

Influence of Surface Modification on the Dispersion of Nanoscale α -Al₂O₃ Particles in a Thermoplastic Polyurethane Matrix

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ABSTRACT: In this study, two types of nanoscale α -Al₂O₃ particles were used for preparation of α -Al₂O₃/thermoplastic polyurethane (TPU) composites. These α -Al₂O₃ particles were either coated or uncoated with stearic acid. For the uncoated α -Al₂O₃/TPU composite, the results of field-emission scanning electron microscopy (FE-SEM) and energy dispersive X-ray spectrometry indicate that uncoated α -Al₂O₃ particles are significantly aggregated together. This aggregation is due to the poor compatibility between the inorganic filler (α -Al₂O₃) and the organic matrix (TPU). The size of clusters is in the range from 5 to 20 μ m. For the coated α -Al₂O₃/TPU composite, FE-SEM

results indicate that most coated α -Al₂O₃ particles are well dispersed in the TPU matrix. This phenomenon results from the effect of surface modifier (i.e., stearic acid) on α -Al₂O₃ particles. Stearic acid can act as a compatibilizer to bridge the boundary between the TPU matrix and the α -Al₂O₃ particle. Stearic acid is not only a suitable surface modifier for the nanoscale α -Al₂O₃ particle, but also a good dispersant for the dispersion of nanoscale α -Al₂O₃ particles in the TPU matrix. © 2008 Wiley Periodicals, Inc. *J Appl Polym Sci* 110: 237–243, 2008

Key words: TPU; α -Al₂O₃; nanocomposite

INTRODUCTION

Polymer nanocomposites have received great attention because they often exhibit much better properties than polymers or polymers filled with micrometer-size inorganic fillers. The degree of dispersion and the type of nanoscale fillers are two key factors to manipulate the properties of nanocomposites. By adding 2–5 wt % nanoscale fillers, the enormous enhancement in properties of a polymer nanocomposite can be observed. Furthermore, the weight of finished polymer nanocomposites can be obviously reduced by comparing with those of the conventional polymer microcomposites.¹ Various nanoscale fillers have been studied to improve the mechanical and thermal properties of polymers, such as clay,² silica,³ calcium carbonate (CaCO₃),^{4–6} and aluminum oxide (Al₂O₃).⁷ The improved properties include toughness, stiffness, damping, chemical resistance, heat resist-

ance, thermal conductivity, coefficient of thermal expansion, and electrical properties.

Thermoplastic polyurethanes (TPU) are block copolymers which contain hard and soft segments. Because of its feasible properties, TPU and its composites have been successfully applied in industries for a long time. The common applications of TPU and its composites include footwear, biomaterial, agriculture, consumer products, transportation, film and sheet, electronics, polymer impact modifier, food processing, recreation, etc.

Recently, TPU unwoven fabric prepared by melt blowing process attracts many researchers' great interests because this material can be produced quickly and can be applied in many polishing applications. To improve the abrasion resistance of TPU unwoven fabric, the nanoscale α -Al₂O₃ particles are quite suitable to be used as the fillers. This is because that α -Al₂O₃ has better abrasion resistance and higher thermal property than other inorganic fillers. Meanwhile, to not stop the holes of spinneret of the melt blowing equipment, not only the nanoscale α -Al₂O₃ particles have to be used but also the dispersion of the nanoscale α -Al₂O₃ particles in the TPU matrix must be as homogenous as possible.

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For TPU composites, most technical papers are focused on the area of clay/TPU nanocomposites. Solution and bulk polymerization methods are two commonly reported synthesis methods for the preparation of clay/TPU nanocomposites.^{8–11} Only few papers discussed the preparation of α -Al₂O₃/TPU microcomposite.¹² No paper or literature revealed about the preparation of α -Al₂O₃/TPU nanocomposite by melt blending process earlier. Therefore, the preparation of α -Al₂O₃/TPU nanocomposite by using a twin-screw extruder (melt blending) rather than solution or bulk polymerization was studied in this article.

