% weight loss of UPE/Al<sub>2</sub>O<sub>3</sub> composite from Figure 3. Figures 3 and 6 shows the TG and DTG curves of UPE/Al<sub>2</sub>O<sub>3</sub> composite with different Al<sub>2</sub>O<sub>3</sub> content. The starting degradation temperature is used to characterize the thermal stability of the UPE composite. The temperature of 5% weight loss of the composite is selected to indicate the starting degradation temperature here. The temperature of 5% weight loss of UPE/Al<sub>2</sub>O<sub>3</sub> (100 phr) composite is 467.0°C, about 10.5°C higher than that of pure UPE (456.5°C), seen from Figure 5, showing that the addition of Al<sub>2</sub>O<sub>3</sub> is useful to improve the thermal stability of UPE/Al<sub>2</sub>O<sub>3</sub> composite. The increasing trend of the temperature of 5% weight loss of the composite slows down with the increasing Al<sub>2</sub>O<sub>3</sub>, indicating that the enhancement of the stability of the UPE composite is not so obvious as the Al<sub>2</sub>O<sub>3</sub> filler content increases to a certain degree. The DTG curves of the composites shift to the high temperature direction in Figure 6, confirming the increasing enhancement of the stability of the composites when Al<sub>2</sub>O<sub>3</sub> filler is added into the UPE matrix.



**Figure 6.** DTG curves of UPE/Al<sub>2</sub>O<sub>3</sub> composites. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

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Figure 7. DSC curves of UPE/Al<sub>2</sub>O<sub>3</sub> composites before and after thermal treatment. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

In our previous study,<sup>32</sup> the temperature of 5% weight loss of epoxy/Al<sub>2</sub>O<sub>3</sub> (100 phr) composite is 366°C, about 34°C higher than that of pure epoxy (332°C), showing that the addition of Al<sub>2</sub>O<sub>3</sub> is useful to improve the thermal stability of the epoxy composite. But the improvement of the 5% weight loss temperature of epoxy/Al<sub>2</sub>O<sub>3</sub> (100 phr) composite is higher than that of

UPE/Al<sub>2</sub>O<sub>3</sub> (100 phr) composite, which is related to the structure of the matrix. The bond energy of C—O structure in epoxy main chain, is lower than that of C—C structure in UPE main chain, So the 5% weight loss temperature of epoxy is  $332^{\circ}$ C, lower than that of UPE (456.5°C). After adding the same amount of alumina microparticles, it is more helpful to the

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Figure 8. Influences of  $Al_2O_3$  content and thermal treatment on the melting point of UPE/Al\_2O\_3 composites. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

improvement of thermal stability of polymer composites with weak main chain structure.

#### Influence of Al<sub>2</sub>O<sub>3</sub> Content and Thermal Treatment on Melting Point and Degree of Crystallinity of UPE/Al<sub>2</sub>O<sub>3</sub> Composites

UPE is a kind of semicrystalline polymer. Thermal treatment influences the growth of UPE crystal to a certain extent, and UPE crystal and thermal conductivity often have a certain relationship, so it is necessary to study the relationship of UPE crystal and thermal treatment in order to improve thermal conductivity of UPE composites. Figure 7 shows DSC curves of UPE/Al<sub>2</sub>O<sub>3</sub> composites before and after thermal treatment. As can be seen from Figure 7, the melting peak values of UPE/ Al<sub>2</sub>O<sub>3</sub> composites after thermal treatment (melting point) all shift to the higher temperature and the melting peak areas (melting heat, related to degree of crystallinity) are all bigger than that of UPE/Al<sub>2</sub>O<sub>3</sub> composites before thermal treatment, indicating that the melting point (related to crystalline regularity) and melting heat (related to degree of crystallinity) of UPE/ Al<sub>2</sub>O<sub>3</sub> composites are all improved. The improvement is useful to improve the thermal conductivity of UPE/Al<sub>2</sub>O<sub>3</sub> composites. Detailed data can be seen from Figures 8 and 9.

