Ji-Zhao Liang*

Heat distortion temperature of PPS/PC blend, PPS/PC nanocomposite and PPS/PC/GF hybrid nanocomposite

Abstract: The polyphenylene sulfide (PPS) blended with polycarbonate (PC), reinforced glass fiber (GF) and nanometer calcium carbonate (nano-$CaCO_3$) filled PPS ternary composite, as well as the PPS/PC/GF/nano-$CaCO_3$ hybrid composite, were prepared by means of a twin-screw extruder, and the heat distortion temperature (T_d) of these materials was measured to identify the influence of the PC and nano-$CaCO_3$ content on the heatproof properties. The T_d values for the PPS/PC blend were lower than that of the neat PPS, when the PC weight fraction (ϕ_{PC}) was less than 20%, and increased with increase in ϕ_{PC}. The T_d values for the PPS/GF/nano-$CaCO_3$ ternary composite, on which the particle surface was treated with a titanate coupler, were higher than that of the composite with the particle surface treated with a stearate coupler. When the nano-$CaCO_3$ weight fraction (ϕ_f) was less than 6%, the T_d values for the PPS/PC/GF/nano-$CaCO_3$ hybrid composites increased with increasing ϕ_f; at greater than the maximum of 6%, T_d decreased. There was a certain synergistic effect of the GF and nano-$CaCO_3$ on the heatproof properties in the PPS/PC composite.

Keywords: glass fiber; heat distortion temperature; nano-$CaCO_3$; polycarbonate; polymer composite; polyphenylene sulfide.

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1 Introduction

Polyphenylene sulfide (PPS) has high strength and good dimension stability, heatproof, flame retardant and chemical resistance, as well as good processing properties. However, its application is limited to a great extent, due to its poor impact toughness and cost [1]. To improve the impact toughness and reduce the cost, blending [2–4], fiber reinforcing [5], and particle filling composite [6, 7] are usually used in industry. Akhtard and White [2] studied the properties and characteristics of binary and ternary blends of PPS with poly (bisphenol A) sulfone and polyetherimide. Lim et al. [3] researched the thermal properties and morphological study of PPS-polycarbonate (PC) blends. Choi and Lim [4] investigated the effect of an epoxy on compatibility of PPS/PC blend. Chen et al. [5] studied the friction and wear mechanisms of the PA66/PPS blend reinforced with carbon fiber (CF), and noted that the abrasive wear caused by ruptured CFs (for lower CF content) and the load bearing ability of CFs (for higher CF content) are the major factors affecting the wear volume. Recently, PPS was modified by using nanometer inorganic particles, like nano-SiO_X [6], and nano-apatite (NAP) [7] and the effect was good. Lu et al. [6] measured impact strength and the crystallization property of nano-SiO_X/PPS composites with heat-treated PPS. Yang et al. [7] studied the properties of a biocomposite of NAP/poly (1,4-phenylene-sulfide)-poly(2,4-phenylene sulfide acid) (PPSA). The results showed that the NAP/PPS-PPSA biocomposite not only had good homogeneity, but also had high NAP content of 60%, which was a potential bioactive material to be used as load-bearing implants or fixation in bone repair.

For inorganic rigid particle-filled polymer composites, the physical, heatproof and mechanical properties depend, to a great extent, upon interfacial morphology, like the interfacial adhesion between the filler and the matrix, interfacial structure, and the dispersion of the inclusions in the matrix [8–11]. More recently, the authors [12–14] measured the mechanical properties including tensile, flexural and impact properties of the glass fiber (GF)-reinforced PPS/nanometer calcium carbonate (nano-$CaCO_3$) ternary composites.

