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Toughening mechanism of PA1010/ester-based TPU blends

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Abstract

To improve the notched impact strength of polyamide-1010 (PA1010), it was modified with a thermoplastic poly (ester urethane) elastomer (ester-based TPU). The notched impact strength of PA1010/ester-based TPU blends was investigated by using an impact tester and the fracture morphology of PA1010/ester-based TPU blends was investigated by means of SEM. In the impact experiments, it was found that the notched impact strength of the blends is obviously higher than that of pure PA1010, and the fracture surfaces of the blends show a corrugated and oriented structure. The results indicate that the brittle-to-tough transition of the blends occurs when the content of ester-based TPU is 20 wt.% and there is a new toughening mechanism, which is the multi-layer crack extension mechanism, besides the crazing with a shear-yield mechanism in the process of fracture for the blend samples under impact.

Keywords: Polyamide 1010; Thermoplastic poly (ester urethane) elastomer; Impact property; Fracture morphology; Toughening mechanism

1. Introduction

Polyamide-1010 (PA1010) is one of the important polyamide engineering plastics, which has been produced commercially in China since in the 1970s. It has high strength, high elasticity and good abrasion resistance [1], but it also has some inherent drawbacks. For example, PA1010 has a lower notched impact strength compared with polyamide-11, polyamide-12 and polyamide-1212 [2,3]. The notched impact strength of PA1010 can be improved by incorporating a toughening agent, such as thermoplastic poly urethane elastomer, into PA1010 [4,5]. In a previous study [6], the toughening mechanism of the addition of ester-based TPU into PA1010 was discussed by us, and a conclusion was made that there could be a new toughening mechanism in the toughening process of PA1010 with the addition of ester-based TPU besides the crazing with a shear-yield mechanism. However, the above conclusion was made based on the samples of anneal treatment, which is different from the samples in the present study. Because PA1010 is a semicrystalline polymer [7], the toughness of PA1010 blends will be decreased after anneal treatment, which will influence the evaluation of the toughening effect of the addition of ester-based TPU. In order to eliminate the influence of anneal treatment and give a detailed statement on the toughening mechanisms of PA1010/ester-based TPU blends, the investigation on the notched impact strength and the fracture morphology of the blends was carried out in this study.

2. Experimental

2.1. Materials

PA1010 was supplied by Jilin Nylon Chemical Engineering Limited Liability Co. (P.R. China), whose relative viscosity was 2.6. The type of ester-based TPU was JZ85, which was supplied by Tianjin Plastics Group Limited Co. (P.R. China). The parameters of JZ85 ester-based TPU were as follows: Shore hardness $A = 85$; $M_w = 310{,}692$ g/mol; $M_w/M_n = 2.76$. The soft segments of JZ85 ester-based TPU are comprised of poly (ethylene adipate) diol (PEA, $M_n = 2000$ g/mol) and the hard segments are comprised of diphenylmethane diisocyanate (MDI) and 1,4-butanediol (BOD).

Table 1
The correlation between the notched impact strength and the compositions of PA1010/ester-based TPU blends

PA1010/ester-based TPU (wt.%)	100/0	90/10	80/20
Notched impact strength (KJ/m^2)	6.3	16.0	≥237.3