Figure 8 shows influences of Al<sub>2</sub>O<sub>3</sub> content on the melting point of UPE/Al<sub>2</sub>O<sub>3</sub> composites. As can be seen from Figure 8, melting point of pure UPE after thermal treatment is 142.4°C,  $3.9^{\circ}$ C higher than that of pure UPE before thermal treatment (138.5°C). The two melting point curves of UPE/Al<sub>2</sub>O<sub>3</sub> composites with thermal treatment and without thermal treatment are all nearly parallel to the X axis, showing that the melting points of UPE/Al<sub>2</sub>O<sub>3</sub> composites almost have no changes with the increasing Al<sub>2</sub>O<sub>3</sub> content which can be proved by the melting points. The melting points of UPE/Al<sub>2</sub>O<sub>3</sub> composites without thermal treatment are 137.0°C (Al<sub>2</sub>O<sub>3</sub> 40 phr) and 137.6°C (Al<sub>2</sub>O<sub>3</sub> 100 phr) and the melting points of UPE/Al<sub>2</sub>O<sub>3</sub> 40 phr) and 141.4°C (Al<sub>2</sub>O<sub>3</sub> 100 phr), all almost have no changes with the increasing Al<sub>2</sub>O<sub>3</sub> content. But the melting points of UPE/Al<sub>2</sub>O<sub>3</sub> composites after thermal treatment are all higher than that of UPE/Al<sub>2</sub>O<sub>3</sub> composites without thermal treatment, indicating that thermal treatment is very beneficial to the improvement of the melting point of the composites. Thermal treatment (the slow cooling arrangement) makes the crystals have much time to grow regularly. The melting point is closely related to crystal regularity of UPE, the better of crystal regularity, the higher of the melting point, so thermal treatment is also beneficial to improve the crystal regularity of UPE. When UPE is in high crystal regularity, the thermal phonon can quickly pass through the lattice and transfer more heat, then the thermal conductivity of UPE will be enhancement. From the analysis above, on can conclude that thermal treatment can improve the thermal conductivity of UPE. The data will be listed in the following figures.

Figure 9 represents influences of Al<sub>2</sub>O<sub>3</sub> content and thermal treatment on the real degree of crystallinity of UPE/Al<sub>2</sub>O<sub>3</sub> composites. From 9, it can be seen that the real degree of crystallinity of UPE/Al<sub>2</sub>O<sub>3</sub> composites changing trend is same as the melting point curves changing trend. Not only X<sub>rc</sub> of UPE/ Al<sub>2</sub>O<sub>3</sub> composites after thermal treatment, but also X<sub>rc</sub> of UPE/ Al<sub>2</sub>O<sub>3</sub> composites before thermal treatment all have no changes with the increasing Al<sub>2</sub>O<sub>3</sub> content. X<sub>rc</sub> of pure UPE without thermal treatment is about 54.6%, and X<sub>rc</sub> of UPE/Al<sub>2</sub>O<sub>3</sub> composites are about 53.3% (40 phr), 55.4% (100 phr), which are almost the same. But X<sub>rc</sub> of UPE/Al<sub>2</sub>O<sub>3</sub> composites after thermal treatment are all higher than X<sub>rc</sub> of UPE/Al<sub>2</sub>O<sub>3</sub> composites before thermal treatment. X<sub>rc</sub> of UPE/Al<sub>2</sub>O<sub>3</sub> composites after thermal treatment are 66.4% (pure UPE), 64.5% (Al<sub>2</sub>O<sub>3</sub> 40 phr), 65.7% (Al<sub>2</sub>O<sub>3</sub> 100 phr), respectively, illustrating that thermal treatment is very useful to increase X<sub>rc</sub> of UPE in UPE/ Al<sub>2</sub>O<sub>3</sub> composites on one side, and Al<sub>2</sub>O<sub>3</sub> microparticles almost have no effect on the improvement of Xrc of UPE in UPE/Al2O3 composites at the same time. When X<sub>rc</sub> of UPE in UPE/Al<sub>2</sub>O<sub>3</sub> composites is improved by thermal treatment, the crystal of UPE will be increased, the thermal phonon path will be



**Figure 9.** Influences of  $Al_2O_3$  content and thermal treatment on the real degree of crystallinity of UPE/ $Al_2O_3$  composites. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]



**Figure 10.** Crystal bridge structure of UPE-polarized optical microscopy images for pure UPE at 70°C. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

widened and more phonon can pass the crystal in a certain time, and then the thermal conductivity of UPE will be enhanced.

