Work of Fracture of Polystyrene/High Density Polyethylene Blends Compatibilized by Triblock Copolymer

S. C. TJONG,[1] S. A. XU,[1,2] R. K. Y. LI[1]

[1] Department of Physics and Materials Science, City University of Hong Kong, 83 Tat Chee Avenue, Kowloon, Hong Kong

[2] Institute of Polymer Science and Engineering, East China University of Science and Technology, 130 Mei-Long Road, Shanghai 200237, People's Republic of China

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ABSTRACT: The fracture toughening behavior of polystyrene/high density polyethylene blends compatibilized by 10 wt % of a styrene-ethylene-butylene-styrene triblock copolymer (SEBS) was assessed using single-edge notched tension (SENT) and double-edge notched tension (DENT) specimens of various gauge lengths over a wide range of tensile rates. The fracture of DENT and SENT specimens was completely ductile under the plane-stress condition. A linear relationship was observed between the specific total work of fracture and the ligament length (L) for a given L range. The results showed that the essential work (w_e) was independent of the tensile rate (R) range of 1–30 mm/min, and it then decreased considerably when R was increased to 50 mm/min and above. However, the nonessential work exhibited a rate independent trend behavior. In addition, w_e and the specific nonessential work of fracture (βw_P) were basically independent of the gauge length (G), provided that G was greater than the width of the sample. Finally, it was also shown that the w_e and βw_P values for SENT specimens are obviously greater than those for DENT specimens. © 2000 John Wiley & Sons, Inc. J Appl Polym Sci 77: 2074–2081, 2000

Key words: essential work; polystyrene; polyethylene; fracture toughness; ligament length

INTRODUCTION

Polymeric materials are widely used as structural material for engineering applications. It is of practical interest to understand the deformation and fracture toughening behavior of polymers and their blends.[1] For the characterization of the fracture behavior of brittle polymers, such as polystyrene (PS) or poly(methyl methacrylate) (PMMA), linear elastic fracture mechanics (LEFM) is one of the most frequently used methods.[2] LEFM deals with the fractures occurring at nominal stresses that are well below the uniaxial yield stress of the material. Under this condition, plastic flow at the tip of the crack is intimately associated with the fracture process, which is brittle in nature.[3] The fracture toughness in the LEFM concept can be represented in terms of the stress-intensity factor, K, or the strain-energy release rate, G. The stress-intensity factor is based on the stresses around a crack tip, and the strain-energy release rate is a measure of the energy available to extend a crack of a unit area.[4] Failure generally occurs when K (or G) reaches a critical value. Therefore, the critical stress-intensity factor (K_C) or the critical strain-energy release rate (G_C) is sufficient to characterize the fracture behavior of brittle polymers.[3] However, these two

Correspondence to: Prof. S. C. Tjong.

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parameters can be best characterized only when the plane-strain conditions exist. To achieve this state, the size or the geometry of the specimens must satisfy certain requirements. According to the ASTM standard,[5] the limitation imposed on the specimen size is given as follows,

$$a,\ B,\ W - a \geq 2.5\left(\frac{K_C}{\sigma_Y}\right)^2 \tag{1}$$

where a is the crack length; B and W are the specimen thickness and width, respectively; $W - a$ is the ligament length; and σ_Y is the uniaxial yield stress of the material. For brittle material such a size restraint in determining K_C presents no practical difficulties.[6] However, the restriction of the small scale yielding places a severe limitation on the application of LEFM in characterizing the fracture toughness of ductile and semiductile materials.[3] In this case, two approaches appear to be more appropriate to characterize the failure of ductile polymers,[7] which are the J integral and the essential work of fracture.

The J-integral approach was proposed by Rice.[8] It is a path independent line integral expressed in terms of energy,

$$J = -\frac{1}{B}\frac{dU}{da} \tag{2}$$

where U is the potential energy of the loaded body. The critical value of the J integral is the J_C. In J_C measurement a certain size criteria of the specimen must also be satisfied to generate a plane-strain constraint along the crack front. According to the ASTM method for J_C determination, the specimen size must meet the following requirement[9]:

$$B,\ W,\ W - a \geq 25(J_C/\sigma_Y) \tag{3}$$

For polymeric materials with a high value of σ_Y, this requirement is easy to meet and their fracture can be characterized by the J-integral approach.[10,11] On the contrary, for polymers having a low σ_Y, such as polypropylene (PP) and polyethylene (PE), the size limitation presents some practical difficulties.[12] Another approach used to characterize the fracture toughness of ductile materials is the essential work concept, which was originally proposed by Broberg.[13] When a ductile specimen containing a crack is loaded, the plastic flow occurs in an outer plastic zone that borders the fracture process zone (Fig. 1). The total work of fracture, W_f, is considered to be made of two components: the essential work (W_e) required to fracture the polymer in the process zone and nonessential or plastic work (W_p) dissipated by various deformation mechanisms in the outer plastic zone. Therefore, W_f can be expressed as