PC is an engineering resin used extensively in industry owing, to excellent strength, toughness and processing properties. Nano-$CaCO_3$ is usually used to modify polymers in industry, due to its low cost and abundant source. Heat distortion temperature (or heat deflection temperature) is one of the major characterizations of the heatproof properties of materials. The objectives in this paper are to investigate the influence of the PC content and the content of the nano-$CaCO_3$ particles, as well as

their surface treatment, on the heatproof properties of the PPS/PC blend, PPS/GF/nano-$CaCO_3$ ternary composite, and PPS/PC/GF/nano-$CaCO_3$ hybrid composite under experimental conditions.

2 Experimental

2.1 Raw materials

The PPS resin used in this work was PPS30, produced by Honghe Special Engineering Plastics Co. Ltd. (Sichuan, China). The melting temperature and density of the resin were 285°C and 1.5 g/cm^3, respectively.

The PC was supplied by Bayer Co. Ltd., Germany; its trademark was Makrolon, PC2807. The density and melt flow rate (1.2 kg, 300°C) of the resin were 1.2 g/cm^3 and 9.5 g/10 min, respectively.

The GF used in this work was a long fiber, of which the diameter was 10 μm; it was a type of glass filament yarn supplied by Beijing Glass-Reinforced Epoxy Composite Materials Co. Ltd. (Beijing, China). The product type was Z-G1-2000, and the surface had been pretreated by the supplier.

Nano-$CaCO_3$ was produced by Anyuan Technical Chemical Industry Co. Ltd. (Jiangxi, China). The trademark of the nano-$CaCO_3$ was CC-A, and the mean diameter and density of the particles were 40 nm and 2.5 g/cm^3, respectively.

2.2 Preparation of composites and specimens

After the particles surface of the nano-$CaCO_3$ was treated in a high speed mixer, they were mixed with the PPS and PC resins, as well as the GF, according to designed blending ratios. For the PPS/PC blends, the PC weight fractions were 10%, 20%, 30%, and 40%, respectively. For the GF reinforced and nano-$CaCO_3$-filled PPS composites, the GF weight fraction was fixed as 40%, and the weight fractions of the nano-$CaCO_3$ were 2%, 4%, 6%, and 8%, respectively. The surface of the nano-$CaCO_3$ particles was treated with the stearic acid coupling agent and the titanate coupling agent before compounding, and the corresponding composite systems were named as PPS/GF/nano-$CaCO_3$/S and PPS/GF/nano-$CaCO_3$/T, respectively. Finally, the PPS/PC, PPS/GF/nano-$CaCO_3$ and PPS/PC/GF/nano-$CaCO_3$ blends were melted and blended in a twin-screw extruder (model TSSJ-40) to make the PPS blend and PPS composites. The diameter and length-diameter ratio of the extruder screw were 40 mm and 32:1, respectively. The extruder barrel temperature range was from 260°C to 290°C. The particulate composites were dried for 10 h at 100°C before tests.

The specimens for heat resistant tests were prepared by means of a plastics injection machine (model CJ80NC) supplied by Zhende Plastics Machinery Co. Ltd. (Shunde, China). The injection temperature ranged from 270°C to 290°C, and the injection pressure ranged from 6 MPa to 8 MPa. The size of the specimens was 15 mm×15 mm×10 mm.

2.3 Instrument and methodology

The automotive heat deflection-Vicat softening point tester (model XWR-300) supplied by Jingjian Testing Instrument Co. Ltd. (Chengde, China) was used in this work to measure the heat distortion temperature of the blend and composites. The heat distortion temperature tests were conducted according to ISO75-2 standard, the heating rate was 120°C/h, and the flexural load was 1.82 MPa and 4.5 MPa, respectively. The heat transfer medium was dimethyl silicone oil.

The fracture surfaces of the specimens from the experiments were examined by means of an LEO (model 1530 VP) scanning electron microscope (SEM) supplied by Carl-Cest Instrument Company (Germany) to observe the dispersion or distribution of the filler particles in the PPS matrix. The specimens were gold-coated before SEM examination.

