Effect of core–shell composite particles on the sintering behavior and properties of nano-Al_2O_3/polystyrene composite prepared by SLS

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Abstract

Nano-Al_2O_3 particles coated with polystyrene (PS) by emulsion polymerization were used as fillers to reinforce PS based composites prepared by selective laser sintering (SLS). The influences of the treated and untreated nanoparticles on the sintering behavior and mechanical properties of the laser sintered specimens were investigated. It was found that there were many uneven holes in the untreated composites. However, for the treated composites, due to the nanoparticle surfaces treated by emulsion polymerization, the absorbance of laser was improved and the nanoparticles dispersed well in the polymer matrix; a full dense structure was obtained and the properties were enhanced, such as the notched impact strength increased 50%, the maximum value was 12.1 kJ/m^2; the tensile strength increased up to 300%, the maximum value was 31.2 MPa, comparing to the unfilled PS. FE-SEM studied the tensile fractured surfaces of the sintered specimens. It was noted that the fractured surfaces of composites with treated nanoparticles were rougher than those of unfilled PS and those of the untreated composite. Drawing from the results, it can be confirmed that a full dense structure can be obtained and the polystyrene matrix was strengthened and toughened when the nanoparticles were coated with PS by emulsion polymerization. This work forms a theoretical and technique basis for the production of selective laser sintered nano-Al_2O_3/PS functional products.
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1. Introduction

It is known owing to their excellent comprehensive properties, engineering plastics, such as polystyrene (PS), have been widely used in many fields. However, when PS is used alone, it has a disadvantage of low notched impact strength, which obstructs the application of PS. Hence, inorganic nanoparticle was used to reinforce the PS matrix [1]. Nanoparticle filled polymers have been the subject of active studies in the past decades due to their unique physical and chemical properties [2–4]. At the present time, there are already reports on the preparation of polymer based nanocomposite [5–7]. For example, Ash et al. [5] have a report on alumina/polymethylmethacrylate (PMMA) nanocomposites which were produced by incorporating alumina nanoparticles, and synthesized using the forced gas condensation method into methylmethacrylate. Wang et al. [6,7] have a research about reverse ATRP grafting from silica surface to prepare well-defined organic/inorganic hybrid nanocomposite.

On the other hand, the demand for faster and less expensive product development has resulted in an impressive number of rapid prototyping (RP) methods being developed worldwide [8]. Selective laser sintering (SLS) is one of the few RP technologies, which can shorten the design manufacturing cycle and possess the capability to produce parts directly from powders. Most of the researches reported previously were focused on the sintered powders, including metal, ceramic, amorphous polymer system and so on [9–12]. Some researchers [13,14] have discussed the metal matrix composite prepared by SLS. Comparatively fewer researchers have studied polymer nanocomposite. Furthermore, Kim and Creasy [15] considered that a fully dense part might not be possible using nanocomposite powder with the rapid prototyping process. But they did not give a study about

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the effects of the nanoparticles on the sintering behavior during the SLS processing. In the process of SLS, the sintering temperature was related to the absorbed energy of the materials, which made the powders fuse. Gibson and Shi [16] considered that both mechanical properties and appearance of the components sintered by SLS were influenced by powder materials and fabrication parameters. Based on the previous works, the PS based nanocomposites were prepared by SLS. However, nanoparticles have a great inclination to agglomerate because of the high surface energy and inorganic nanoparticles may have a low absorbance and high reflectance of laser beam, which can influence the sintering behavior and mechanical properties of nano-Al_2O_3/PS composites prepared by SLS. Therefore, in this paper, the nano-alumina particles are modified by emulsion polymerization to form nano-Al_2O_3/PS composite particles with core–shell structure. The effects of core–shell composite particles on the sintering behavior and mechanical properties of specimens prepared by SLS were investigated. The size and morphology of the core–shell composite nanoparticle were observed by a JME-100CX II transmission electron microscope (TEM). The distribution status of the nano-alumina particles in the PS matrix and the surface morphology and the tensile fractured surface of the sintered specimens were characterized by SEM and FE-SEM, respectively.

2. Experimental

2.1. Materials

Polystyrene (PS, 99.7% purity) was provided by Wuhan Chemical Co., China, and the maximum particle size is 50 μm. The nano-alumina particles (99.9% purity) with an average size of 60 nm were produced by Jiangsu Hehai Nano-ST Co., China. Prior to use, the particles were dried in an oven at 110 °C under vacuum for 24 h in order to get rid of the physically absorbed and weakly chemically absorbed species. Styrene (St) and other chemical agents used were of AR grade.