Normally, it is difficult to disperse inorganic nanoparticles into an organic matrix uniformly by melt blending method without the surface modification. Therefore, two types of nanoscale α -Al₂O₃ particles were used for comparison study in this research. One is uncoated α -Al₂O₃ and the other is coated α -Al₂O₃. The uncoated α -Al₂O₃ stands for the α -Al₂O₃ particles without surface modification and the coated α -Al₂O₃ stands for the α -Al₂O₃ particles with surface modification by stearic acid. Meanwhile, to obtain better dispersion of nanoscale α -Al₂O₃ particles in the TPU matrix, a premixing process between the TPU pellets and α -Al₂O₃ particles is needed. The premixing process was conducted in a dry mixer. The purpose of the premixing process is to let the uncoated α -Al₂O₃ or the coated α -Al₂O₃ particles coating on the surface of TPU pellets as many as possible. After the premixing process, the mixture was removed from the dry mixer and then the twin extruder was installed for extrusion processing. A field-emission scanning electron microscopy (FE-SEM) was applied to reveal the dispersion of uncoated or coated α -Al₂O₃ particles in the TPU matrix, respectively. In addition, an energy dispersive X-ray spectrometry (EDX) was also conducted to confirm the existence of the aluminum element in the α -Al₂O₃/TPU composites.

EXPERIMENTAL

Materials

The nanoscale α -Al₂O₃ powder was kindly supplied by the Particulate Materials Research Center (PMRC) at the National Cheng-Kung University, Tainan, Taiwan. The primary crystalline phase of α -Al₂O₃ was no less than 99.0 wt %. Its particle size ranged from 50 to 200 nm. Its specific surface area was about 200 m²/g. The coated α -Al₂O₃ was prepared by suspending nanoscale α -Al₂O₃ particles in an ethanol solution with 3 wt % stearic acid [CH₃(CH₂)₁₆COOH]. After 3 h stirring, the coated α -Al₂O₃ was filtered and then dried. The polyester-type TPU (Kou Ching Chemical, Taiwan, KC-TPU E85100) was

kindly provided by the Taiwan Textile Research Institute (TTTRI), Taipei, Taiwan.

TEM examination

The uncoated α -Al₂O₃ powder was homogeneously dispersed into an alcohol solution to form a mixture. Then, the mixture was dropped and dried on a copper grid. The particle size and shape of the uncoated α -Al₂O₃ were examined by a field emission gun transmission electron microscopy (FEG-TEM) (FEI, USA, model Philips Tecnai G2 F20 FEG-TEM). The accelerating voltage was set as 200 kV.

Preparation of α -Al₂O₃/TPU composites

A twin extruder (Zenix Industrial, Taiwan, model ZPT-32HT) with 10 temperature zones was used to prepare the TPU/ α -Al₂O₃ composite. Before the processing, the polyester-based TPU pellets were dried in a circulating air oven at 80°C for 12 h to remove most of moisture. Then, 4.5 kg fresh dried TPU pellets and 0.5 kg nanoscale α -Al₂O₃ particles were mixed in a dry mixer at room temperature. To obtain better dispersion of nanoscale α -Al₂O₃ particles in the TPU matrix, this premixing step is needed. After about 30 min mixing, all TPU pellets were coated by the nanoscale α -Al₂O₃ particles. Then, the mixture was removed from the mixer and then put in the twin extruder for extrusion processing. The extrusion processing was performed at a screw speed of 60 rpm. Meanwhile, the temperature during the extrusion processing was set as 170°C at zones 1–5, 175°C at zones 6–7, and 180°C at zones 8–10. The extruded product was immediately quenched in a water bath and then pelletized into granules with no more than 3 mm long.

In this study, two types of nanoscale α -Al₂O₃ particles were used. They were coated and uncoated α -Al₂O₃ particles. The uncoated α -Al₂O₃ particles were incorporated into the TPU to form a 10 wt % uncoated α -Al₂O₃/TPU composite. Similarly, the coated α -Al₂O₃ particles were incorporated into the TPU to form a 10 wt % coated α -Al₂O₃/TPU composite.

