

Toughening effect of K resin on the fracture of polyamide 6/K resin blends

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Polyamide 6 (PA6) is a semi-crystalline thermoplastic used in a wide range of engineering applications because of its attractive combination of good processability, mechanical property and chemical resistance. However, it has high moisture absorption and low resistance to crack propagation in the presence of a notch. Polymer blending is an efficient way to improve some deficient properties of these existing polymers, therefore, blends of PA6 with polycarbonate, polyphenylene oxide and glass microbead have been studied in some details. However, blending polyolefin and rubber elastomers such as styrene/butadiene/styrene copolymers, hydrogenated styrene/butadiene triblock copolymers, and ethylene-propylene-diene rubber with PA6 are the dominating approach to obtain high-toughened polyamide 6 materials [1–6]. Because of the low elastic modulus of rubber elastomers, this kind of materials will distinctly decrease stiffness K resin is a styrene-butadiene copolymer with high content styrene and much higher modulus than rubber elastomers. Until recently, very little quantitative information was available on K resin blends [7].

Recently, the essential work of fracture (EWF) method has been gaining more attention and acceptance for the toughness description of ductile polymers,

toughened polymer blends and composites, because of the simplicity of the experimental process and data manipulation [8–14]. In this paper, our work focuses on the investigation of effect of K resin on the fracture properties of PA6/K blends over the entire composition range. At the same time, the influence of incorporation of K on the fracture behavior was analyzed using the EWF method. Then, how the distribution of fracture energy in different stages affected the variation of EWF parameters was also discussed.

PA6 used in this study was obtained from UBE Industries Ltd (Japan), trademark 5033B K-Resin[®] (KR03) was supplied by Phillips Co (Korea).

Prior to use PA6 was dried for 12 h under vacuum at 100 °C to eliminate hydrolytic degradation during processing. The mixture of PA6 and K resin was melt blended in a twin-screw extruder with a temperature profile: 200, 210, 225, and 230 °C. The materials were palletized. After drying to remove the attached moisture during extrusion and palletizing, the pellets were injected into rectangular samples.

A single-edge V-shaped notch of 2 mm depth and tip radius 0.1 mm was milled in part of rectangular specimens for Charpy test. Part of the rectangle samples were compression-molded into sheets of about 0.6 mm thickness at 230 °C (except 190 °C for K) and 10 Mpa. The EWF test specimens (length × width = 80 × 20 mm) were cut from the compression-molded sheets. The pre-cracks on one side of the specimens were milled perpendicularly to the tensile direction.

The Charpy impact test was performed on a XJJ-50 plastic impact machine. The tests were carried out at ambient temperature and 55% relative humidity. The impact velocities used in the Charpy impact tests was 20 m/s.

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Electron microscopic observation of the specimens was performed with a JEOL JSM-6360 system. The specimens were fractured under cryogenic conditions using liquid nitrogen. The fractured surface so obtained was then etched with a suitable solvent: either formic acid to remove the PA6 phase or styrene to dissolve the K phase.

The EWF tests of specimens were performed by single edge notched tension (SENT) on an Instron universal testing machine equipped with a 500 N load cell and at 20 °C, while the crosshead speed was set as 10 mm/min. The load–displacement curves were recorded and the absorbed energy until failure was calculated by computer integration of the loading curves.

Figure 1 showed the dependence of the Charpy impact strength on the PA6/K ratio. It can be seen that, adding a little content K to PA6 can decrease the impact performance, this results from incompatibility between the PA6 and K phases of the blends. But with the addition of K, the impact strength of blend increased continuously, the PA6/K 50/50 blend exhibits much higher impact strength compares to pure resin and other PA6/K blends. Similar trend was observed in the ultimate elongation of the blends. This confirms that a co-continuous morphology should be responsible for the observed very high impact strength at this composition.