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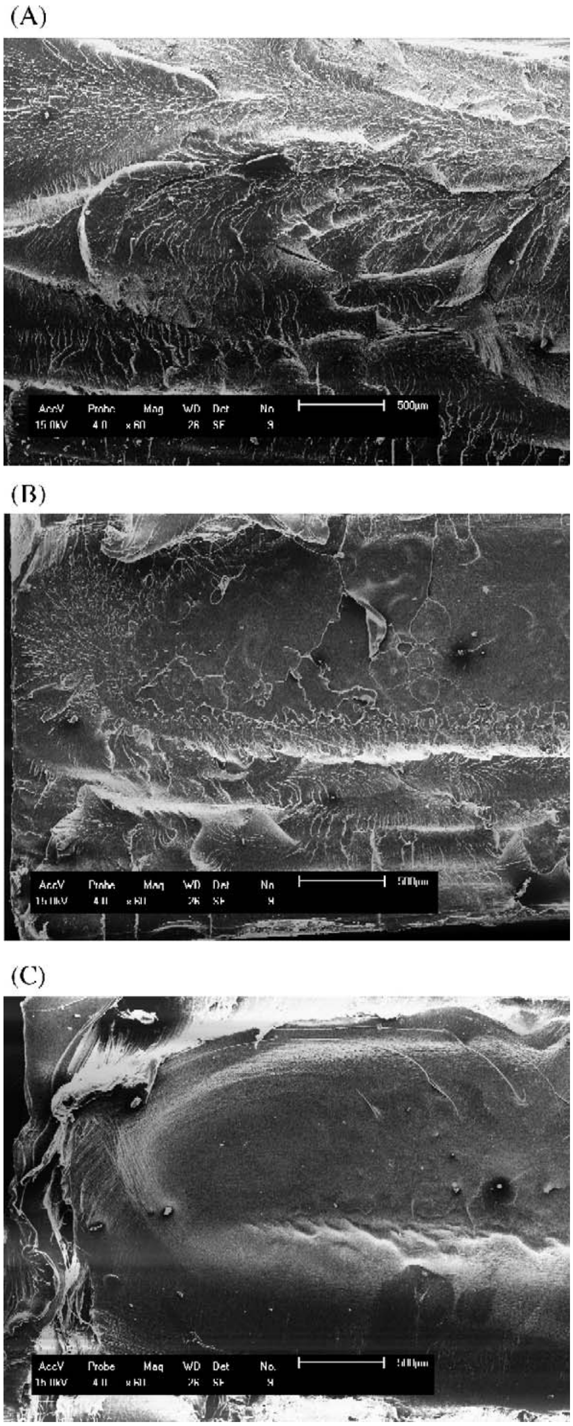

Fig. 1. The microscopic graphs of the whole fracture morphologies of the PA1010/ester-based TPU blend samples with different compositions under impact: (A) PA1010/TPU = 100/0 (scale bar = 500 μm); (B) PA1010/TPU = 90/10 (scale bar = 500 μm); (C) PA1010/TPU = 80/20 (scale bar = 500 μm).

2.2. Sample preparation

The pellets of PA1010 and ester-based TPU were dried at 100 °C in a vacuum oven for 8 h and 2 h, respectively, before melt blending. PA1010/ester-based TPU blend samples were prepared by using a Haake PTW 16/25p twin-screw extruder operating in a temperature range of 190–210 °C and at a screw speed of 45 rpm. The weight ratios of the PA1010/ester-based TPU blend samples were 100/0, 90/10 and 80/20, respectively.

2.3. Impact property measurements

Charpy notched samples with dimensions of 55 mm × 6 mm × 4 mm were molded by injection. The notched impact strength was measured by using an XJ-6 pendulum impact tester at room temperature. The average values of at least five tests are reported.

2.4. Observations of fracture morphology under impact

A Shimadzu SSX-550 Superscan scanning electron microscope was used. The Charpy notched impact fracture surfaces of the samples were gold-sputtered prior to scanning.

3. Results and discussion

3.1. Impact property

The correlation between the notched impact strength and the compositions of the PA1010/ester-based TPU blends is shown in Table 1. It can be seen from Table 1 that without the addition of ester-based TPU,

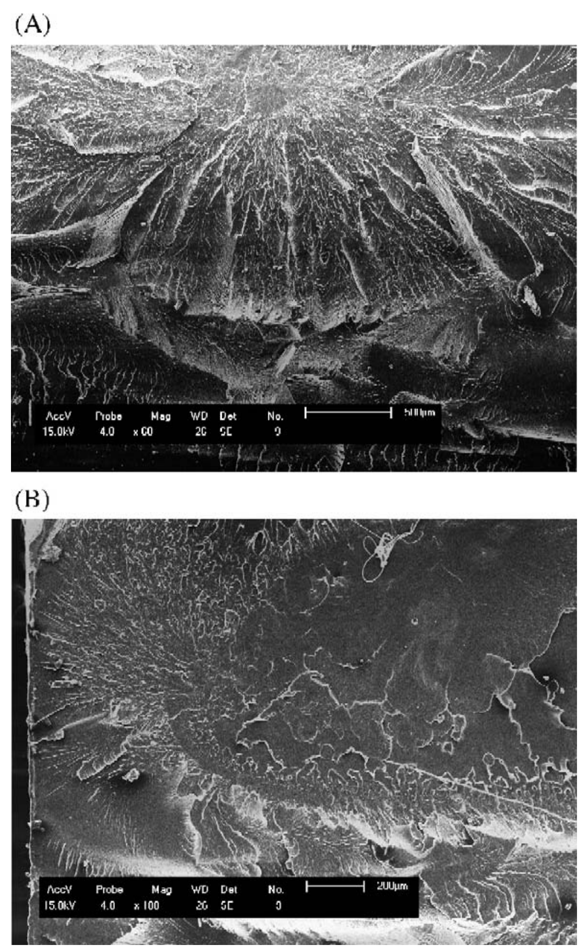

Fig. 2. The microscopic graphs of the crack morphology of PA1010/ester-based TPU blends under impact: (A) PA1010/TPU = 100/0 (scale bar = 500 μm); (B) PA1010/TPU = 90/10 (scale bar = 200 μm).

