

Comparison of the Toughening Effects of Different Elastomers on Nylon 1010

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ABSTRACT: The toughness of three different elastomer-toughened nylon 1010 blends was investigated via standard notched Izod impact test and single edge notched three-point bending test. The toughness of nylon 1010 blends varies much with different elastomer types and components. All three kinds of nylon/elastomer/maleated-elastomer blends showed high impact strength (over 50 kJ m⁻²) as long as at appropriate blending ratios. With increasing maleated elastomer content, brittle-ductile transition was observed for all three kinds of elastomer-toughened nylon 1010 blends. The number average dispersed particle size (d_n) of ethylene-1-octene copolymers or ethylene-vinyl acetate copolymers toughened nylon

1010 blends significantly decreased from over 1 to 0.1 μm with increasing corresponding maleated elastomer content. Investigation on the fracture toughness showed the dissipative energy density gradually increased with decreasing d_n , while the limited specific fracture energy increased with increasing d_n when d_n was below 1 μm and then sharply decreased with further increasing d_n . The energy consumed in the outer plastic zone was the main part of the whole energy dissipated during the fracture process. © 2011 Wiley Periodicals, Inc. *J Appl Polym Sci* 121: 3340–3346, 2011

Key words: nylon 1010; elastomer; morphology; toughness

INTRODUCTION

Toughness is one of the most important properties for polymer materials. Nylon is a kind of pseudo-ductile polymer with high crack initiation energy but low crack propagation energy, and thus has high unnotched impact strength but low notched impact strength.¹ Therefore, toughening of nylon is an important topic for polymer processing and modification. The toughening of semicrystalline nylon such as nylon 6 or nylon 66 by blending with elastomers and their functional versions was extensively studied.^{2–4} The toughening effects of elastomers on nylon depended on such factors as matrix molecular weight,⁵ matrix crystallinity,^{6,7} dispersed particle size,⁸ and elastomer type.^{9–11}

Nylon 1010 is an important engineering plastic with good performance such as good low temperature toughness and self lubrication as well as relatively low water absorption ratio, and thus is widely used in the automotive and electronics

fields. The toughening of nylon 1010 by blending with suitable elastomers was reported by a few researchers.^{12–14} Chen¹² reported that the notched impact strength of nylon 1010 significantly increased by blending with saturated polyolefin elastomers functionalized with maleic anhydride. Zhang¹³ studied the toughening effect of thermoplastic polyurethane elastomer (TPU) on nylon 1010, and found the highest notched impact strength of the nylon 1010/TPU blends was achieved at the TPU content of 20 wt %. In our previous work,^{14,15} the ethylene-vinyl acetate rubber (EVM) was used as an impact modifier to toughen nylon 1010, and the results showed that EVM could significantly increase the notched impact strength of nylon 1010. In this work, styrene-ethylene-butadiene-styrene block copolymers (SEBS), ethylene-1-octene copolymers (POE), EVM and their maleated versions (SEBS-g-MAH, POE-g-MAH, and EVA-g-MAH) were used as impact modifiers to tough nylon 1010. The toughening effects of different elastomers on nylon 1010 are worth to be compared. The fracture behavior of nylon/elastomer/maleated elastomer blends would be investigated by means of modified essential work of fracture, and the corresponding parameters would be correlated with the blends morphology.

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EXPERIMENTAL

Raw materials

The nylon 1010 pellets were produced by Shanghai Salient Chemical, with the crystallinity of 26% measured by differential scanning calorimeter and the intrinsic viscosity of 83.4 mL g^{-1} (25°C , 96% H_2SO_4). EVM (Levapren 400, $\text{ML}_{1+4}^{100^\circ\text{C}} = 20 \pm 4$) with the vinyl-acetate content of 40 wt % was produced by Lanxess GmbH, (Germany). POE (Engage 8180, $\text{ML}_{1+4}^{120^\circ\text{C}} = 35$) with the octene content of 28 wt % was produced by Dow Chemical Company (Japan). SEBS with the styrene content of 32 wt % was produced by Kuraray Company. EVA-g-MAH (MV0106) and POE-g-MAH (CMG9805) were produced by Shanghai Sunny with the grafting degree of 0.5–1.2 wt % and 0.8 wt %, respectively. SEBS-g-MAH was produced by Kuraray Company (Japan) with the grafting degree of 1.7–2.0 wt %.