FE-SEM examination

The surface morphologies of the uncoated α -Al₂O₃ and coated α -Al₂O₃ were examined. Meanwhile, the surface morphologies of 10 wt % uncoated α -Al₂O₃/TPU and 10 wt % coated α -Al₂O₃/TPU composites were also examined to reveal the dispersion of the uncoated or coated α -Al₂O₃ particles in the TPU matrix. The cross section samples were prepared by immersing the α -Al₂O₃/TPU composite into liquid nitrogen for 45 s. Then, samples were fractured and

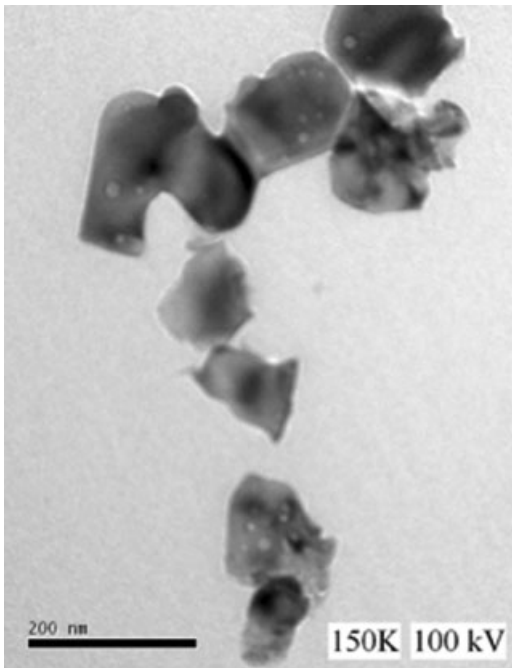


Figure 1 TEM photograph ($\times 150,000$) of the uncoated α -Al₂O₃ particles.

each taken sample was coated with the gold palladium film and examined by a FE-SEM (Jeol, Japan, model JSM 6700F). Meanwhile, to confirm the exist-

tence of α -Al₂O₃ particle in the TPU matrix, an EDX was conducted.

RESULTS AND DISCUSSION

Figure 1 displays the TEM photograph of uncoated α -Al₂O₃. The result shows that the particle size of uncoated α -Al₂O₃ ranges from 50 to 200 nm. Meanwhile, the uncoated α -Al₂O₃ particles exhibit irregular shapes under the TEM examination.

Figure 2(a,c) displays FE-SEM photographs ($5000\times$) of uncoated α -Al₂O₃ and coated α -Al₂O₃ particles, respectively. The uncoated α -Al₂O₃ particles on Figure 2(a) are significantly agglomerated. This phenomenon is resulted from the polarity of the surface of uncoated α -Al₂O₃ particles. Thus, uncoated α -Al₂O₃ particles can easily absorb moisture. Then, the significant agglomeration of uncoated α -Al₂O₃ particles occurs. However, the coated α -Al₂O₃ exhibits almost no significant agglomeration. This improvement is due to the surface modification of the α -Al₂O₃ particle with stearic acid. The surface of the coated α -Al₂O₃ particle becomes hydrophobic. This phenomenon can effectively reduce the agglomeration among the coated α -Al₂O₃ particles during the extrusion processing. Figure 2(b,d) displays FE-SEM photographs ($50,000\times$) of uncoated α -Al₂O₃ and coated α -Al₂O₃ particles, respectively. The