From the analysis above, one can conclude that thermal treatment not only can increase the melting point (regularity of the crystal of UPE in UPE/Al<sub>2</sub>O<sub>3</sub> composites), but also can increase  $X_{rc}$  of UPE in UPE/Al<sub>2</sub>O<sub>3</sub> composite (the amount of crystal of UPE, which all can enhance the thermal conductivity of UPE in UPE/Al<sub>2</sub>O<sub>3</sub> composites, then the thermal conductivity of UPE/Al<sub>2</sub>O<sub>3</sub> composites will be increased. The thermal conductivity data of UPE/Al<sub>2</sub>O<sub>3</sub> composites are listed in the following figures.

The thermal conductivity enhancement mechanism can be described vividly by the polarized optical microscopy images in Figure 10. Figure 10 describes crystal bridge structure of UPEpolarized optical microscopy images for pure UPE at 70°C. It can be seen that a lot of small crystal particles entangled with each other to form crosslinked crystal bridge in UPE. The spread speed of thermal phonons is faster in the crystalline region than that in the amorphous region. When X<sub>rc</sub> increases and the crystal becomes regulary influenced by thermal treatment in UPE matrix, the crystal bridge in UPE will become broad and regulary, then thermal phonons will transfer more heat from one side to the other side of the crystal bridge, the thermal conductivity of UPE matrix will be enhanced. In UPE/ Al<sub>2</sub>O<sub>3</sub> composites, the thermal conductivity of Al<sub>2</sub>O<sub>3</sub> is about 30 W/(m•K), much higher than that of UPE matrix (about 0.5 W  $(m K)^{-1}$ ), so the interface effect and the low thermal conductivity of UPE are the two major factors to influence the thermal conductivity of UPE/Al2O3 composites. Because the alumina size is in micron level, so surface effect can be neglected. So to increase the thermal conductivity of UPE matrix becomes the key factor to enhance the thermal conductivity of UPE/Al<sub>2</sub>O<sub>3</sub> composites. So when the thermal conductivity of UPE matrix in UPE/Al<sub>2</sub>O<sub>3</sub> composites is enhanced, the thermal conductivity of UPE/Al2O3 composites will be enhanced

at the same time. It is a feasible and effective way to solve the thermal conductivity of polymer-inorganic filler composite from the improvement of matrix material with low thermal conductivity. To improve the crystal of materials ( $X_{rc}$  and regulary of crystal) is a good method to improve the thermal conductivity of UPE matrix.

## Influence of $Al_2O_3$ Content and Thermal Treatment on the Density of UPE/ $Al_2O_3$ Composites

From the thermal conductivity (formula 3) $\lambda = \alpha \times Cp \times \rho$ , it can be seen that the thermal conductivity of UPE/Al<sub>2</sub>O<sub>3</sub> composite ( $\lambda$ ) is proportional to the density of the composite ( $\rho$ ). So it needs to study the density changes with the increasing Al<sub>2</sub>O<sub>3</sub> content and thermal treatment. Influences of Al<sub>2</sub>O<sub>3</sub> content on the densities of UPE/Al<sub>2</sub>O<sub>3</sub> composites are listed in Figure 11. From Figure 11, it can be seen that the density of UPE/ Al<sub>2</sub>O<sub>3</sub> composite increases with the increasing Al<sub>2</sub>O<sub>3</sub> content from 1.01 g cm<sup>-3</sup> (Al<sub>2</sub>O<sub>3</sub> 20 phr) to 1.401 g cm<sup>-3</sup> (Al<sub>2</sub>O<sub>3</sub> 100 phr), about 9.9% (Al<sub>2</sub>O<sub>3</sub> 20 phr) and 52.9% (Al<sub>2</sub>O<sub>3</sub> 100 phr) higher than the density of pure UPE (0.916 g cm<sup>-3</sup>). According to formula (3), the density will attribute to the enhancement of the thermal conductivity of UPE/Al<sub>2</sub>O<sub>3</sub> composite to some extent.