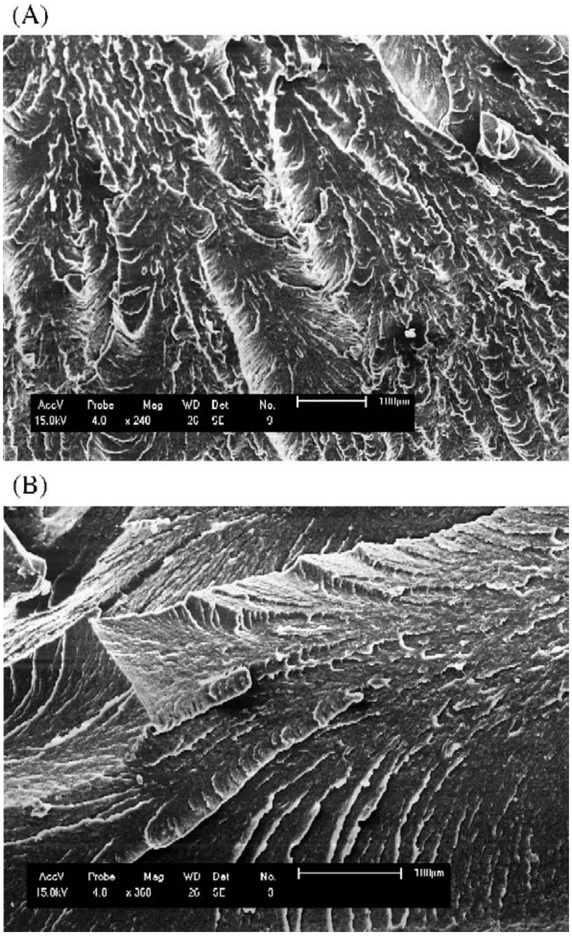

Fig. 3. The microscopic graphs of the shear lip of PA1010/ester-based TPU blends under impact: (A) PA1010/TPU = 100/0 (scale bar = 100 μm); (B) PA1010/TPU = 90/10 (scale bar = 100 μm).

the notched impact strength of PA1010 is 6.3 KJ/m^2, while it will increase to 16.0 KJ/m^2 when the content of ester-based TPU is 10 wt.%, and the notched impact strength can be as high as 237.3 KJ/m^2 when the content of ester-based TPU is 20 wt.%. Therefore, it can be concluded that the addition of ester-based TPU into PA1010 can remarkably improve the toughness of PA1010. It also can be seen from Table 1 that there is a sharp increase in the toughness of PA1010/ester-based TPU blends when the content of ester-based TPU is up to 20 wt.%, which is a sign of a brittle-to-tough transition.

3.2. Observation of fracture morphology under impact

In order to illustrate the toughening mechanisms of the addition of ester-based TPU into PA1010, detailed observations on the fracture morphologies of PA1010/ester-based TPU blends samples under impact were carried out.

Fig. 1 shows the microscopic graphs of the whole fracture morphologies of the PA1010/ester-based TPU blend samples with different compositions under impact. From Fig. 1, it can be seen that the whole fracture morphology of pure PA1010 sample is relatively scraggly. However, a smooth zone can be observed besides a scraggly zone in the whole fracture morphology of the (90/10) PA1010/ester-based TPU blend. In the whole fracture morphology of the (80/20) PA1010/ester-based TPU blend sample, there exists only a smooth zone. The scraggly zones of pure PA1010 and the (90/10) PA1010/ester-based TPU blend samples were further observed. It was found that the scraggly zones in the whole fracture morphologies of these samples consist of cracks and shear lips. Fig. 2 shows the microscopic graphs of the cracks of the pure PA1010 sample and the (90/10) PA1010/ester-based TPU blend sample under impact. From Fig. 2, it can be seen that the cracks are circle, centrosymmetrical, and radial [8]. Fig. 3 shows the microscopic graphs of the shear lips of the pure PA1010 sample and the (90/10) PA1010/ester-based TPU blend sample under impact. From Fig. 3, it can be seen that the shear lips are curly [9]. Fig. 4 shows the microscopic graphs of