3 Results and discussion

3.1 PPS/PC blend system

As previously stated, the heat distortion temperature of polymer materials is the temperature at which the deformation reaches the stipulated deformation of the specimen under the test conditions, with a given load and a certain heating rate; it is one of the major indexes for characterizing the heatproof properties of materials. Figure 1 shows the dependence of the heat distortion temperature (T_d) on the PC weight fraction (ϕ_{PC}) for the PPS/PC blend system. Where the flexural stress was 1.82 MPa, A1 and A2 present, respectively, two kinds of compatibility agents. It can be seen that the value of T_d first decreases, then increases with an increase of ϕ_{PC} in the case of a low PC concentration. This is because the heatproof property of

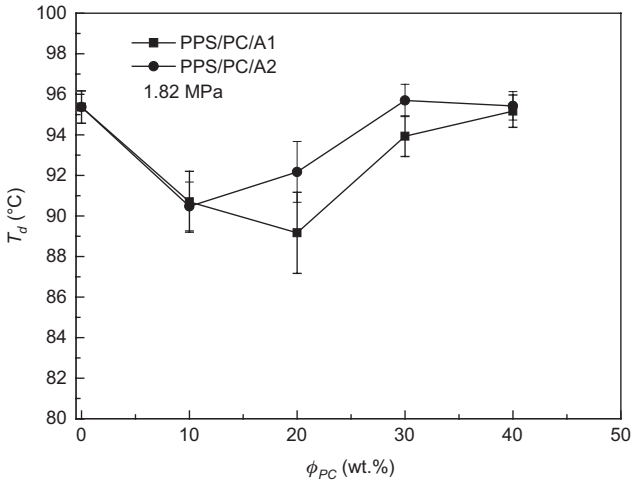

Figure 1 Dependence of heat distortion temperature on polycarbonate (PC) content of polyphenylene sulfide (PPS)/PC blend systems (1.82 MPa).

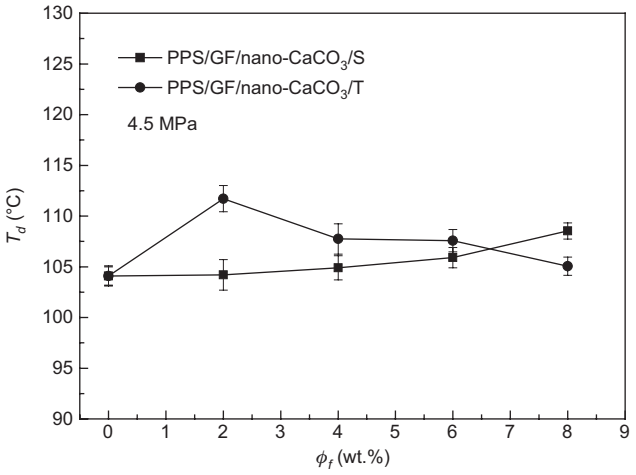

Figure 2 Correlation between heat distortion temperature and nanometer particle weight fraction of polyphenylene sulfide/glass fiber/nanometer calcium carbonate (PPS/GF/nano-$CaCO_3$) ternary composite systems (4.5 MPa).

the PC resin is much lower than that of PPS resin; the heat distortion temperature of the composite will be reduced if there are less physical nodes of the macromolecular chains between the PPS and PC resins, in the case of a low PC content. With an increase of the PC content, the physical nodes of the macromolecular chains between the PPS and PC resins will increase, and the heatproof property will be improved correspondingly, leading to an increase in the heat distortion temperature of the composite.

For the PPS/PC/A1 system, the value of T_d is a minimum at ϕ_{PC} of 20%; for the PPS/PC/A2 system, the value of T_d is a minimum at ϕ_{PC}=10%. The values of T_d of the PPS/PC/A2 system are higher than those of the PPS/PC/A1 system. This indicates that the influence of the type and content of compatibility agent on the heatproof properties of the PPS/PC blend systems is significant. That is, there is a certain synergistic effect of the suitable compatibility agent on the heatproof properties of the PPS/PC blend systems.