The morphology of the blends, as obtained by SEM, are shown in Fig. 2. Differ from other blends, the PA6/K 50/50 blend is shown in Fig. 2c. There is evidence of co-continuity; the K phase has been dissolved, leaving behind a three-dimensional porous network in and around the PA6 phase. These results indicate that a

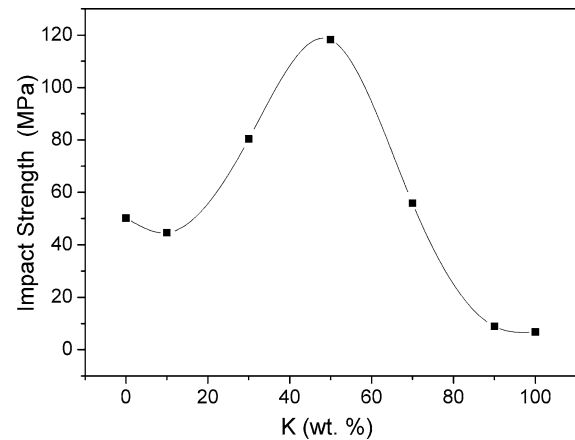


Fig. 1 Charpy impact strength of PA6/K blends with varied content of K resin

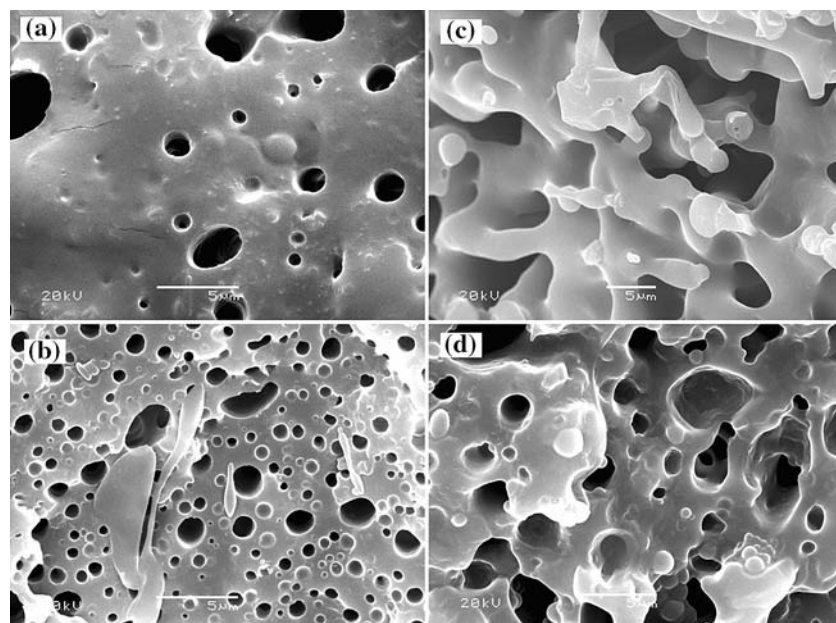
phase inversion phenomenon has occurred at around 50 wt. % K and that a co-continuous morphology is observed at this composition.

The fracture toughness of all the PA6/K blends was evaluated by the EWF method [18–20]. According to the EWF analysis, the total work of fracture (W_f), or the energy absorbed in the fracture of a test specimen, can be divided into the essential work of fracture (W_e) and the non-essential work of fracture (W_p). The W_e is surface related and proportional to ligament length, l , the W_p is volume related and proportional to the square of the ligament length, l^2 . Hence it can be written as

$$W_f = W_e + W_p \tag{1}$$

$$W_e = w_e l t, \quad W_p = \beta w_p l^2 t \tag{2}$$

Fig. 2 SEM micrographs showing the morphology of the blends: (a) PA6/K 90/10; (b) PA6/K 70/30; (c) PA6/K 50/50; (d) PA6/K 30/70