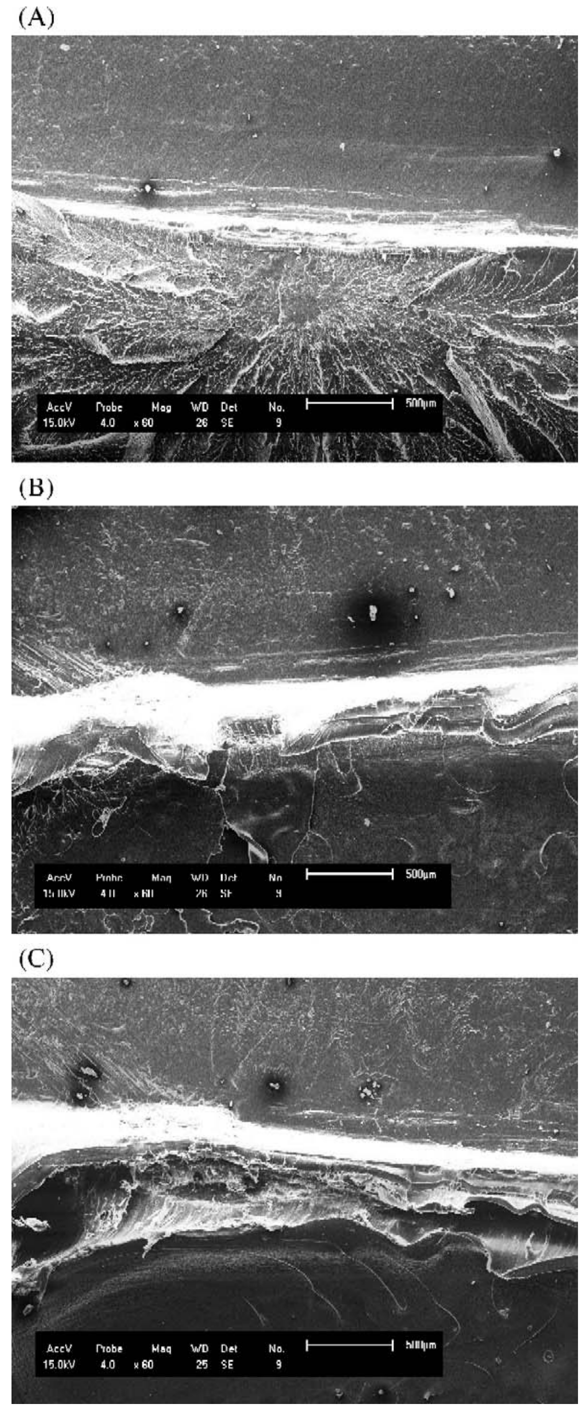

Fig. 4. The microscopic graphs of the fracture morphology of PA1010/ester-based TPU blends under impact (near the notch): (A) PA1010/TPU = 100/0 (scale bar = 500 μm); (B) PA1010/TPU = 90/10 (scale bar = 500 μm); (C) PA1010/TPU = 80/20 (scale bar = 500 μm).