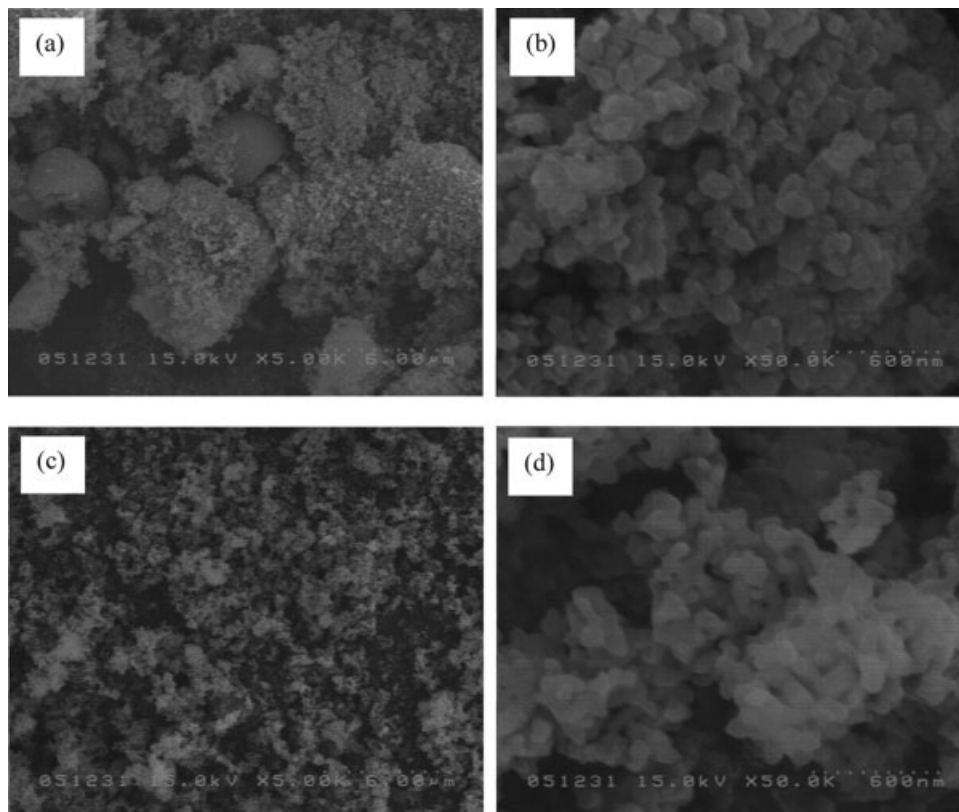


Figure 2 FE-SEM photographs of α -Al₂O₃ particles: (a) uncoated α -Al₂O₃ ($\times 5000$), (b) uncoated α -Al₂O₃ ($\times 50,000$), (c) coated α -Al₂O₃ ($\times 5000$), (d) coated α -Al₂O₃ ($\times 50,000$).

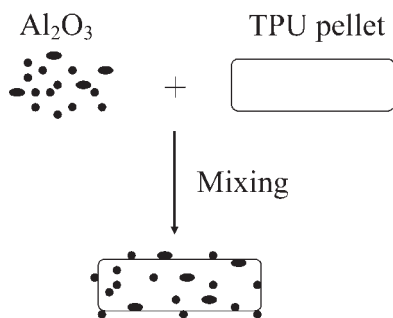


Figure 3 TPU pellets coated by nanoscale α -Al₂O₃ particles after premixing process.

particle sizes between uncoated α -Al₂O₃ and coated α -Al₂O₃ seem similar and both of them are in the range from 50 to 200 nm as shown in Figure 1. However, because of the successful surface modification, the surface of coated α -Al₂O₃ particle looks smoother than that of the uncoated α -Al₂O₃ particle.

To obtain better dispersion of nanoscale α -Al₂O₃ particles in the TPU matrix, the premixing process between the TPU pellets and α -Al₂O₃ particles is required. Figure 3 illustrates the TPU pellets coated by nanoscale α -Al₂O₃ particles after premixing process. Both the uncoated α -Al₂O₃ and the coated α -Al₂O₃ particles are inclined to coat on the surface of TPU pellets due to the interaction between the α -Al₂O₃ particles and TPU. This is due to the TPU molecule containing both hydrophobic and hydrophilic structures. The premixing process takes about 30 min in this study.

Figure 4(a–c) displays the FE-SEM photographs of the fractured surface of the 10 wt % uncoated α -Al₂O₃/TPU composite. The adopted magnifications in Figure 4(a–c) are 500 \times , 5000 \times , and 80,000 \times , respectively. The arrows shown in Figure 4(a,b) are used to point out the aggregation of uncoated α -Al₂O₃ nanoparticles. Although the uncoated α -Al₂O₃ particles are inclined to coat on the surface of TPU pellets after premixing process, they can easily agglomerate during the extrusion processing due to the polarity of the surface of uncoated α -Al₂O₃ particles. Since the surface of uncoated α -Al₂O₃ particle is not modified, the compatibility between the uncoated α -Al₂O₃ and the TPU matrix is very poor. Thus, the aggregation of uncoated α -Al₂O₃ particles is easily observed in Figure 4(a). Meanwhile, the aggregation of uncoated α -Al₂O₃ particles results in clusters significantly. At the magnification of 5000 \times , only a small portion of uncoated α -Al₂O₃ particles is observed in nanoscale dispersion [area pointed by dashed arrow; same as area I shown in Fig. 4(b)]. Most of uncoated α -Al₂O₃ particles are aggregated together to form clusters with various sizes [same as area II shown in Fig. 4(b)]. The sizes of clusters are in the range from 1 to 20 μ m. For the magnification

up to 80,000 \times , as shown in Figure 4(c), it is confirmed that the cluster is formed by many nanoscale uncoated α -Al₂O₃ particles.