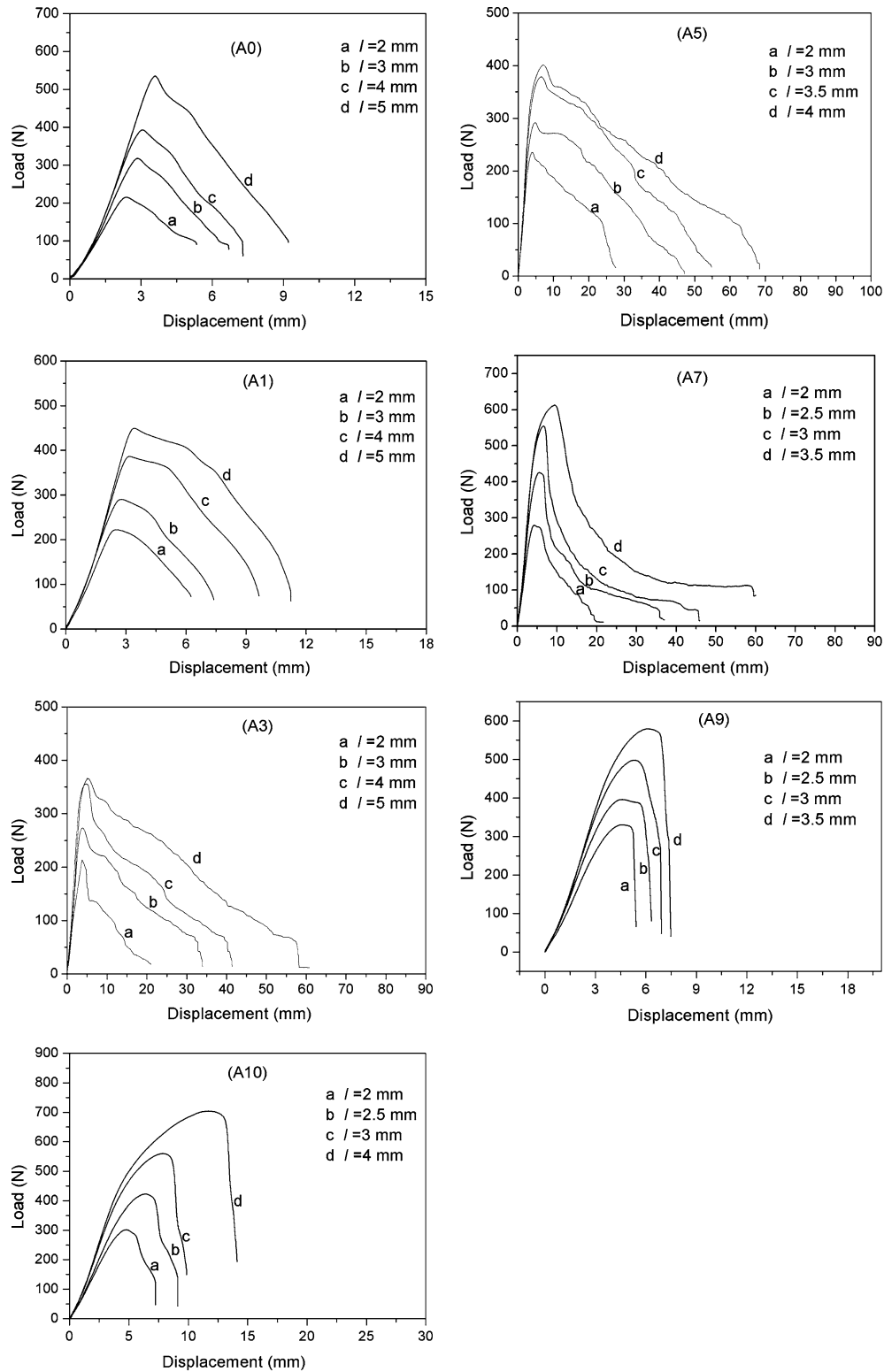


Fig. 3 Load–displacement curves for PA6/K blends at different mass ratio: (PA6 content: A0, 0%; A1, 10%; A3, 30%; A5, 50%; A7, 70%; A9, 90%; A10, 100%)

Where w_e and βw_p are the specific essential work of fracture and specific non-essential work of fracture, respectively. The parameter β is a geometry-depen-

dent plastic zone shape factor and t is the specimen thickness. The specific total fracture work, w_f , is given by:

$$w_f = W_f/l_t = w_e + \beta w_p l \tag{3}$$

According to Eq. (3), plotting w_f against ligament yield a straight line whose intercept with the w_f -axis gives w_e and whose slope is βw_p . The detail of the method was reported in many literatures [8–14].

Figure 3 showed the load–displacement curves of SENT specimens for PA6/K blends during EWF tests as a function of ligament length. Apparently, similar trends were observed for all the materials. The load increased quickly with slight increase of the displacement before the definite upper point in the initial stage. For the blends containing 0%, 10%, 70%, 90% and 100% K resin, after a peak, a smooth drop in load occurred with further increase of displacement and suddenly a rapid load drop at the end stage of the curves indicated the fracture of the specimens. It can be seen in all load–displacement curves that irrespective of the initial crack lengths, the force maximum and the elongation at break were approximately linearly increasing with the ligament length, although the stability of crack propagated of PA6/K 30/70 and PA6/K 50/50 blends were slight worse than pure resin. The curves showed that the ligament fully yielded and the crack propagated in a stable manner on the whole. With a general comparison of the curves at the same ligament length, it was found that the elongation at break increased with K content to reach a peak around 50 wt. %, which indicated the changing of ductility of the blend.