Sample preparation

Nylon/elastomer/maleated elastomer blends were prepared using a counter-rotating twin-screw extruder with a diameter of 25 mm and a length/diameter ratio of 41. The barrel temperatures were set at 195, 200, 205, 210, 210, 210, 210, and 205°C , and the rotor speed was 250 rpm. Prior to the melt mixing, the nylon 1010 was vacuum dried in an oven at 90°C for 12 h. Elastomers and maleated elastomers were vacuum dried at 80°C for 4 h.

The standard Izod impact specimens were prepared according to the ISO 180 in a plastic injection molding machine. The barrel temperatures were set at 205°C (hopper) and 220°C (nozzle), and the mold temperature was 45°C . The injection pressure was 40 MPa.

Measurements

Notched Izod impact strength was tested using a Ray-Ran Universal Pendulum Impact Tester (UK) at a pendulum speed of 3.5 m s^{-1} according to ISO 180. Single edge notched three point bending test (SEN3PB) specimens with dimensions of $80 \times 10 \times 4 \text{ mm}^3$ were cut from the injection-molded plaques. The notches of different depths were made first by the formation of saw cut slots having rectangular shape and then by sharpening with a fresh razor blade. The total crack length varied from 20 to 80% of the specimen width, and the ligament length (l) was measured from the original crack tip to the beginning of the hinge.

Morphology of cryogenically fractured surfaces of specimens was observed using scanning electron microscope (Hitachi-S-2150, Japan). The fractured surfaces of nylon/POE/POE-g-MAH and nylon/SEBS/SEBS-g-MAH blends were etched in boiling

toluene to remove the dispersed phase. The fractured surfaces of nylon/EVM/EVA-g-MAH blends were etched in a boiling toluene/methyl ethyl ketone (60/40, wt) mixture to remove the EVM/EVA-g-MAH phase before observation.

The dispersed particle size of nylon/elastomer/maleated elastomer blends was calculated by using a Mivnt microscopy image analysis software. At least two hundreds particles were chosen for analysis. The number average dispersed particle size (d_n) was calculated according to the following equation:

$$d_n = \frac{\sum_{i=1}^n n_i d_i}{\sum_{i=1}^n n_i} \quad (1)$$

where d_i is the particle size and n_i is the number of particles with a diameter of d_i .

RESULTS AND DISCUSSION

Notched impact strength

The type and component of elastomers significantly affect the notched impact strength of nylon/elastomer/maleated elastomer blends at ambient temperature (Fig. 1). The notched impact strength of nylon/EVM/EVA-g-MAH blends in Figure 1 was from previous work.¹⁵ For all the binary nylon/elastomer blends, the notched impact strength is relatively low (less than 20 kJ m^{-2}), and nylon/EVM (80/20) blend has the highest notched impact strength among all the binary nylon/elastomer blends. Nylon/POE/POE-g-MAH and nylon/EVM/EVA-g-MAH blends have a brittle-ductile transition (BDT) when the maleated elastomer content increases from 0 to 5 wt

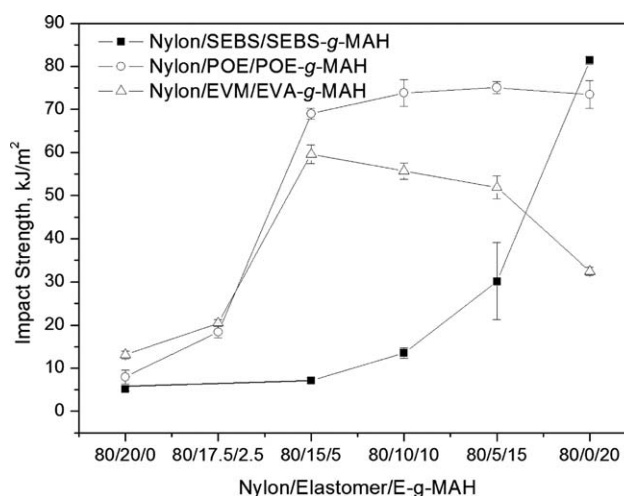


Figure 1 Notched Izod impact strength of different nylon/elastomer/maleated elastomer blends (the notched impact strength of nylon/EVM/EVA-g-MAH blends is from Ref. 15).