Figure 5(a,b) display the EDX analyses of the fractured surfaces of the 10 wt % uncoated α -Al₂O₃/TPU composite. These two images were taken from the areas I and II identified in Figure 4(b),

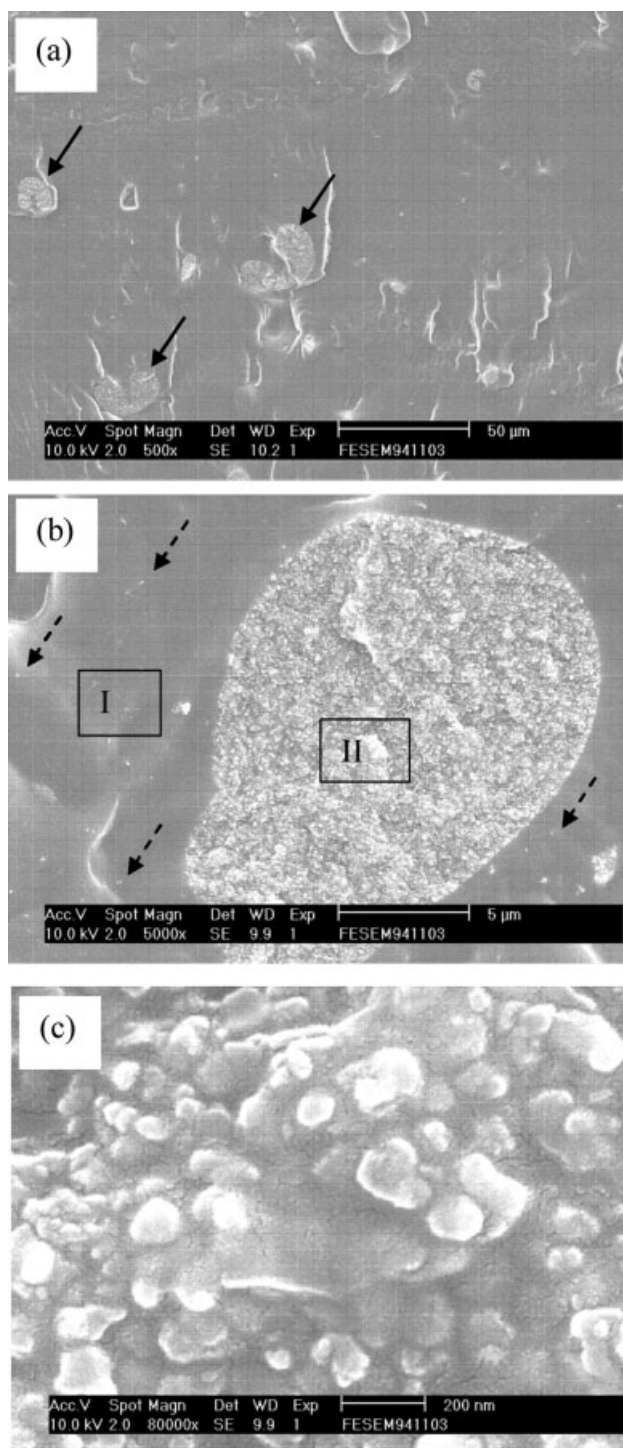


Figure 4 FE-SEM photographs of the fractured surfaces of 10 wt % uncoated α -Al₂O₃/TPU composite: (a) \times 500, (b) \times 5000, (c) \times 80,000.