The plots of w_f versus l of PA6/K blends are shown in Fig. 4. It is worthwhile noting that the w_f – l diagrams gave very good linear relationships for all the materials studied in this work, as proved by the linear regression coefficient (R^2) being in most cases higher than 0.92.

The values of w_e and βw_p obtained from the interception and slope of the straight lines extrapolated to zero ligament length, together with the regression coefficient, are listed in Table 1. It is notable especially that w_e value of PA6 is the lowest, only 4.1 kJ/m², while w_e value of K is 55.4 kJ/m² and almost 13 times as high as that of pure PA6. It seems contrary to the result of conventional Charpy impact test. The specific essential fracture work, w_e , reflects the resistance to crack propagation of materials. In fact, it is well-known that PA6 has low resistance to crack propagation in the presence of a notch. The values of w_e denote that PA6 is easy to fracture during long service time at low stress condition, but K resin not. The higher impact toughness has been found in Charpy impact test, due to the fact that the βw_p value, i.e., the energy dissipated in the plastic deformation, of PA6 is higher than K resin.

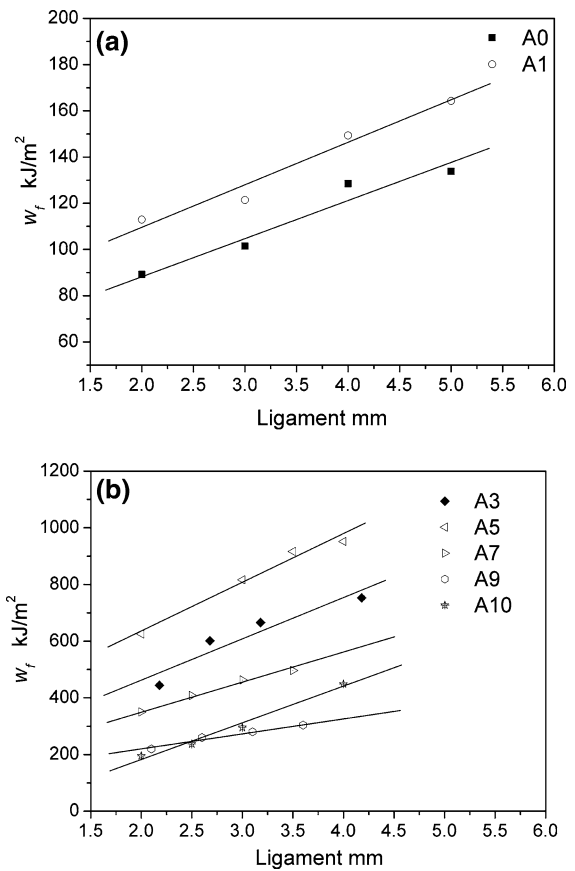


Fig. 4 Specific work of fracture against ligament length for PA6/K blends: (PA6 content: A0, 0%; A1, 10%; A3, 30%; A5, 50%; A7, 70%; A9, 90%; A10, 100%)

Most strikingly, from the values listed in Table 1, it is clear that the specific essential work of fracture, w_e , values for PA6/K blends with different K content were greatly higher than that of the pure PA6. We must call attention to the fact, though the specific non-essential work of fracture, βw_p , has not been improved, that adding a little K to PA6 can significantly enhance the crack resistance of PA6/K blends. R. Adhikari et al. systematically investigated the crack resistance behavior of binary styrene-butadiene block copolymer

Table 1 Fracture parameters for the PA6/K blends composites with varied content of PA6

Specimen	w_e (kJ/m ²)	βw_p (MJ/m ³)	R^2
PA6/K 100/0	4.1	100.1	0.97
PA6/K 90/10	143.3	44.5	0.95
PA6/K 70/30	182.1	92.7	0.92
PA6/K 50/50	297.1	169.7	0.98
PA6/K 30/70	148.9	152.0	0.94
PA6/K 10/90	68.9	19.7	0.97
PA6/K 0/100	55.4	16.6	0.96

blends, and demonstrated the existence of a novel toughening concept for polymers in incompatible polymer blends [21]. If blending the functionalized K resin with PA6, we believe that super-tough materials will be obtained. Further result is reserved for a future publication.

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