Figure 12 shows influences of thermal treatment on the density of UPE/Al<sub>2</sub>O<sub>3</sub> composites. Seen from Figure 12, the density of UPE/Al<sub>2</sub>O<sub>3</sub> composites after thermal treatment also increases with the increasing Al<sub>2</sub>O<sub>3</sub> content, the density of UPE/Al<sub>2</sub>O<sub>3</sub> composites after thermal treatment increases from 1.054 g cm<sup>-3</sup> (Al<sub>2</sub>O<sub>3</sub> 20 phr) to 1.583 g cm<sup>-3</sup> (Al<sub>2</sub>O<sub>3</sub> 100 phr), about 13.0% (Al<sub>2</sub>O<sub>3</sub> 20 phr) and 69.7% (Al<sub>2</sub>O<sub>3</sub> 100 phr) higher than the density of pure UPE after thermal treatment (0.933 g cm<sup>-3</sup>), all higher than the density and the density increasing rate of UPE/ Al<sub>2</sub>O<sub>3</sub> composites before thermal treatment with the same Al<sub>2</sub>O<sub>3</sub> content, indicating that thermal treatment can increasing the density of UPE/Al<sub>2</sub>O<sub>3</sub> composites. Thermal treatment (slow cooling) can increase the degree of crystallinity of UPE in UPE/



Figure 11. Influences of  $Al_2O_3$  content on the densities of UPE/ $Al_2O_3$  composites. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]



**Figure 12.** Influences of thermal treatment on the densities of UPE/Al<sub>2</sub>O<sub>3</sub> composites. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Al<sub>2</sub>O<sub>3</sub> composite while the increasing degree of crystallinity of UPE matrix makes the volume shrinkage, so thermal treatment can increase the density of UPE/Al<sub>2</sub>O<sub>3</sub> composite. The increasing degree of crystallinity of UPE matrix can be seen from the above data of degree of crystallinity of UPE matrix in Figure 9.

#### Influence of Al<sub>2</sub>O<sub>3</sub> Content and Thermal Treatment on Thermal Conductivity of UPE/Al<sub>2</sub>O<sub>3</sub> Composites

Thermal conductivity of UPE/Al<sub>2</sub>O<sub>3</sub> composites was measured by the laser flash method, as shown in Figures 13 and 14. Figure 13 shows temperature dependency for thermal conductivity of UPE/Al<sub>2</sub>O<sub>3</sub> composites with various Al<sub>2</sub>O<sub>3</sub> contents. Thermal conductivity of pure UPE is found to be about 0.496 W (m K)<sup>-1</sup> (25°C), 0.503 W (m K)<sup>-1</sup> (50°C), 0.495 W (m K)<sup>-1</sup> (75°C), 0.489 W (m K)<sup>-1</sup> (100°C), and 0.466 W (m K)<sup>-1</sup> (125°C), exhibiting temperature dependences of thermal conductivity on pure UPE. Before 100°C, UPE is in the



Figure 13. Temperature dependency for thermal conductivity of UPE/  $Al_2O_3$  composites with various  $Al_2O_3$  contents. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]



Figure 14. Thermal conductivity and thermal conductivity enhancement of UPE/Al<sub>2</sub>O<sub>3</sub> composites with various Al<sub>2</sub>O<sub>3</sub> content at  $25^{\circ}$ C. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary. com.]

semi-crystalline state as the DSC curves in Figure 7 showed, the molecular chain movement is restricted, so the thermal conductivity almost has no obvious changes with increasing temperature. After 100°C, UPE begins to melt. At 125°C, UPE is in the semi-melting state completely, part of UPE molecular chain begins to melt and the melting makes UPE crystal reducing, and then the molecular chain movement is in the disorder state and disorder the heat transfer, so the thermal conductivity decreases.

Thermal conductivities of UPE/Al<sub>2</sub>O<sub>3</sub> composites before 100°C are not so ordered as that of pure UPE, the more the Al<sub>2</sub>O<sub>3</sub> microparticles are added in UPE, the decreasing trend of thermal conductivity with temperature increasing is more obvious before 100°C. Thermal conductivities of UPE/Al<sub>2</sub>O<sub>3</sub> composite (100 phr) are 1.55 W (m K)<sup>-1</sup> (25°C), 1.47 W (m K)<sup>-1</sup> (50°C), 1.42 W (m K)<sup>-1</sup> (75°C), 1.33 W (m K)<sup>-1</sup> (100°C), and 1.38 W (m K)<sup>-1</sup> (125°C). About 1.33 W (m K)<sup>-1</sup> (100°C) is only about 85.8% of 1.55 W (m K)<sup>-1</sup> (25°C). These may be illustrated from the interface reflection effect of micro Al<sub>2</sub>O<sub>3</sub> on the heat transfer.