2.2. Preparation of core–shell composite nanoparticles and the mixing powders

Nano-alumina particles were coated with PS by emulsion polymerization according to the steps described elsewhere [17].
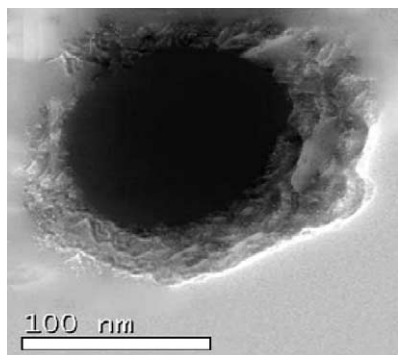

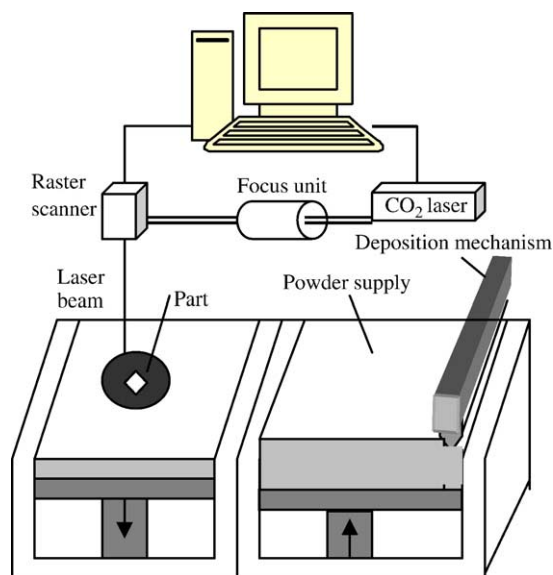Fig. 1. TEM of single nano-Al_2O_3/PS composite particle.

Fig. 2. Schematic of the direct laser sintering apparatus.

TEM of a single nano-Al_2O_3/PS composite particle is shown in Fig. 1. From Fig. 1, it can be clearly seen that it is a typical core–shell structure and the colour in the center is dark with the dimension of 60 nm; around the center is light, with the dimension of 10–20 nm.

There were three kinds of mixing powders in this experiment. They were the unfilled PS and the filled PS with 5 wt.% untreated and 5 wt.% treated nano-alumina particles, respectively. They were blended as following: at first, the PS powders were put into the nanoparticles; then the mixed powders with right dose of light absorption additives and anti-friction additives, which can improve the thermal receptivity of PS and reduce the distortion and increase the strength of the specimens, were put into the high-speed mixer. The agitation process continued for 30 min at 80 °C, then the mixing powders were discharged, dried in oven, and were used in the experiment.

2.3. SLS of the powders

The sintering machine used in this experiment is HRPS-IIIA laser sintering machine made by Wuhan Binhu Mechanical and Electrical Co. Ltd., China, which consists of a powder handling system, a continuous wave CO_2 laser irradiation with related optics and a process computer. The conditions for laser irradiation are those: the spot diameter of the laser beam on the powder bed is 0.5 mm, the maximum laser power and maximum scan speed is 50 W and 4000 mm/s, respectively. Fig. 2 depicts a schematic diagram of the instrument. In the SLS process, the computer system dealt with the three-dimensional object model created by the computer through cascades of thin slices. Then the three-dimensional object is created layer by layer from heat-fusible powdered materials with energy supported by the CO_2 laser. A very thin layer of heat-fusible powdered materials was delivered onto the top of the built cylinder by a roller. The laser beam traced across this layer and sintered the specific areas according to the instructions of

the CAD file. After the sintering process was finished, the platform descended slightly and another thin layer of material was delivered on the sintered layer. Then, the laser beam repeated the above process to create another layer. The thermal effect of the laser energy increases the temperature of the bed, bonding the loose powder together. The process continues, layer by layer, until the three-dimensional object is complete. The unsintered powder stays in the container during the process, serving as a natural support for the object [18].

3. Results and discussions

3.1. Morphologies

In order to study the variation in the sintering behavior between the powders and laser beams due to the surface modification of the nano-alumina, the surfaces of the sintered specimens were investigated by SEM. The SEM images of sintered specimens' surfaces are shown in Fig. 3. All samples were sintered using a fixed laser power of 24.5 W, scan speed of 1100 mm/s, scan space of 0.2 mm and layer thickness of 0.1 mm in air atmosphere at room temperature. Fig. 3(a,b) shows the surface morphology of the laser sintered sample with 5 wt.% uncoated and coated nanoparticle fillers, respectively. It can clearly be seen that the microstructural feature is different, such as porosity and voids. In Fig. 3(a), it can be seen that there are many holes in the matrix with the uncoated nanoparticles. As compared to the untreated nano-Al_2O_3/PS composites (Fig. 3a), a full dense compact structure is obtained (see in Fig. 3b).