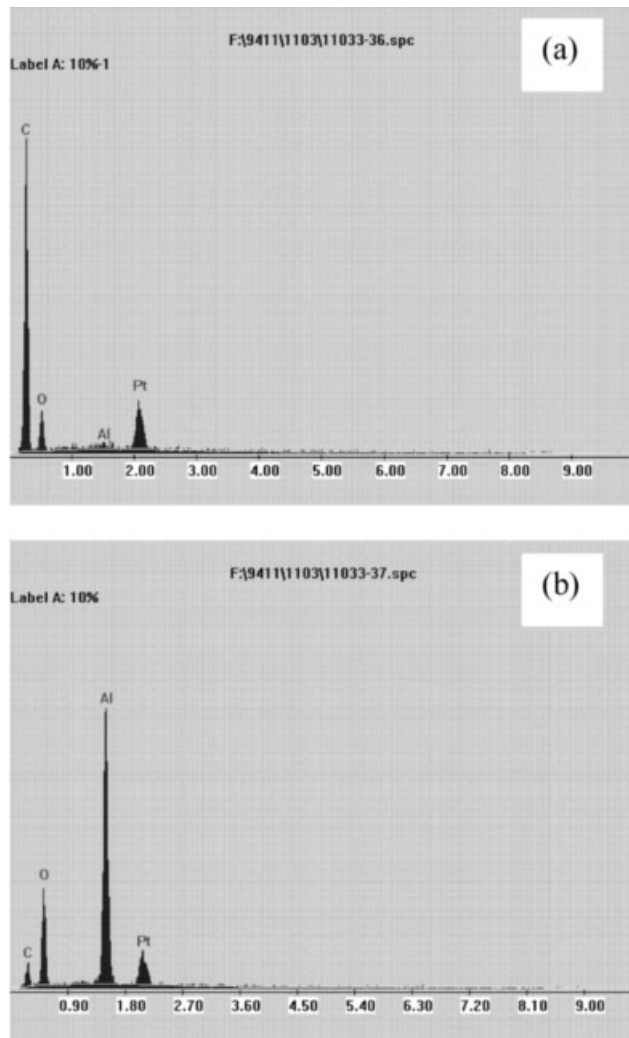


Figure 5 EDX analyses of the fractured surfaces of 10 wt % uncoated α -Al₂O₃/TPU composite: (a) area I shown on Figure 4(b); (b) area II shown on Figure 4(b).

respectively. The EDX analysis shows that there is low content of aluminum element in area I. This result also indicates that only few uncoated α -Al₂O₃ particles are well dispersed in area I. However, the EDX spectrum on area II shows very strong signal of aluminum element. This result reconfirms that the cluster is formed by the aggregation of many uncoated α -Al₂O₃ particles.

Figure 6(a–c) illustrate the FE-SEM photographs of the fractured surfaces of pure TPU, 10 wt % uncoated α -Al₂O₃/TPU, and 10 wt % coated α -Al₂O₃/TPU composites, respectively. Comparing Figure 6(a,c) with Figure 6(b), Figure 6(a,c) illustrates no hole on the fractured surface of TPU. However, holes are significantly observed in Figure 6(b). This phenomenon is resulted from the poor compatibility between uncoated α -Al₂O₃ particles and the TPU matrix. Therefore, the holes are formed when the

uncoated α -Al₂O₃ particle clusters are popped out from the fractured surface as it is made.

Figure 7(a–c) shows the FE-SEM photographs of the fractured surfaces of the 10 wt % coated α -Al₂O₃/TPU composite at different magnifications (500 \times , 5000 \times , and 80,000 \times). Comparing Figure 4(a)