When the temperature increases, the molecular chain motion between  $Al_2O_3$  and UPE matrix increases, impeding the phonon transfer heat from  $Al_2O3$  microparticles to the UPE matrix, but also hindering the phonon transfer heat to  $Al_2O3$  microparticles from the UPE matrix, thus thermal conductivity gradually reduced with the increasing temperature before  $100^{\circ}$ C.The higher the  $Al_2O3$  content in UPE, the greater the area of the interface, the surface effect is more obvious, so UPE/Al\_2O3 composite thermal conductivity varies with temperature trend is more obvious. At  $125^{\circ}$ C, thermal conductivity slightly upturned, which may be due to the higher specific heat of the composite.

Figure 14 represents thermal conductivity and thermal conductivity enhancement of UPE/Al<sub>2</sub>O<sub>3</sub> composites with various



**Figure 15.** Temperature dependency for thermal conductivity of UPE/ $Al_2O_3$  composites after thermal treatment. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Al<sub>2</sub>O<sub>3</sub> content at 25°C. Thermal conductivity of  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> is about 30 W (m K)<sup>-1,26</sup> so the addition of Al<sub>2</sub>O<sub>3</sub> into UPE is beneficial to increase the thermal conductivity of the composites. The thermal conductivity of UPE/Al<sub>2</sub>O<sub>3</sub> composites increases with the increasing Al<sub>2</sub>O<sub>3</sub> content at 25°C and increases to 0.675 W (m K)<sup>-1</sup> (Al<sub>2</sub>O<sub>3</sub> 20 phr), and then 1.554 W (m K)<sup>-1</sup> (Al<sub>2</sub>O<sub>3</sub> 100 phr), about 1.35 times and 3.11 times (or 35% (Al<sub>2</sub>O<sub>3</sub> 20 phr) and 211% (Al<sub>2</sub>O<sub>3</sub> 100 phr) enhancement) of thermal conductivity of pure UPE (0.496 W (m K)<sup>-1</sup>), respectively, displaying great thermal conductivity enhancement.

From Figure 11 (influences of Al<sub>2</sub>O<sub>3</sub> content on the densities of UPE/Al<sub>2</sub>O<sub>3</sub> composites), it shows that Al<sub>2</sub>O<sub>3</sub> content increases the densities of UPE/Al<sub>2</sub>O<sub>3</sub> composites. The densities are increased by 9.9% (Al<sub>2</sub>O<sub>3</sub> 20 phr) and 52.9% (Al<sub>2</sub>O<sub>3</sub> 100 phr), respectively, all lower than the thermal conductivity of UPE/Al<sub>2</sub>O<sub>3</sub> composites increased ratio of the corresponding. But according to the thermal conductivity formula  $\lambda = \alpha^* C_P^* \rho$ , the increase of the thermal conductivity of UPE/Al<sub>2</sub>O<sub>3</sub> composites ( $\lambda$ ) is contributed by three factors ( $\alpha$ ,  $C_B$  and  $\rho$ ), specific heat ( $C_p$ ) is generally reduced with the increasing Al<sub>2</sub>O<sub>3</sub> content, suggesting that increased Al<sub>2</sub>O<sub>3</sub> content improves the thermal diffusion coefficient ( $\alpha$ ) and then enhances thermal conductivity of UPE/Al<sub>2</sub>O<sub>3</sub> composite.

In our previous study, the thermal conductivity of epoxy/ Al<sub>2</sub>O<sub>3</sub> composites increases with the increasing Al<sub>2</sub>O<sub>3</sub> content at 25°C and increases to 1.382 W (m K)<sup>-1</sup> (the mass fraction of Al<sub>2</sub>O<sub>3</sub> = 69.0%), 5.62 times or 462% enhancement of the thermal conductivity of the pure epoxy (0.246 W (m K)<sup>-1</sup>), displaying great thermal conductivity enhancement. But 1.382 W (m K)<sup>-1</sup> is lower than the conductivity of 1.554 W (m K)<sup>-1</sup> (the mass fraction of Al<sub>2</sub>O<sub>3</sub>=50% or Al<sub>2</sub>O<sub>3</sub> = 100 phr), suggesting that UPE as polymer matrix is better than epoxy to enhance the conductivity of polymer/Al<sub>2</sub>O<sub>3</sub> composite, because the regular crystal structure of UPE is more beneficial than the amorphous structure of epoxy resin to transfer thermal phonon. The high thermal conductivity will be beneficial to transfer the heat to the outside of the insulating device, pipe or other using area in the using process, slowing down the degradation of the UPE matrix, prolonging the service life, and also reducing the cost of the product.