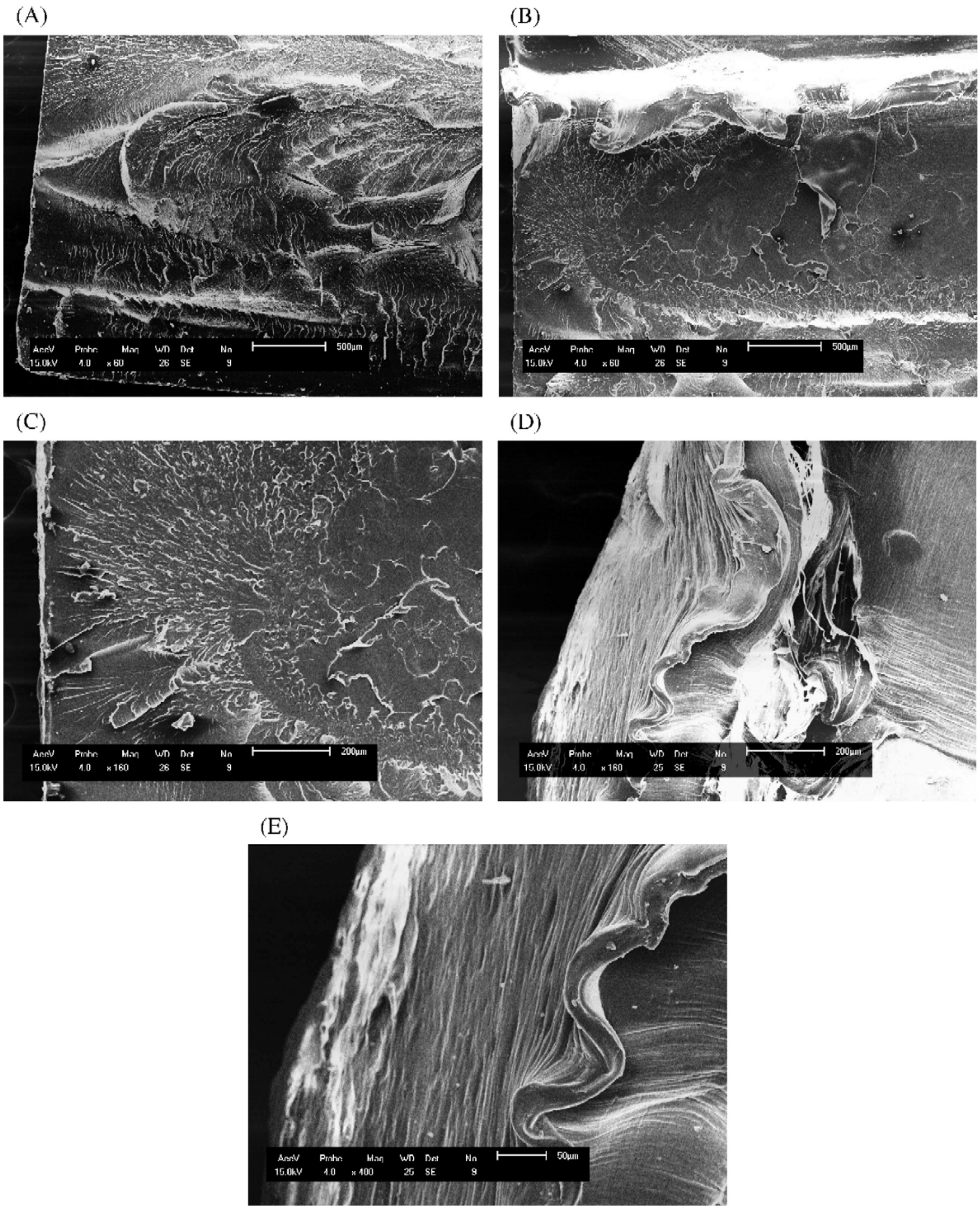

Fig. 5. The microscopic graphs of the fracture morphology of PA1010/ester-based TPU blends under impact (on the edge): (A) PA1010/TPU=100/0 (scale bar=500 μm); (B) PA1010/TPU=90/10 (scale bar=500 μm); (C) PA1010/TPU=90/10 (scale bar=200 μm); (D) PA1010/TPU=80/20 (scale bar=200 μm); (E) PA1010/TPU=80/20 (scale bar=50 μm).

the fracture morphologies of the three PA1010/ester-based TPU blend samples under impact (near the notch). From Fig. 4, it can be seen that the fracture surface of the pure PA1010 sample is smooth; but the fracture surfaces of the two PA1010/ester-based TPU blends samples are relatively rough and multi-layered. The roughness degrees or the curly degrees of the multi-layered fracture surfaces increase with increasing the content of ester-based TPU. In addition, in the single-axis tensile experiments, both the pure PA1010 sample and the PA1010/ester-based TPU blend samples show a thin-neck. The appearance of curly surfaces and a thin-neck suggest that there exists a shear-yield mechanism in the fracture process for both the pure PA1010 sample and the PA1010/ester-based TPU blend samples under impact [10].