This can be explained by that: firstly, as has been known selective laser sintering mechanism is the interaction between the laser beam and the powder by means of reflect transmission and refraction. The powder is heated by absorption of the energy induced by the laser. However different materials have different absorbance and reflectance. For example, the absorbance of organic substance is more than 0.9 and the
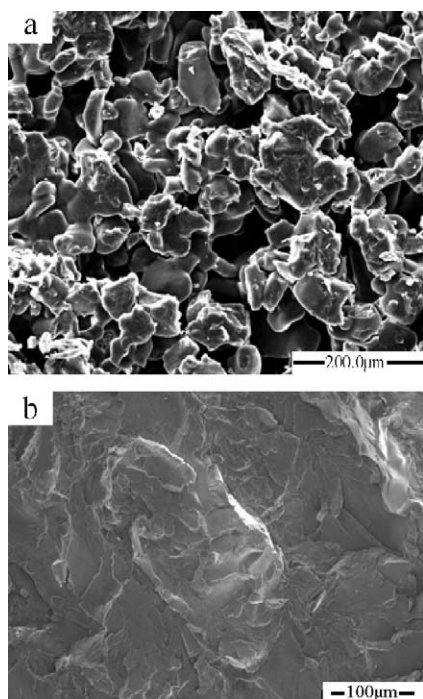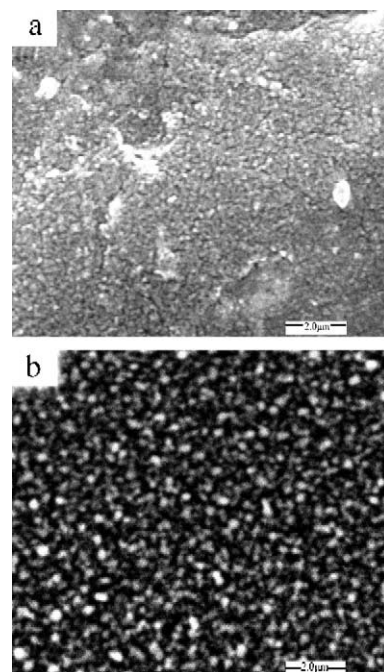

Fig. 4. Dispersion of the nano-Al_2O_3 in the matrix (a, untreated and b, treated).

reflectance is little, but those of inorganic substance are different; its reflectance is very high and its absorbance is about 0.5. When the nanoparticles are coated with PS by emulsion polymerization, they are more effective than uncoated nanoparticles on the absorbance of laser beam during the SLS processing, which results in a higher work temperature. Secondly, due to the difference of surface polarities between PS and nano-alumina, it is concluded that the untreated nano-alumina fillers do not bond the matrix well, which reveals that the filler-matrix interface is weak in adhesion and particle re-agglomeration occurs when aggregates are brought together by the non-homogeneous flow field. However, PS coating on the nano-alumina has a similar solubility parameter to the PS matrix, which leads to good compatibility and interfacial adhesion between the filler particles and the matrix. In addition, the uncoated nanoparticle may hinder polymer flow, which makes the polymer have a higher viscosity. Based on the aforesaid reasons, the different morphologies shown in Fig. 3 demonstrate due to surface treatment by emulsion polymerization, that the absorbance of laser energy and the adhesion between fillers and matrix are improved, and more nanoparticles are embedded in the polymer matrix without gaps between fillers and matrix. It can be concluded that a full dense structure can be obtained by SLS.

It is well known that the nanoparticle dispersion plays a major role in the observed properties of composites. Sometimes the composites perform even worse than conventional microparticles filled version, if the nanoparticles dispersed poorly [19–21]. Fig. 4 shows the dispersions of the treated and untreated nano-alumina in the matrix. As portrayed by Fig. 4, it is clearly seen that there is an obvious difference of dispersion between the untreated and the treated nanoparticles in the PS matrix. In Fig. 4(a), it can be seen that the untreated nanoparticles agglomerate due to their high surface energy. Even though mixing can de-agglomerate the nanoparticle aggregates, they might quickly re-agglomerate due to their high surface energy and the different surface polarities between the filler and the matrix when the mixing powders with untreated nano-alumina were sintered.