Figure 15 shows temperature dependency for thermal conductivity of UPE/Al<sub>2</sub>O<sub>3</sub> composites after thermal treatment. Thermal conductivities of pure UPE after thermal treatment are 0.593 W (m K)<sup>-1</sup> (25°C), 0.584 W (m K)<sup>-1</sup> (50°C), 0.552 W (m K)<sup>-1</sup> (75°C), 0.507 W (m K)<sup>-1</sup> (100°C), and 0.494 W (m K)<sup>-1</sup> (125°C), all higher than that of pure UPE before thermal treatment, respectively. But thermal conductivities of pure UPE almost all decrease with the increasing temperature.

The reduction of the thermal conductivity of UPE/Al<sub>2</sub>O<sub>3</sub> composites after thermal treatment with the increasing temperature is more obvious than the thermal conductivity of UPE/Al<sub>2</sub>O<sub>3</sub> composites. The thermal conductivity of UPE/Al<sub>2</sub>O<sub>3</sub>(100 phr) composites after thermal treatment reduces to  $1.70 \text{ W} (\text{m K})^{-1}$  $(125^{\circ}C)$ , about 0.26 W (m K)<sup>-1</sup> lower than 1.96 W (m K)<sup>-1</sup> (25°C), but all higher than that of UPE/Al<sub>2</sub>O<sub>3</sub>(100 phr) composites before thermal treatment and the reduction ratio 13.3% (1-1.70/1.96) is almost equal to the reduction ratio 14.2% (1-85.8%) of the thermal conductivity of UPE/Al<sub>2</sub>O<sub>3</sub>(100 phr) composite before thermal treatment. The thermal conductivity decreased with the temperature increasing phenomenon is consistent to the literature,<sup>32</sup> is due to the temperature increase which intensifies the molecular chain segment movement to impede phonon conduction and interface thermal resistance effect.

Figure 16 represents thermal conductivities of UPE/Al<sub>2</sub>O<sub>3</sub> and UPE/Al<sub>2</sub>O<sub>3</sub> (thermal treatment) composites at 25°C. From Figure 16, it can be seen that the thermal conductivities of UPE/Al<sub>2</sub>O<sub>3</sub> composites after thermal treatment are all higher than that of UPE/Al<sub>2</sub>O<sub>3</sub> composites (before thermal treatment) when the Al<sub>2</sub>O<sub>3</sub> contents in the composites are the same. This can be



Al<sub>2</sub>O<sub>3</sub> content (phr)

**Figure 16.** Thermal conductivities of UPE/Al<sub>2</sub>O<sub>3</sub> and UPE/Al<sub>2</sub>O<sub>3</sub> (thermal treatment) composites at 25°C. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

illustrated by the degree of crystallinity data above. From the above the degree of crystallinity data in Figure 9, it can be seen that the degree of crystallinity of pure UPE after thermal treatment 66.4% is higher than that of pure UPE before thermal treatment 54.9%. Then the thermal conductivity of pure UPE after thermal treatment 0.593 W (m K)<sup>-1</sup> is higher than that of pure UPE before thermal treatment 0.496 W (m K)<sup>-1</sup>.