From Fig. 4, it can be found that the fracture surfaces of the pure PA1010 sample and the PA1010/ester-based TPU blend samples (near the notch) show a stress-whitening phenomenon, which demonstrates that there exists the crazing mechanism under impact for all the samples. On the basis of the above analysis, it can be concluded that there exists the crazing of shear-yield mechanism for all the samples under impact. Because of the existence of the crazing of shear-yield mechanism, the toughening effect of the addition of ester-based TPU into PA1010 will

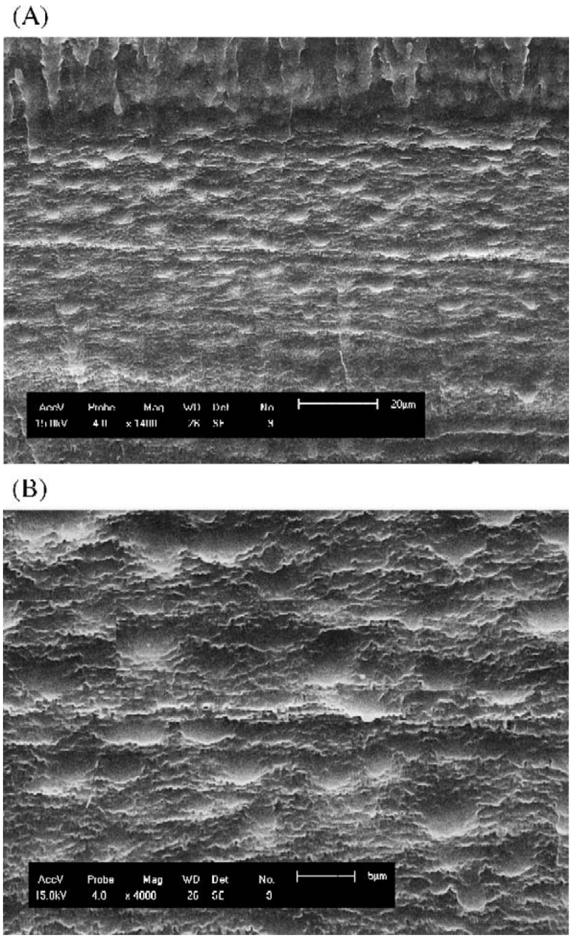

Fig. 6. The microscopic graphs of the fracture morphology in the smooth zone of PA1010/ester-based TPU blends under impact: (A) PA1010/TPU = 90/10 (scale bar = 20 μm); (B) PA1010/TPU = 90/10 (scale bar = 5 μm).

certainly depend upon the particle size distribution of ester-based TPU [11]. The detailed mechanism of this toughening effect is as follows. On the one hand, the particle size of ester-based TPU cannot be too small, otherwise the particle of ester-based TPU cannot effectively prevent crazings from developing into devastating cracks; on the other hand the particle size of ester-based TPU cannot be too big, otherwise the contacting area between the particles of ester-based TPU and the matrix of PA1010 will greatly decrease, which will reduce the number of the induced crazings. Therefore, the toughening effect of the addition of ester-based TPU into PA1010 depends upon the particle size distribution of ester-based TPU for the crazing of shear-yield mechanism.

Fig. 5 shows the microscopic graphs of the fracture morphologies of all the three PA1010/ester-based TPU blend samples under impact (on the edge). From Fig. 5, it can be seen that the edges of the pure PA1010 sample and the (90/10) PA1010/ester-based TPU blend sample show a single-layer structure (seen in Fig. 5A–C). However, the edges of the (80/20) PA1010/ester-based TPU blend sample show a corrugated and coiled structure [12,13], and the circumference of the corrugated and coiled structure shows an obviously oriented multi-layered morphology (seen in Fig. 5D and E) [6]. Fig. 6 shows the microscopic graphs of the smooth zone of the fracture surface for the (90/10) PA1010/ester-based TPU blend sample under impact. It can be found that the smooth zone shows an oriented tendency, although it is not very obvious. Figs. 7 and 8 show the microscopic graphs of the different areas of the smooth zone of the fracture surface of the (80/20) PA1010/ester-based TPU blend under impact. It was found that the smooth zone shows an obviously oriented tendency (seen in Figs. 7A and 8A). Some regions of the obviously oriented zone consist of oriented fibrillar clusters, which are perpendicular to the impact direction (seen in Fig. 7B) [12,13]. Other regions of the obviously oriented zone consist of the appreciably regular striations (seen in Fig. 8B), among which there are spaces (seen in Fig. 8C). It is noteworthy that there exist single fibre spans among the spaces (seen in Fig. 8D). Because the fracture surface of the (80/20) PA1010/ester-based TPU blend shows a corrugated and coiled structure and an obviously oriented tendency, it can be deduced that there exists a new toughening mechanism (namely multi-layer crack extension mechanism) in the process of fracture of the (80/20) PA1010/ester-based TPU blend sample under impact [12,13]. For the PA1010/ester-based TPU (90/10) blend sample, the fracture surface under impact shows a less obvious oriented tendency than the fracture surface for the (80/20) PA1010/ester-based TPU blend sample, which means that the new toughening mechanism plays a less important role. For pure PA1010, the fracture surface does not show an oriented tendency, which means that the new toughening mechanism does not exist in the fracture process. On the basis of the above analysis, it can be concluded that the multi-layer crack extension mechanism only exists in the fracture process of PA1010/ester-based TPU blends under impact. Because the fracture of PA1010/ester-based TPU blend samples under impact follows the multi-layer crack extension mechanism, the toughening effect of the addition of ester-based TPU on PA1010 depends upon the extension area and the