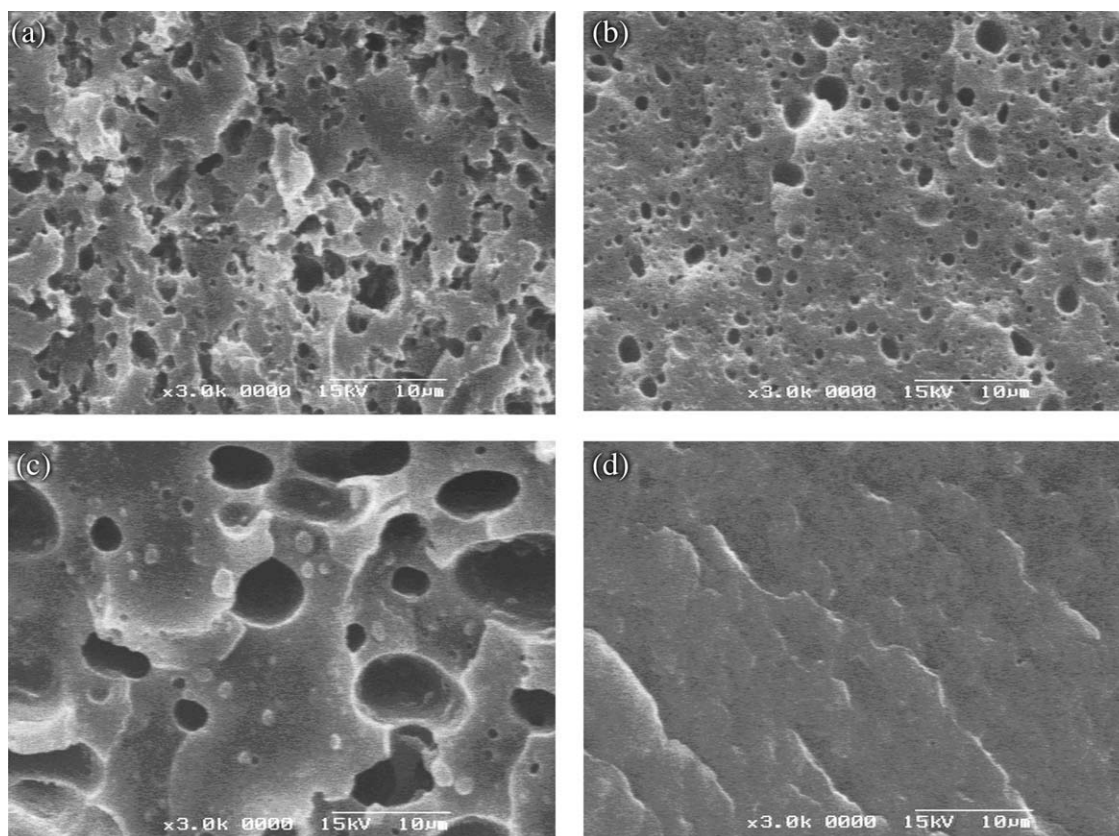


Figure 2 Morphology of different nylon/elastomer/maleated elastomer blends; (a–b) nylon/SEBS/SEBS-g-MAH blends: (a) 80/20/0 (b) 80/0/20; (c–d) nylon/POE/POE-g-MAH blends: (c) 80/20/0 (d) 80/0/20.

%. To be more accurate, the BDT occurs when the maleated elastomer content increases from 2.5 to 5 wt % for both nylon/EVM/EVA-g-MAH and nylon/POE/POE-g-MAH blends. With further increasing maleated elastomer content, the notched impact strength of nylon/POE/POE-g-MAH blends has little change while the notched impact strength of nylon/EVM/EVA-g-MAH blends gradually decreases but is still much higher than that of nylon 1010 (4.4 kJ m^{-2}). The decrease in the notched impact strength of nylon/EVM/EVA-g-MAH with increasing EVA-g-MAH content should be attributed to the relative high crystallinity of EVA-g-MAH, as reported in the previous work.¹⁵ The notched impact strength of nylon/SEBS/SEBS-g-MAH blends gradually increases with increasing SEBS-g-MAH content, and a BDT is observed when the SEBS-g-MAH content increases from 15 to 20 wt %. The nylon/SEBS-g-MAH (80/20) blend has the highest notched impact strength (81.4 kJ m^{-2}) at ambient temperature among all the blends studied in this work.