3.2 PPS/GF/nano-$CaCO_3$ ternary composite systems

The correlation between the T_d and the nano-$CaCO_3$ weight fraction for the GF-reinforced PPS ternary nanocomposites, at a flexural stress of 4.5 MPa, is illustrated in Figure 2. When the GF weight fraction is 40%, it may be observed that the value of T_d for the PPS/GF/nano-$CaCO_3$/T composite system increases, with an increase of the nano-$CaCO_3$ fraction (ϕ_f) when ϕ_f is less than 3%, it reaches the maximum at ϕ_f=2%, and then decreases with increasing ϕ_f. For the PPS/GF/nano-$CaCO_3$/S system, the value of T_d increases slightly with an increase in ϕ_f. Moreover, the values of T_d of the PPS/GF/nano-$CaCO_3$/T composite system are higher than those of the PPS/GF/nano-$CaCO_3$/S system, except at individual data points. This indicates that the surface treatment of nano-$CaCO_3$ with the titanate coupling agent is more beneficial in improving the compatibility between the particle and the matrix than with the stearic acid coupling agent, resulting in increased heat distortion temperature of the composite.

In general, the macromolecular chain movement of polymer composites would be blocked by the fillers, and this blocking action would be enhanced with an increase of the filler content, resulting in raising the heat distortion temperature of the composite systems. It is known from Figure 2, that when the PPS is reinforced with GF and filled with nano-$CaCO_3$, the blocking action of the fillers to the macromolecular chain movement will be significant. Consequently, the heat distortion temperature of the PPS/GF/nano-$CaCO_3$ ternary composite systems increases with an increase of the filler weight fraction.

3.3 PPS/PC/GF/nano-$CaCO_3$ hybrid composite systems

Figure 3 displays the relationship between the T_d and the nano-$CaCO_3$ weight fraction for the GF-reinforced PPS/PC hybrid nanocomposites when the flexural stress is 4.5 MPa. When the GF weight fraction is 40%, it may be found that the value of the T_d increases nonlinearly with increasing ϕ_f when ϕ_f is smaller than 6%; the value of the

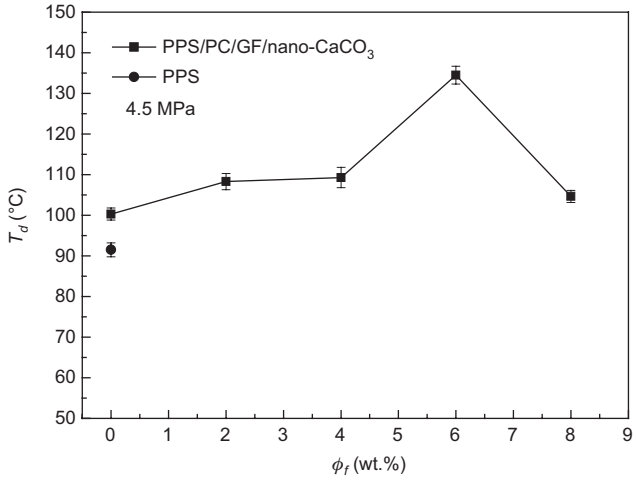

Figure 3 Correlation between heat distortion temperature and nanometer particle weight fraction of polyphenylene sulfide/polycarbonate/glass fiber/nanometer calcium carbonate (PPS/PC/GF/nano-$CaCO_3$) hybrid composite systems (4.5 MPa).