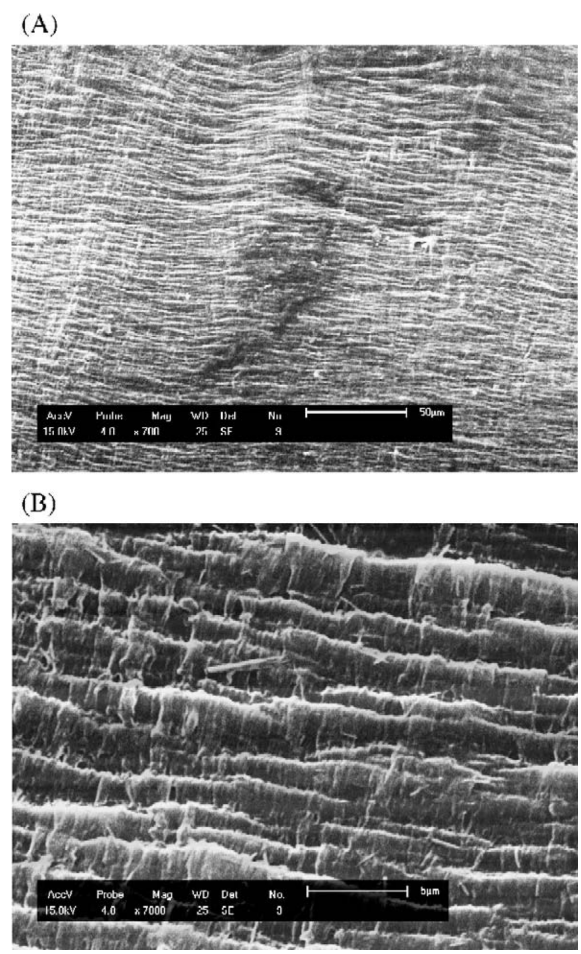

Fig. 7. The microscopic graphs of the fracture morphology in the smooth zone of PA1010/ester-based TPU blends under impact: (A) PA1010/TPU = 80/20 (scale bar = 50 μm); (B) PA1010/TPU = 80/20 (scale bar = 5 μm).