Morphology

The morphology of nylon/elastomer/maleated elastomer blends is also significantly affected by the elastomer types and components (Fig. 2). Both

EVM¹⁵ and POE are found to be dispersed as spherical particles, and the dispersed particle size of nylon/EVM/EVA-g-MAH and nylon/POE/POE-g-MAH blends significantly decreases with increasing maleated elastomer content. SEBS exists as irregular particles in nylon/SEBS (80/20) blend, and with increasing SEBS-g-MAH content the dispersed particles of nylon/SEBS/SEBS-g-MAH blends become more spherical but the corresponding particle size changes a little.

The d_n of blends was calculated according to eq. (1) (Fig. 3). For nylon/EVM/EVA-g-MAH and nylon/POE/POE-g-MAH blends, d_n significantly decreases with increasing maleated elastomer content, which was attributed to the increased interfacial interactions caused by the reaction between maleic anhydride group and nylon 1010 chain. The nylon/EVM/EVA-g-MAH blends have much smaller d_n than the corresponding nylon/POE/POE-g-MAH blends. The d_n of nylon/SEBS/SEBS-g-MAH blends, however, is around $1 \mu\text{m}$ and merely has a little change with increasing SEBS-g-MAH content. The elastomer particle size distribution is also very important in determining the toughness of elastomer-toughened plastics. Huang et al.¹⁶ reported that the bimodal distribution of dispersed particle size was observed in nylon 6/POE/POE-g-MAH blends

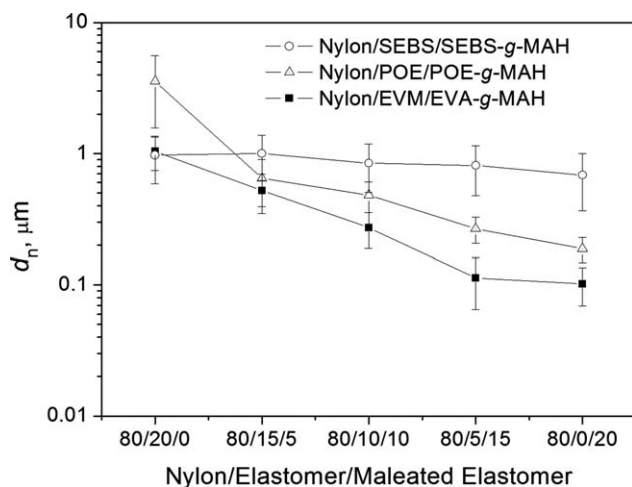


Figure 3 The d_n of different nylon/elastomer/maleated elastomer blends.

if the maleation level was too high and such bimodal distribution would usually play a negative role in the toughening process. The nylon/POE/POE-g-MAH (80/10/10) and nylon/EVM/EVA-g-MAH (80/10/10) blends have a unimodal distribution of dispersed particle size (Fig. 4). The particle size distribution of nylon/SEBS/SEBS-g-MAH (80/10/10) blend, however, looks like bimodal, implying a poor compatibility between SEBS and SEBS-g-MAH and contributing to the relative low notched impact strength of the nylon/SEBS/SEBS-g-MAH (80/10/10) blend.

Fracture behavior

Although the standard notched Charpy and Izod impact tests are commonly used to characterize the toughness of polymers due to their simple convenient test methods, they merely reveal the total energy dissipation during the whole test and fail to provide a more detail information on the toughness of materials.¹⁷ In this work, the modified essential work of fracture (EWF) model¹⁸ is used to characterize the fracture behavior of the nylon/elastomer/maleated elastomer blends. In the modified EWF model, the total fracture energy per unit area (U/A) is given by

$$U/A = u_0 + u_d l \quad (2)$$

where l is the ligament length, u_0 is the limited specific fracture energy related to energy dissipated in the inner fracture process zone, and u_d is the dissipative energy density related to the energy dissipated in the outer plastic zone. Since the two parts of specimens could not be completely separated after the SEN3PB test, the actual ligament length l used in the test is the length of stress whitening zone in the

fracture direction.¹⁹ By plotting U/A against l , the intercept of the linearly fitted line is u_0 and the slope is u_d .