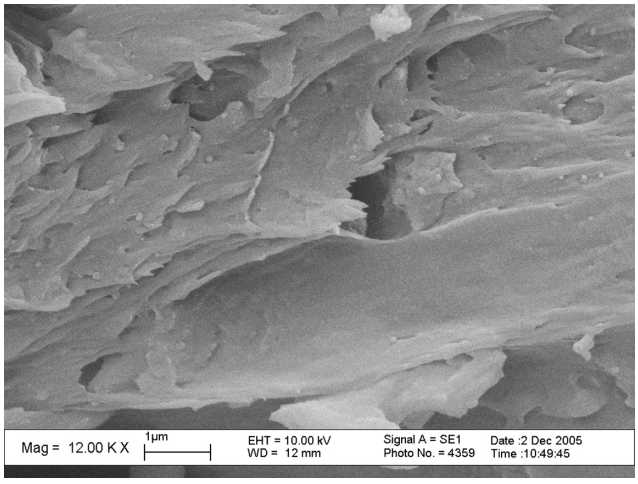

Figure 4 Scanning electron microscope (SEM) photograph of the impact fracture surface of the polyphenylene sulfide/polycarbonate/glass fiber/nanometer calcium carbonate (PPS/PC/GF/nano-$CaCO_3$) ternary composite (ϕ_f=2%).

T_d reaches the maximum at a ϕ_f of 6%; it then decreases with increasing ϕ_f.

As discussed above, the fillers, including fibers and particles, would block the macromolecular chain movement of polymer composites to varying degrees, and this blocking action would be enhanced with an increase of the filler content, resulting in raising the T_d of the composite systems. It is known from Figure 3, that when the PPS/PC blend is reinforced with GF and filled with nano-$CaCO_3$, the blocking action of the fillers to the macromolecular chain movement will be significant. Consequently, the T_d of the PPS/PC/GF/nano-$CaCO_3$ hybrid composite systems increases with an increase of the filler weight fraction. Moreover, if there is a certain synergistic effect between PPS and PC on the heatproof properties of the composite systems, the heatproof properties will be improved.

3.4 Morphology

Figure 4 illustrates the SEM photograph of the impact fracture surface of the PPS/PC/GF/nano-$CaCO_3$ hybrid composite when ϕ_f is 2%. It can be seen that the distribution of the nano-$CaCO_3$ in the PPS matrix is roughly uniform, and the interface between the particles and matrix is relatively rough. Moreover, there is no interfacial debonding between the inclusion and matrix. This indicates that the interfacial adhesion between the particles and the PPS matrix is good in this case. It is generally believed that the uniform dispersion of the filler in the PPS resin matrix is beneficial in enhancing the blocking action of the fillers to the macromolecular chain movement, leading to a higher T_d of polymer composites (see Figure 3). Figure 5 displays the SEM photograph of the specimen impact fracture surface of the PPS/PC/GF/nano-$CaCO_3$ hybrid composite when ϕ_f is 4%. Similarly, the dispersion and distribution of the nano-$CaCO_3$ particles in the PPS matrix are also uniform, and there are some platforms on the fracture surface. As stated above, the uniform dispersion of the filler particles and PPS matrix is beneficial in enhancing the blocking action of the fillers to the macromolecular

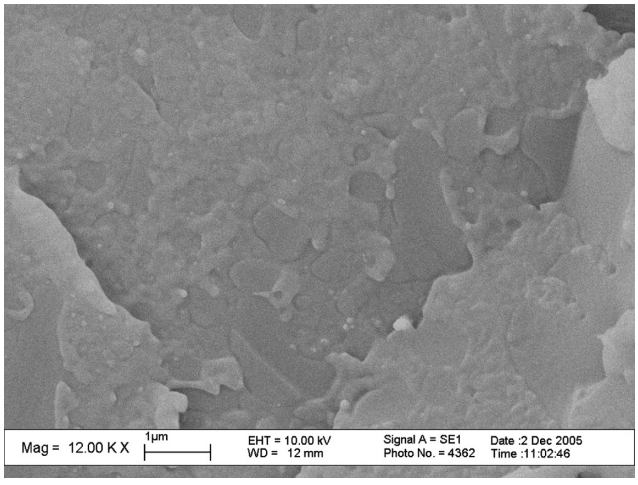

Figure 5 Scanning electron microscope (SEM) photograph of the impact fracture surface of the polyphenylene sulfide/polycarbonate/glass fiber/nanometer calcium carbonate (PPS/PC/GF/nano-$CaCO_3$) ternary composite (ϕ_f=4%).