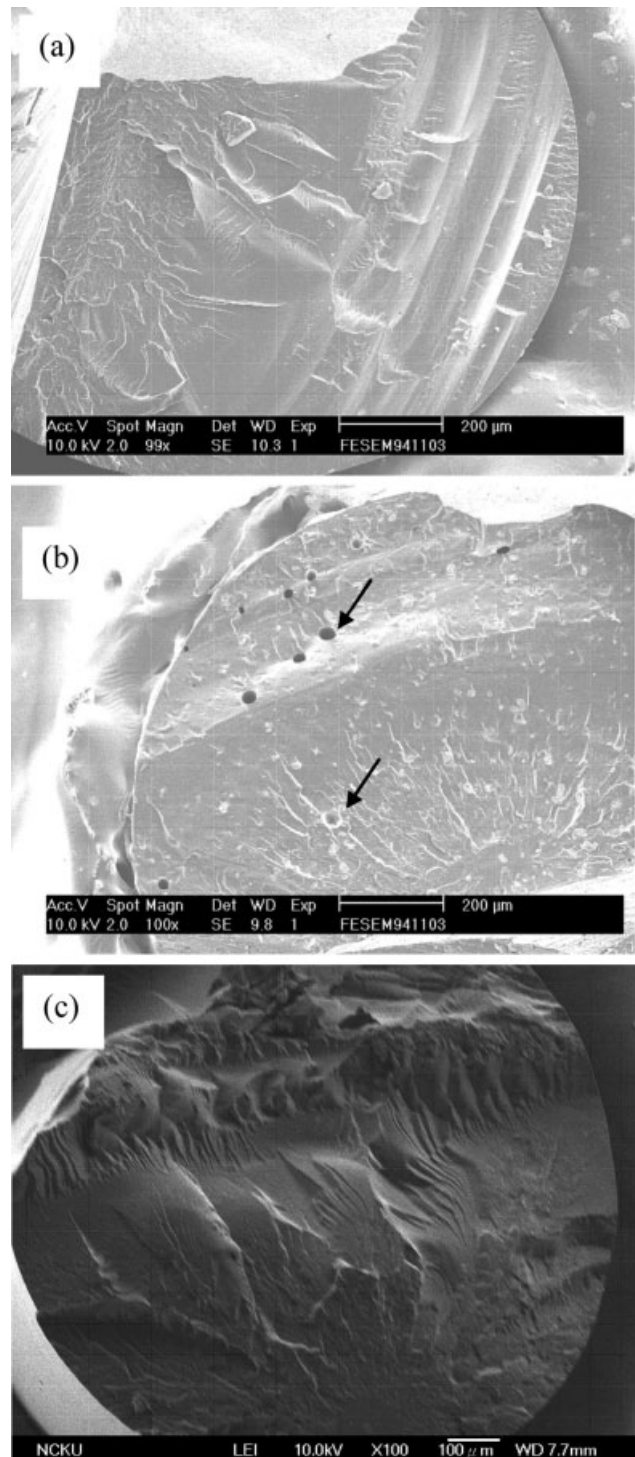


Figure 6 FE-SEM photographs of the fractured surfaces of (a) TPU, (b) 10 wt % uncoated α -Al₂O₃/TPU composite, and (c) 10 wt % coated α -Al₂O₃/TPU composite.