Taking nylon/POE/POE-g-MAH blends as examples, the POE/POE-g-MAH ratio significantly affects the load-displacement curves in SEN3PB test (Fig. 5). All the load-displacement curves of nylon/POE (80/20) and nylon/POE-g-MAH (80/20) blends are similar, indicating the geometry similarity during the growth of crack between samples with different l . All SEN3PB tests were automatically stopped when the load dropped below a threshold value (3 N). For nylon/POE (80/20) blend, the load reaches the maximum value and sharply decreases to the threshold value with little decay, indicating the crack propagation is fast with a small amount of energy dissipation. For nylon/POE-g-MAH (80/20) blend, the load slowly decreases to the threshold value from the maximum load, indicating a large amount of energy dissipation during the crack propagation.

The total fracture energy (U) was calculated by integrating the corresponding load-displacement curves, and then the U/A was plotted against l . Figure 6 plots the fitted line between U/A and l of nylon/POE/POE-g-MAH blends as an examples. A good linearity was obtained for all the blends, indicating the applicability of the modified EWF method. The intercept, u_0 , is associated with the energy dissipated in the inner fracture process zone while the slope, u_d , is associated with the energy dissipated in the outer plastic zone. The u_d of the nylon/POE (80/20) blend is near to zero, indicating that the energy is mainly consumed in the inner fracture process zone and little energy is dissipated in the outer plastic zone. The u_d of nylon/POE/POE-g-MAH blends sharply increases when the POE-g-MAH content increases from 0 to 5 wt %. The

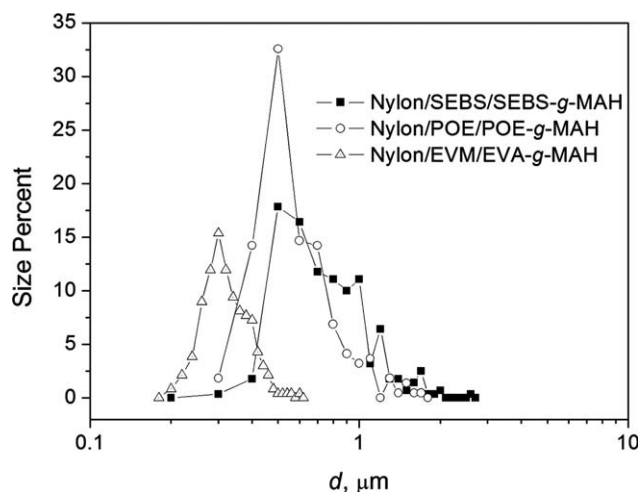


Figure 4 Particle size distribution of nylon/elastomer/maleated elastomer blends.