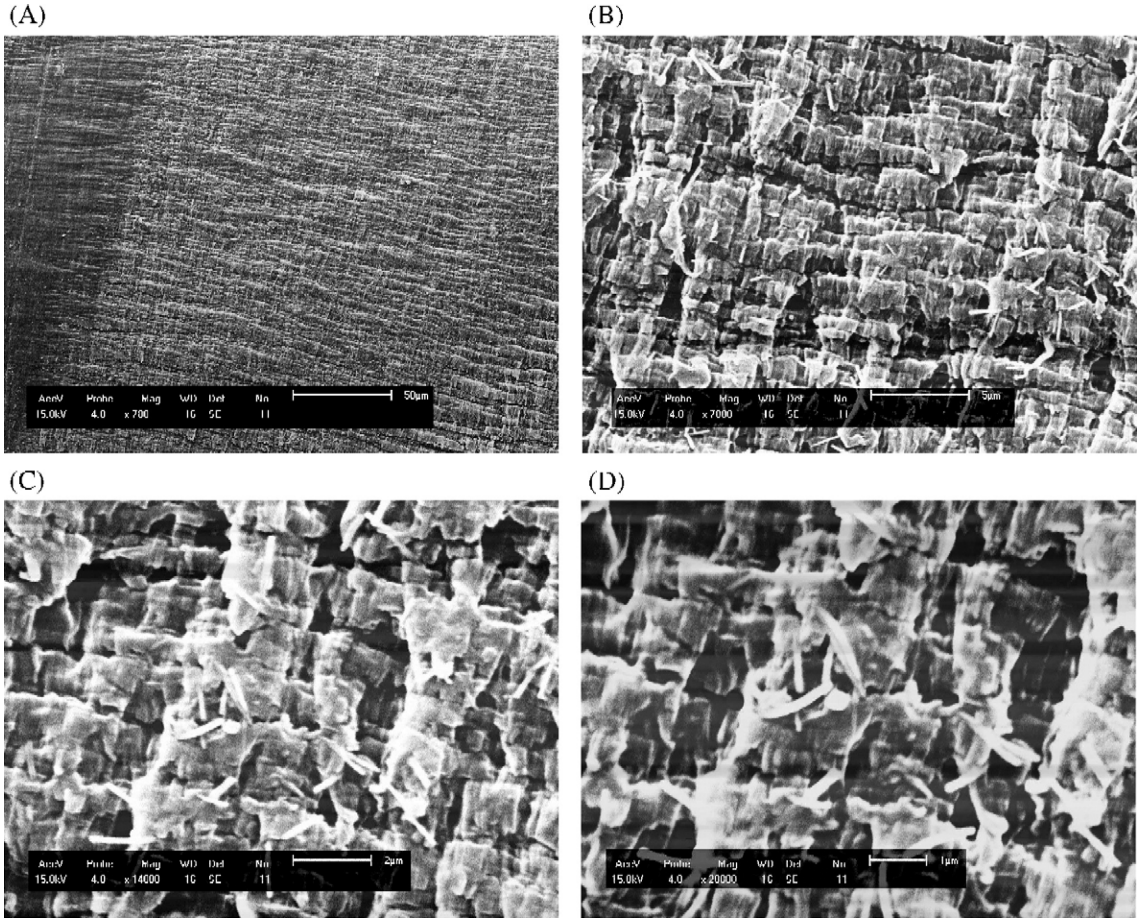

Fig. 8. The microscopic graphs of the fracture morphology in the smooth zone of PA1010/ester-based TPU blends under impact: (A) PA1010/TPU = 80/20 (scale bar = 50 μm); (B) PA1010/TPU = 80/20 (scale bar = 5 μm); (C) PA1010/TPU = 80/20 (scale bar = 2 μm); (D) PA1010/TPU = 80/20 (scale bar = 1 μm).

oriented degree of the fibrillar clusters as well as the amount of single fibre. Impact energy can be changed into "surface extension energy" and "molecular orientation energy" as well as "fibre formation energy", which is the real cause of brittle-to-tough transition. From the above analysis, it can be seen that in the fracture process of pure PA1010 under impact, there only exists the crazing with a shear-yield mechanism, but there exists the multi-layer crack extension mechanism besides the crazing with a shear-yield mechanism in the process of fracture for the (80/20) PA1010/ester-based TPU blend. By comparing with the fracture surfaces of the (90/10) PA1010/ester-based TPU blend and the (80/20) PA1010/ester-based TPU blend, it can be found that the extension area, the oriented degree of the fibrillar clusters and the amount of single fibre increase with increasing the content of ester-based TPU, which means that the contribution of the multi-layer crack extension mechanism becomes bigger and the contribution of the crazing with a shear-yield mechanism becomes smaller with increasing the content of ester-based TPU. Namely, the dominant status of one toughening mechanism will be converted into another with increasing the content of ester-based TPU.

4. Conclusions

By investigating the toughening mechanisms upon the addition of ester-based TPU into PA1010, the following conclusions can be obtained: (1) the brittle-to-tough transition of PA1010/ester-based TPU blends occurs when the content of ester-based TPU is 20 wt.%; (2) there exist two toughening mechanisms in the toughening process upon the addition of ester-based TPU into PA1010, which are the crazing with a shear-yield mechanism and the multi-layer crack extension mechanism; (3) the dominant status of one toughening mechanism will be converted into another with increasing the content of ester-based TPU, namely, the effect of the crazing with a shear-yield mechanism will be gradually weakened, and the effect of the multi-layer crack extension mechanism will be gradually strengthened with increasing the content of ester-based TPU; (4) the toughening effect of the addition of ester-based TPU into PA1010 not only depends upon the particle size distribution of ester-based TPU, but also depends upon the extension area and the oriented degree of the fibrillar clusters as well as the amount of single fibre.

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