chain movement, leading to a higher T_d of polymer composites (Figure 3). Figure 6 demonstrates the SEM photograph of the specimen impact fracture surface of the PPS/PC/GF/nano-$CaCO_3$ hybrid composite, when ϕ_f is 6%. It can be observed that the dispersion and distribution of the nano-$CaCO_3$ particles in the PPS matrix are relatively poor. In general, poor dispersion and distribution of the filler in the resin matrix will weaken the blocking action of the fillers to the macromolecular chain movement, leading to a slight variation in the T_d of the polymer composites (Figure 3).

Figure 7 demonstrates the SEM photograph of the specimen impact fracture surface of the PPS/PC/GF/nano-$CaCO_3$ hybrid composite, when ϕ_f is 8%. Similarly, the dispersion and distribution of the nano-$CaCO_3$ particles in the PPS matrix are relatively poor. As discussed above, poor dispersion and distribution of the filler in the resin matrix will weaken the blocking action of the fillers to the macromolecular chain movement, leading to a reduction of the T_d of the polymer composites (Figure 3). To clearly observe the interfacial morphology between the GF and the PPS matrix, the SEM photograph was taken with a magnification factor of 500 for the PPS/PC/GF/nano-$CaCO_3$ hybrid composite, when ϕ_f is 8%, as shown in Figure 8. It may be observed that the surface of the fiber extracted from the matrix is stained with some PPS resin. This indicates that the interfacial adhesion between the fiber and the matrix is good; it will be beneficial in improving the heatproof properties of the PPS composites.

As discussed above, the activity and relative movement of the matrix macromolecular chains are blocked when the inorganic particles are filled into the resin, thus the heatproof property of the composites will be improved. Moreover, if the inclusions play the role of the heterogeneous nucleation in the matrix to increase the crystalline degree, the heatproof property of the composites will be greatly enhanced. More recently, the author [15] investigated the effects of the nanometer filler content on the crystalline degree of the PPS/GF/nano-$CaCO_3$ composites using a differential scanning calorimeter, and found that the crystalline degree of the PPS/GF/nano-$CaCO_3$/T system is somewhat higher than (or close to) that of the

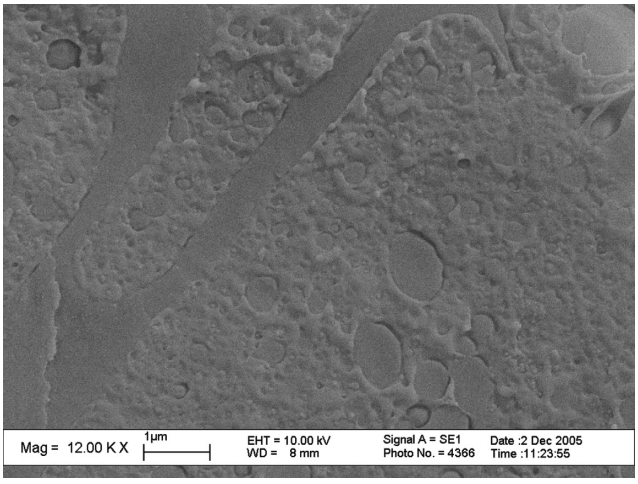

Figure 7 Scanning electron microscope (SEM) photograph of the impact fracture surface of the polyphenylene sulfide/polycarbonate/glass fiber/nanometer calcium carbonate (PPS/PC/GF/nano-$CaCO_3$) ternary composite (ϕ_f=8%, magnification=12,000).