However, much finer dispersion of the fillers can be observed (Fig. 4b), when the nanoparticles are coated with PS. In Fig. 4(b), the round white dots were nanoparticles. The nanoparticles dispersed
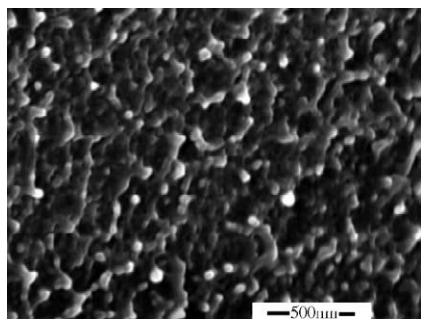

Fig. 3. SEM images of sintered specimen surfaces with 5 wt.% untreated Al_2O_3 (a) and with 5 wt.% treated Al_2O_3 (b).

Fig. 5. Dispersion of the treated nano-Al$_2$O$_3$ in the treated composite.

homogeneously and there was no agglomeration. This can be explained by the polystyrene coating on the nanoparticle forming a stable hindrance layer between particles which inhibits the agglomeration and thus improves greatly the dispersion of the nanoparticles.

In order to acquire more knowledge about the dispersion of the treated nano-alumina in the PS matrix, FE-SEM image with magnification at 50,000× is shown in Fig. 5. A uniform dispersion of nanoparticles in the PS matrix on a nanometer level is obtained. The adhesion between fillers and matrix is enhanced by chain entanglement due to the chemical bonding between the coating PS and the matrix.

3.2. Mechanical properties

When nano-alumina particles are incorporated into PS, the processability and the properties of the composites will be affected. Fig. 6 shows the result of notched impact strength and tensile strength of unfilled PS and its composites with treated and untreated nano-alumina versus the filled laser power (P) when other fabrication parameters are fixed. As can be seen in Fig. 6a, notched impact strengths and tensile strengths of the treated composites are higher than those of the other two kinds of powders, respectively. It can also be seen that the notched impact strength of treated composites and unfilled PS increases and reaches its maximum when the filled laser power is 29.5 W, but that of untreated composites reaches its maximum when the power is 31 W, followed by a decrease (see in Fig. 6a). Fig. 6b shows that there is a similar tendency for the tensile strength, and the tensile strengths of the pure PS and the treated composite initially increase until the filled laser power reaches 27.5 W, but the maximum of the untreated composite is at 30 W. This may be attributed to that intensifying the filled laser power leads to a higher working temperature and consequently lower the viscosity and surface tension. So, the liquid is easier to flow and fill the pore. Consequently, the properties increase with the increasing of P value. However, when the value of P is excessively high, namely, the energy induced by the laser is excessive, the working temperature is excessively high, which results in the degradation of PS and thus results in the properties' decline. For the untreated nanoparticles, due to the low absorbance and the high reflectance of laser beam, the laser energy
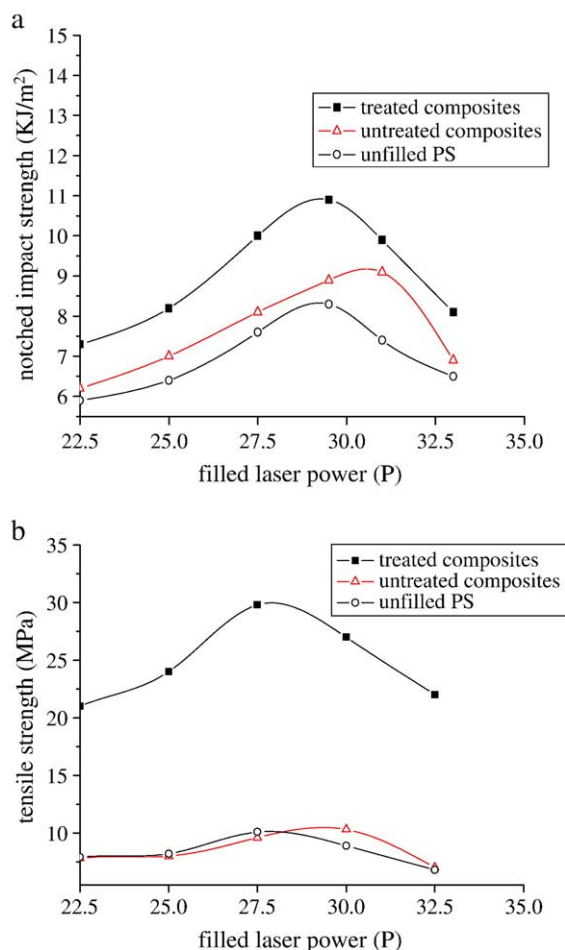