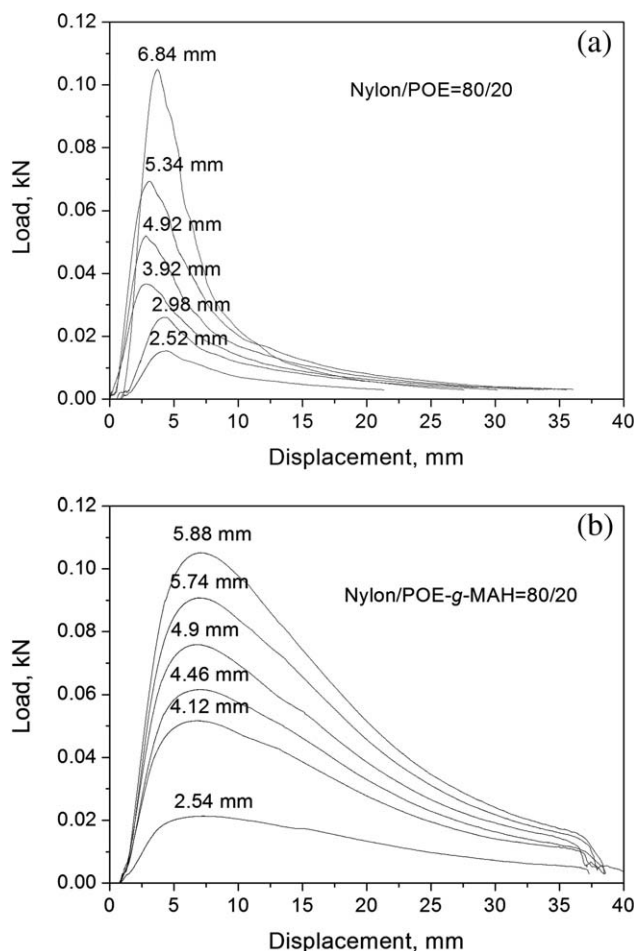


Figure 5 Load-displacement curves for specimens with different ligament lengths of (a) nylon/POE (80/20) and (b) nylon/POE-g-MAH (80/20) blends in SEN3PB test.

increase of u_d indicates increasing energy dissipation in the outer plastic zone and toughness of the corresponding blends.

The EWF parameters are highly dependent on the d_n of nylon/elastomer/maleated elastomer blends

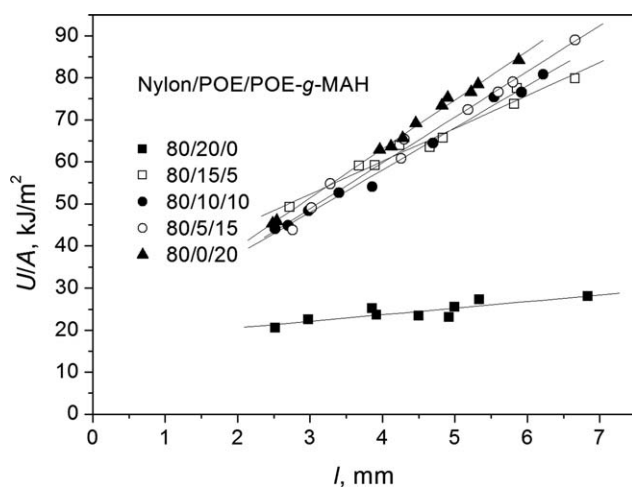


Figure 6 $U/A \sim l$ for nylon/POE/POE-g-MAH blends.

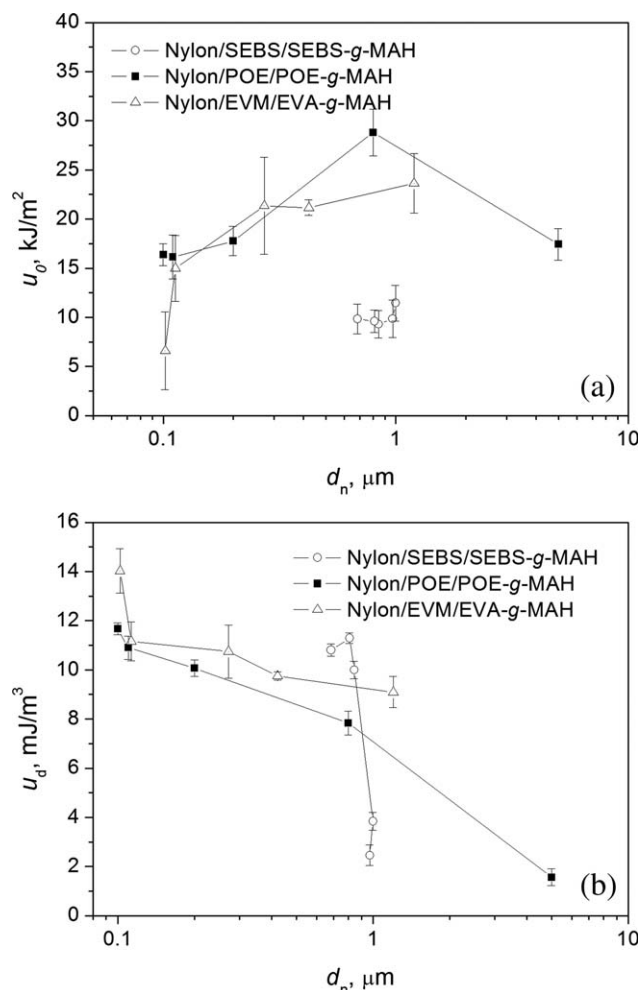


Figure 7 Fracture parameters as a function of d_n for different nylon/elastomer/maleated elastomer blends. (a) u_0 (b) u_d .