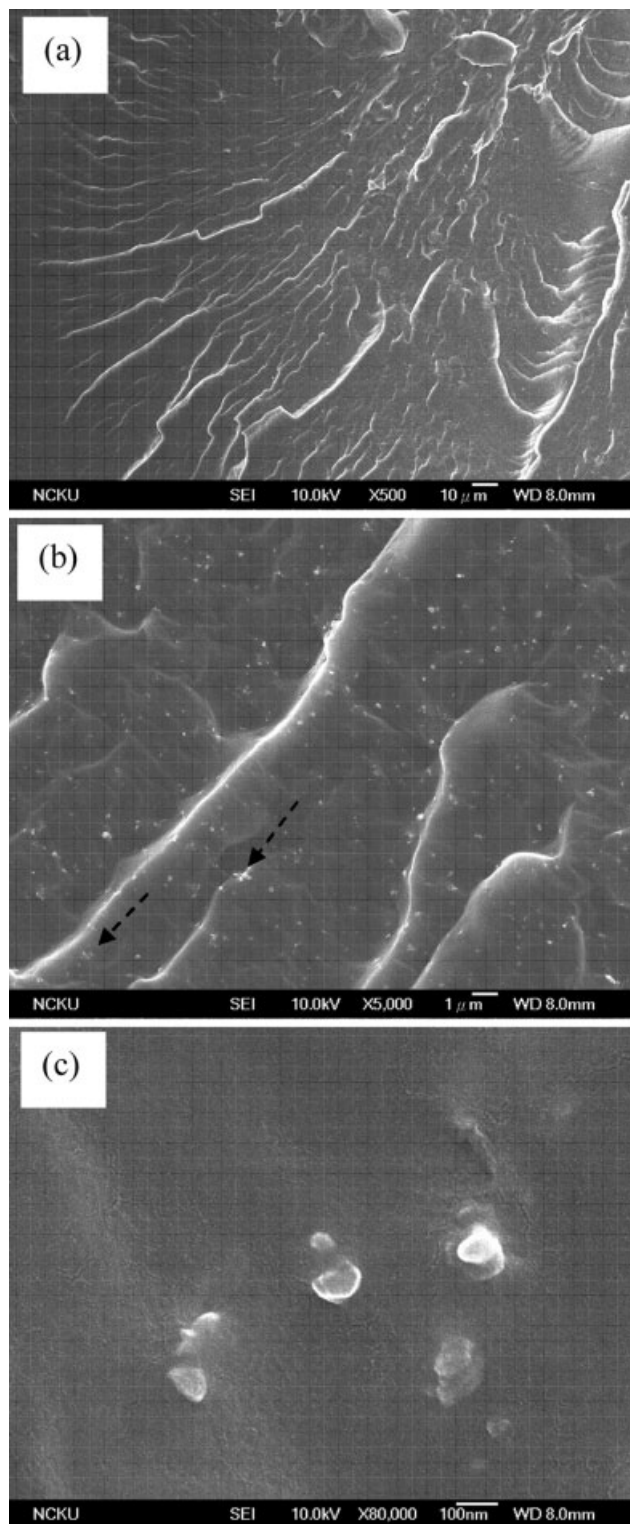


Figure 7 FE-SEM photographs of fractured surfaces of 10 wt % coated α - Al_2O_3 /TPU composite: (a) $\times 500$, (b) $\times 5000$, (c) $\times 80,000$.

with Figure 7(a), no aggregation of the coated α - Al_2O_3 particles is observed in Figure 7(a). There are two possibilities to cause this observation. One is that the coated α - Al_2O_3 particles are inclined to coat

on the surface of TPU pellets after the premixing step. The other is the surface modification of α - Al_2O_3 particles by stearic acid. Thus, the coated α - Al_2O_3 particles are not agglomerated during the extrusion processing. On the contrary, the clusters of uncoated α - Al_2O_3 particles are significantly formed, as shown in Figure 4(a). In contrast to Figure 4(b), Figure 7(b) shows that most of coated α - Al_2O_3 particles are well dispersed in the TPU matrix and only few coated α - Al_2O_3 particles are aggregated to form small clusters (as area pointed by dash arrows). The sizes of these small clusters range from 300 to 800 nm. The results imply that these small clusters are formed by 3 to 5 coated α - Al_2O_3 particles. At higher magnification, as shown in Figure 7(c), it also demonstrates that coated α - Al_2O_3 nanoparticles can be well dispersed in the TPU matrix. On the other hand, the uncoated α - Al_2O_3 particles cannot be well dispersed in the TPU matrix as shown in Figure 4(c).

These observations indicate that stearic acid coated on the surface of α - Al_2O_3 particles can act as a compatibilizer to bridge the boundary between the polymer matrix (TPU) and the nanoscale α - Al_2O_3 particles. Please note that stearic acid is a typical fatty acid which contains essentially long hydrocarbon chains. This hydrocarbon chain contains a carboxyl group at one end and a methyl group at the other. Thus, the carboxyl group of stearic acid can form a physical interaction, i.e., hydrogen bond, with the polar surface of α - Al_2O_3 . Then, the long hydrocarbon chain, $-\text{CH}_3(\text{CH}_2)_{16}$, causes the α - Al_2O_3 surface to become hydrophobic. Therefore, the surface modification of α - Al_2O_3 particles by stearic acid results in not only reducing melt viscosity during the melt blending process but also improving the dispersion of coated α - Al_2O_3 in the TPU matrix. From the FE-SEM results in Figures 6 and 7, it can be concluded that stearic acid is not only a suitable surface modifier for nanoscale α - Al_2O_3 particles, but also a good dispersion promoter between the α - Al_2O_3 particles and TPU matrix.

CONCLUSIONS

Two types of α - Al_2O_3 particles were used for the preparation of α - Al_2O_3 /TPU composites. To obtain better dispersion of nanoscale α - Al_2O_3 particles in the TPU matrix, the premixing process between α - Al_2O_3 particles and the TPU pellets is required. For the uncoated α - Al_2O_3 /TPU composite, FE-SEM results demonstrate that the uncoated α - Al_2O_3 particles are significantly aggregated to form clusters in the TPU matrix. This phenomenon results from the poor compatibility between the uncoated α - Al_2O_3 and the TPU matrix. For the coated α - Al_2O_3 /TPU composite, FE-SEM results demonstrate that many

coated α -Al₂O₃ particles are well-dispersed within nanoscale in the TPU matrix. In addition, the FE-SEM results indicate that stearic acid is not only a suitable surface modifier for nanoscale α -Al₂O₃ particles but also a good dispersion promoter between the α -Al₂O₃ particles and the TPU matrix. In the next study, the α -Al₂O₃/TPU nanocomposite will be melt blown to form an unwoven fabric and the relative properties will be discussed.

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