Fig. 6. (a) Influence of filled laser power on the notched impact strength of different specimens. (b) Influence of filled laser power on the tensile strength of different specimens.
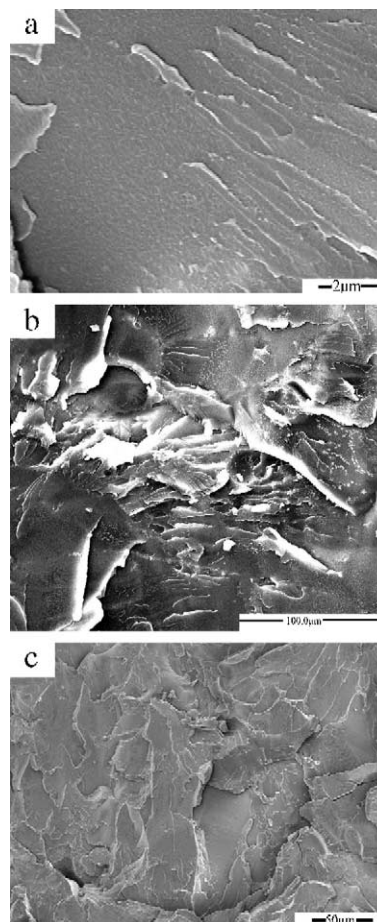
Fig. 7. SEM of the tensile fractured surfaces of unfilled PS (a), untreated composite (b) and treated composite (c).

absorbed by the power is little, which results in the lower sintering temperature and its maximum is obtained at 30 W.

As were compared with the unfilled PS specimens sintered in the same conditions, the tensile strength of the treated composites increased up to 300%, the highest value was 31.2 MPa; the notched impact strength increased 50%, the highest value was 12.1 kJ/m^2.

3.3. Tensile fractured surface

FE-SEM images of the tensile fractured surfaces are presented in Fig. 7.

Fig. 7(a) shows that the fractured surface of unfilled matrix exhibits brittle fracture feature at room temperature. This is mainly due to that PS is a brittle material. As for the untreated composites, it is rather clear that the uncoated nano-alumina fillers do not bond the matrix well, which reveals that the filler-matrix interface is weak in adhesion and there are many uneven holes in the structure (see in Fig. 3a). It had been well known that the appearance of the fractured surfaces of a polymer composite was closely related to propagation of the crack along the filler-matrix interfaces (especially when the interface is weak), so, the crack spreads mainly through the weakest track in the composite. As can be seen in Fig. 7(c), the fractured surfaces of treated composites were rougher than those of unfilled PS specimens and those of the untreated composites, indicating that the treated composites were more ductile than the unfilled PS and the untreated composites. This is a typical multiple cracking phenomenon. Few cracks can be found on the fracture section in Fig. 7(c), indicating a delay of occurrence of microcracking damage and fracture.

It has been well known that the extent of stress concentration around the inclusion in a matrix is proportional to the inclusion size. Furthermore, cracks initiation and propagation depend on the structure of the composites. Structural inhomogeneity, such as aggregation, voids, etc., in a poorly dispersed system would favor initiation of fracture. Compared to the untreated nano-alumina, the strong interfacial interaction between the treated nanoparticles and the matrix firmly made the particles stick to the matrix. Having met with obstruction in front of the particles, the crack has to deviate from its plane, so as to make a detour and propagate between the particles causing additional energy dissipation. Therefore, the treated composites possess much higher toughness than the ones with untreated nanoparticles.

4. Conclusion

Nano-alumina coated with PS by emulsion polymerization dispersed better than the untreated ones in the matrix. From the images of the sintered specimens, it can be concluded that the nano-Al$_2$O$_3$/PS composite particles with core–shell structure can increase the absorbance of the laser beam and improve the interface adhesion of filler-matrix, compared with the untreated nano-alumina. It is confirmed that the polystyrene is toughened and strengthened because the polarity of nano-Al$_2$O$_3$ is modified by the nano-Al$_2$O$_3$/PS composite particles with core–shell. The present work manifests that through proper surface treatment a full dense composite can be prepared by SLS, which forms a theoretical and technique basis for SLS of expanding application area and directly producing the nanocomposite parts with higher physical and mechanical properties.

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