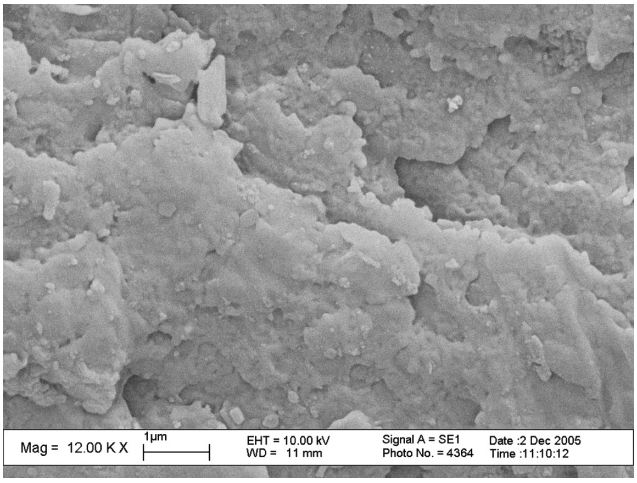

Figure 6 Scanning electron microscope (SEM) photograph of the impact fracture surface of the polyphenylene sulfide/polycarbonate/glass fiber/nanometer calcium carbonate (PPS/PC/GF/nano-$CaCO_3$) ternary composite (ϕ_f=6%).

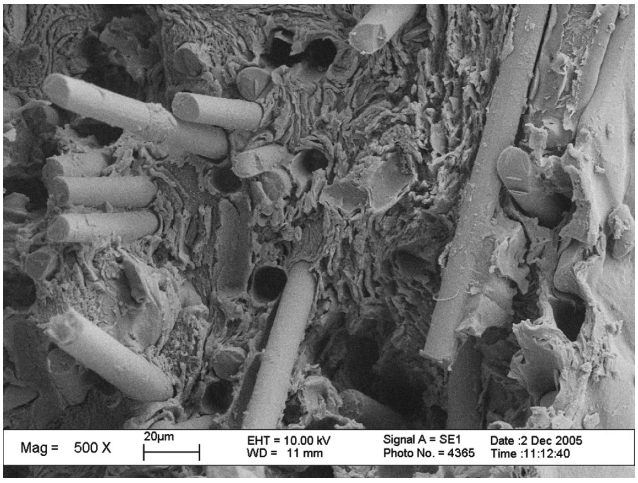

Figure 8 Scanning electron microscope (SEM) photograph of the impact fracture surface of the polyphenylene sulfide/polycarbonate/glass fiber/nanometer calcium carbonate (PPS/PC/GF/nano-$CaCO_3$) ternary composite (ϕ_f=8%, magnification=500×).

PPS/GF/nano-$CaCO_3$/S system, especially when the filler weight fraction ranged from 1% to 4%. These are matched with the results shown in Figure 2.

In conclusion, the filler concentration, the dispersion state of the inclusions in the matrix, the interfacial morphology between the filler and matrix, as well as the crystalline status, are the important factors affecting the heatproof properties of polymer composites.

4 Conclusions

The influences of the PC content, the nano-$CaCO_3$ content and their surface treatment on heatproof properties of the PPS blend and PPS composites, were significant. When the PC weight fraction was less than 20%, the distortion temperature of the PPS/PC blend was lower than that of the neat PPS. There was a certain synergistic effect of the suitable compatibility agent on the heatproof properties of the PPS/PC blend systems.

In the case of a low nano-$CaCO_3$ concentration, the distortion temperature of the PPS/PC/nano-$CaCO_3$/T system was higher than that of the PPS/PC/nano-$CaCO_3$/S system. When the nano-$CaCO_3$ weight fraction was less than 6%, the distortion temperature of the PPS/PC/GF/nano-$CaCO_3$ composites increased with an increase of the nano-$CaCO_3$ weight fraction, and it reached the maximum at ϕ_f of 6%; it then decreased. There was a certain synergistic effect on the heatproof properties in the PPS/PC composite.

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