(Fig. 7). For all the blends examined, u_d gradually increases with decreasing d_n while u_0 increases with increasing d_n when d_n is below 1 μm and then sharply decreases with further increasing d_n . Similar phenomena have also been reported in the nylon 6/ethylene propylene rubber and nylon 6/SEBS blends.¹¹ The nylon/elastomer/maleated elastomer blends with small d_n have low u_0 but high u_d , and also high notched impact strength which indicates that u_d is more important in determining the toughness of blends and the energy consumed in the outer plastic zone is the main part of the total energy dissipation during fracture process. The u_d of nylon/EVM/EVA-g-MAH blends is higher than that of nylon/POE/POE-g-MAH blends at a similar dispersed particle size, which indicates that the former blends show more extensive plastic deformation than the latter blends in ductile fracture. The u_0 of nylon/SEBS/SEBS-g-MAH blends is much lower than that of nylon/EVM/EVA-g-MAH blends. u_0 is the energy dissipated in the inner fracture process zone to form

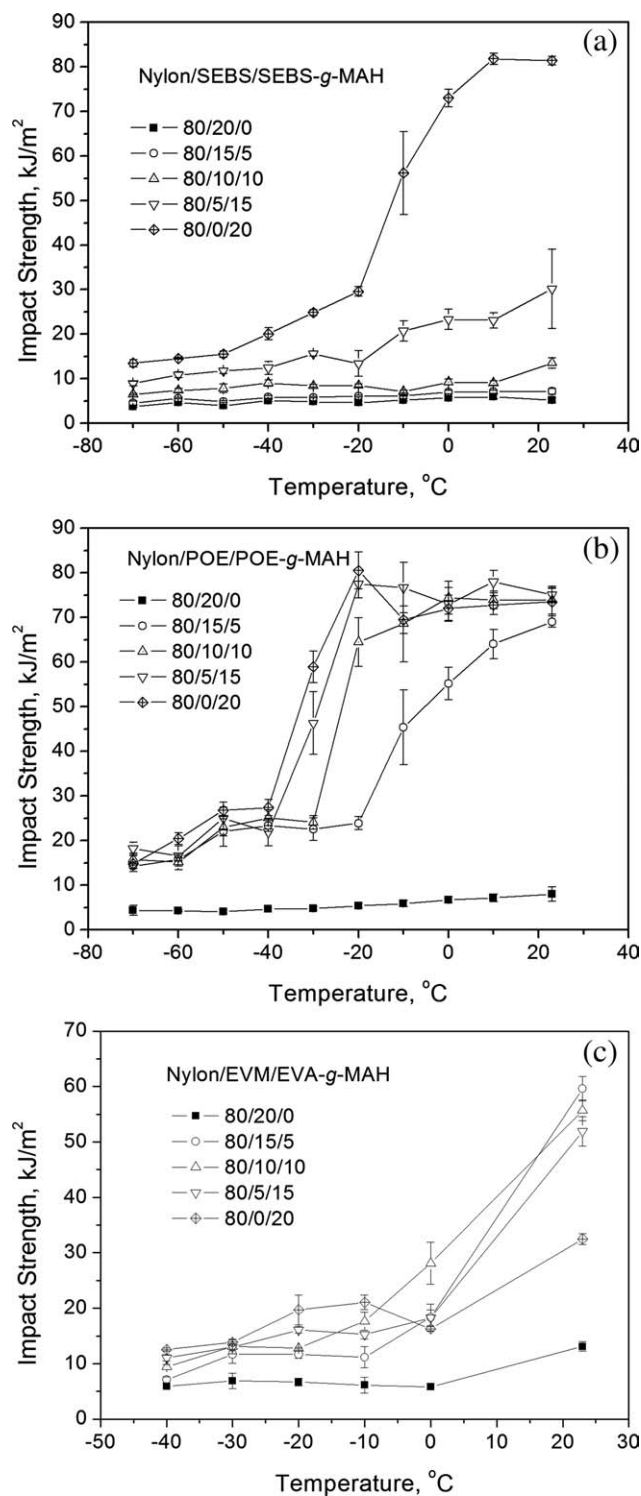


Figure 8 Notched impact strength as a function of testing temperature for different nylon/elastomer/maleated elastomer blends. (a) nylon/SEBS/SEBS-g-MAH; (b) nylon/POE/POE-g-MAH, (c) nylon/EVM/EVA-g-MAH.

new fracture surfaces including rubber particles cavitation, the shear yielding of matrix in the fracture surface etc. Lazzeri and Bucknall²⁰ reported that the shear modulus of rubber is important in determining the cavitation of rubber particles in rubber-tough-

ened plastic. The lower the shear modulus of rubber phase is, the easier its cavitation becomes. Because SEBS is effectively crosslinked by the polystyrene domains¹¹ while EVM is nearly amorphous polymer, EVM should have lower modulus than SEBS. As a result, the cavitation and shear yielding around the crack tip in nylon/EVM/EVA-g-MAH blends would occur more easily than nylon/SEBS/SEBS-g-MAH blends, and thus the former blends have higher μ_0 than the latter.

Low temperature toughness

The notched impact strength at low temperatures of nylon/elastomer/maleated elastomer blends was also investigated. The appearance and position of the BDT of nylon/elastomer/maleated elastomer blends highly depend on the type and component of elastomers (Fig. 8). For the nylon/SEBS/SEBS-g-MAH blends, BDT is observed only in nylon/SEBS-g-MAH (80/20) blend. For the nylon/POE/POE-g-MAH blends, BDT is observed for blends with the