The higher of degree of crystallinity of the polymer matrix, the better of the thermal conductivity of the polymer. When Al<sub>2</sub>O<sub>3</sub> is added into UPE to form UPE/Al2O3 composite, the thermal conductivity of the composite has the same phenomenon as that of pure UPE, such as 0.675 W (m K)<sup>-1</sup> (UPE/Al<sub>2</sub>O<sub>3</sub> 20 phr) < 0.723 W (m K)<sup>-1</sup> (UPE/Al<sub>2</sub>O<sub>3</sub> 20 phr, thermal treatment), 1.554 W (m K)<sup>-1</sup> (UPE/Al<sub>2</sub>O<sub>3</sub> 100 phr) < 1.920 W  $(m \text{ K})^{-1}$  (UPE/Al<sub>2</sub>O<sub>3</sub> 100 phr, thermal treatment). These are due to the UPE/Al<sub>2</sub>O<sub>3</sub> composite structure. When the Al<sub>2</sub>O<sub>3</sub> contents are the same in the two Al<sub>2</sub>O<sub>3</sub>-based polymer composites, the Al<sub>2</sub>O<sub>3</sub> contribution on the thermal conductivity of the UPE/Al<sub>2</sub>O<sub>3</sub> composite are also the same, the thermal conductivity of the polymer matrix and surface thermal resistance effect become the key factor to increase the thermal conductivity of the  $Al_2O_3$ -based composite. Because the surfaces between  $Al_2O_3$ and UPE matrix are the same in the composites with the same Al<sub>2</sub>O<sub>3</sub> content, so the thermal conductivity of the polymer matrix is the main factor discussed in the article. In Figure 16, the thermal conductivities of UPE/Al<sub>2</sub>O<sub>3</sub> composites after thermal treatment are all higher than that of UPE/Al<sub>2</sub>O<sub>3</sub> composites with the same Al<sub>2</sub>O<sub>3</sub> content, so the thermal conductivity of the UPE matrix in UPE/Al<sub>2</sub>O<sub>3</sub> composites after thermal treatment should be higher than the thermal conductivity of the UPE matrix in UPE/Al<sub>2</sub>O<sub>3</sub> composites before thermal treatment.

The higher of degree of crystallinity of the polymer matrix in the UPE/Al<sub>2</sub>O<sub>3</sub> composite, the better of the thermal conductivity of the polymer matrix in the UPE/Al<sub>2</sub>O<sub>3</sub> composite. So the higher thermal conductivity of the UPE/Al<sub>2</sub>O<sub>3</sub> composite can be illustrated by the higher degree of crystallinity of the polymer matrix in the UPE/Al<sub>2</sub>O<sub>3</sub> composite in Figure 9 (Influences of Al<sub>2</sub>O<sub>3</sub> content and thermal treatment on the real degree of crystallinity of UPE/Al<sub>2</sub>O<sub>3</sub> composites). The higher of the degree of crystallinity of the polymer matrix in the composite, the higher of the thermal conductivity of the polymer matrix in the composite, the higher of the thermal conductivity of the composite. In the polymer/inorganic filler composite, enhancing the thermal conductivity of the polymer matrix to broaden the phonon thermal conduction path is a good method to enhance the thermal conductivity of the composite.

#### CONCLUSIONS

To study influence of alumina content and thermal treatment on the thermal conductivity of UPE/ $Al_2O_3$  composite. UPE/ $Al_2O_3$  composites were prepared by casting method and their thermal properties were studied. The main conclusions can be summarized as followed.

a. The TG data and SEM results show good dispersion of Al<sub>2</sub>O<sub>3</sub> microparticles in UPE matrix, showing that Al<sub>2</sub>O<sub>3</sub>

microparticles don't need to be interface treated as Al<sub>2</sub>O<sub>3</sub> nanoparticles in comparison to our previous studies.

- b. The temperature of 5% weight loss and DTG curves of UPE/Al<sub>2</sub>O<sub>3</sub> composites all increase with the increasing Al<sub>2</sub>O<sub>3</sub> content, showing that the addition of Al<sub>2</sub>O<sub>3</sub> is useful to improve the thermal stability of the composites.
- c. Thermal treatment can increase the melting point and the real degree of crystallinity of UPE matrix in UPE/Al2O3 composites, the density is also increased, which are beneficial to the enhancement of the thermal conductivity of UPE/Al<sub>2</sub>O<sub>3</sub> composites. The thermal conductivities of UPE/ Al<sub>2</sub>O<sub>3</sub> composites after thermal treatment are all higher than that of UPE/Al<sub>2</sub>O<sub>3</sub> composites before thermal treatment. Crystal bridge mechanism is used to describe the enhancement of the thermal conductivity of UPE/Al<sub>2</sub>O<sub>3</sub> composites. To improve the crystal of materials (X<sub>rc</sub> and regulary of crystal) is a good method to improve the thermal conductivity of UPE matrix. Improving the thermal conductivity of UPE matrix is helpful to improve the thermal conductivity of UPE/Al<sub>2</sub>O<sub>3</sub> composite. The data are crucial in pipe wear area and other wear area which need well heat dissipation.

These results can give some advice to design formulations for practical applications in pipe and other wear area.

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