POE-g-MAH content no less than 5 wt %, and the BDT temperatures shift towards low temperature with increasing POE-g-MAH content. The nylon/POE-g-MAH (80/20) blend has the lowest BDT temperature (-30 °C) among all the blends studied in this work. For the nylon/EVM/EVA-g-MAH blends, the observed BDT temperatures remain around ambient temperature and are almost independent of the EVA-g-MAH content, which should be attributed to the following two factors. EVA-g-MAH could significantly improve the dispersion of EVM in nylon 1010 matrix, which has a positive effect on the toughness of corresponding blends. On the other hand, the relative high crystallinity of EVA-g-MAH due to its low vinyl acetate content has a negative effect on the toughness.¹⁵ It is the net effect of these two factors that the BDT temperatures of nylon/EVM/EVA-g-MAH blends are independent on the EVA-g-MAH content.

CONCLUSIONS

Nylon 1010 blends with high impact strength (over 50 kJ m^{-2}) were successfully prepared by blending nylon 1010 with styrene-ethylene-butadiene-styrene block copolymers (SEBS), ethylene-1-octene copolymers (POE), ethylene-vinyl acetate rubber (EVM) and their corresponding maleated versions (SEBS-g-MAH, POE-g-MAH, and EVA-g-MAH). All three kinds of elastomer could act as effective impact modifiers to significantly improve the toughness of nylon 1010. The elastomer type and component significantly affected the notched impact strength and also the phase morphology of nylon/elastomer/maleated elastomer blends. The dispersed particle

size gradually decreased with increasing maleated elastomer content, which is mainly attributed to the increased interfacial interactions and contributes to the increased toughness of nylon 1010 blends. Investigation on the fracture behavior of nylon/elastomer/maleated elastomer blends by modified essential work of fracture model showed the fracture parameters were highly dependent on the number average dispersed particle size (d_n). The dissipative energy density (u_d) for all the blends decreased with increasing d_n while the limited specific fracture energy (u_0) increased with increasing d_n in the range of $d_n < 1 \mu\text{m}$ and sharply decreased with further increasing d_n . The energy consumed in the outer plastic zone was the main part of the total energy dissipated during fracture process. The nylon/POE-g-MAH (80/20) blend had the best low temperature toughness among all the blends.

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