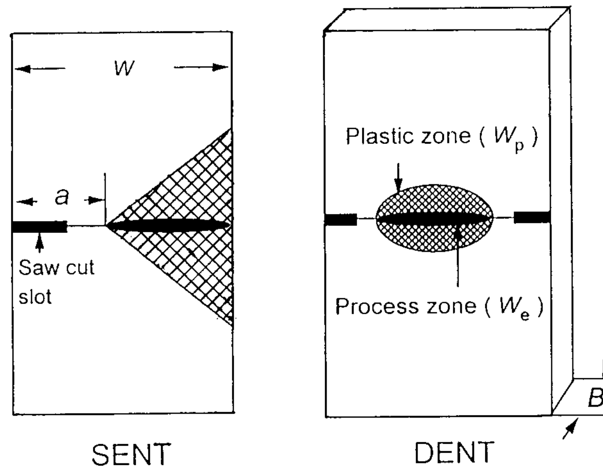

Figure 1 Schematic diagrams showing the single-edge notched tension (SENT) and double-edge notched tension (DENT) specimens.

$$W_f = W_e + W_p \tag{4}$$

Taking into consideration that W_e is surface related whereas W_p is volume related, W_f can be given by the related specific work terms,[13–17]

$$W_f = w_e LB + \beta w_p L^2 B \tag{5}$$

$$w_f = \frac{W_f}{LB} = w_e + \beta w_p L \tag{6}$$

where w_f is the specific total fracture work; w_e and w_p are the specific essential fracture work and specific plastic work, respectively; L is the ligament length; and β is a shape factor of the plastic zone. Based on eq. (6), the specific essential work can be easily obtained from the intercept of the linear plot of w_f versus L. However, the explicit determination of w_p is very difficult because of the lack of knowledge of the shape factor β. In recent years, several researchers have successfully used the essential work concept to characterize the fracture toughness of polymer materials.[3,4,7,18–26]

In this article we attempt to use the essential work concept to characterize the fracture toughening behavior of a ductile high density PE

(HDPE)/PS blend compatibilized by a styrene-ethylene-butylene-styrene triblock copolymer (SEBS) (i.e., PS/HDPE/SEBS 10/80/10). This blend is selected because its tensile ductility is much higher than that of pure HDPE. In a previous study[27] we studied the tensile and impact properties of an HDPE/PS blend compatibilized by a triblock SEBS copolymer. Tensile measurements showed that the elongation at break of the compatibilized HDPE/PS blends was dramatically increased with increasing HDPE content. Charpy impact measurements indicated that the impact strength of the blends increased slowly with HDPE content up to 50 wt %, followed by a significant increase with further increasing HDPE content. Moreover, the elongation at break and the impact strength of some HDPE-rich blends exceed those of pure HDPE.[27]

EXPERIMENTAL

Materials

The homopolymers used in this investigation were commercial grades of PS (Styron 667, Dow Chemical Company) and HDPE (blow film B5429, Mobil, Saudi Arabia). The triblock copolymer SEBS (G1652, Shell) had the respective molecular weights of the PS block and central EB block of 7500 and 37,500 and the PS weight fraction was 28.6%.

Blending Conditions and Sample Preparation

All study materials were separately dried overnight in ovens at 80°C for PS and HDPE and at 60°C for SEBS. The PS/HDPE/SEBS 10/80/10 blend was prepared by mixing the well-dried pellets in a twin-screw extruder (Brabender Plasticorder) operating at 190–200°C. The extrudates were pelletized and then dried at 100°C for 12 h. Using these pellets, plaques with dimensions of 200 × 80 × 3.2 mm were injection molded using a Chen Hsong machine. The barrel zone temperatures were set at 200, 210, and 220°C.

Fracture Tests

The tensile experiments were conducted at room temperature (22°C) using an Instron tensile tester (model 4206). Double-edge notched tension (DENT) specimens and single-edge notched tensile (SENT) specimens with dimensions of 200 × 25 × 3.2 mm were used. They were cut from the injection molded plaques with the longitudinal direction of the specimens parallel to the melt flow direction. The notches were prepared by first forming saw cut slots, which were then sharpened with a razor blade. The razor blade was mounted on a laboratory attachment so that penetration could be carefully controlled. The fresh edge of a razor was then slowly pushed through the material to a depth of about 1 mm. The exact ligament length (L) was measured by a travelling microscope (Topcon Profile Projector). The load applied during extension was monitored with a load cell of an Instron tensile tester.

For DENT specimens the essential work measurements were conducted over wide ranges of tensile rates and gauge lengths (G). The tensile rate ranged from 1 to 100 mm/min, and the gauge length varied from 25 to 150 mm. For SENT specimens the experiments were carried out under a constant tensile rate of 10 mm/min and a gauge length of 100 mm.

RESULTS AND DISCUSSION

Effect of Tensile Rate

The effect of the tensile rate (R) on the work of fracture was investigated using DENT specimens with $G = 100$ mm. Figure 2 depicts the typical load–displacement diagrams of the PS/HDPE/SEBS 10/80/10 blend at various ligament lengths for DENT specimens having a gauge length of 100 mm at 10 mm/min. It is apparent from this figure that all of the specimens fracture in a ductile manner under the testing conditions employed. This implies that all specimens exhibit gross yielding and necking in the tensile process. Careful examination of Figure 2 reveals that the shape of the load–displacement curves for specimens with higher ligament lengths ($L \geq 15.83$ mm) is different from that of lower ligament lengths ($L \leq 12.69$ mm). However, Kocsis et al. reported that the fracture mode of an amorphous copolyester is independent of the ligament length and the shape of the load–displacement curves for specimens at various ligament lengths is similar.[20] They also indicated that the essential work of fracture concept is valid only when the shape of the load–displacement curves of the specimens with various ligament lengths is similar. Therefore, the essential work concept cannot be applied in the whole range of ligaments as shown in Figure 2.

From the areas under the load–displacement diagrams, the specific work of fracture (w_f) is

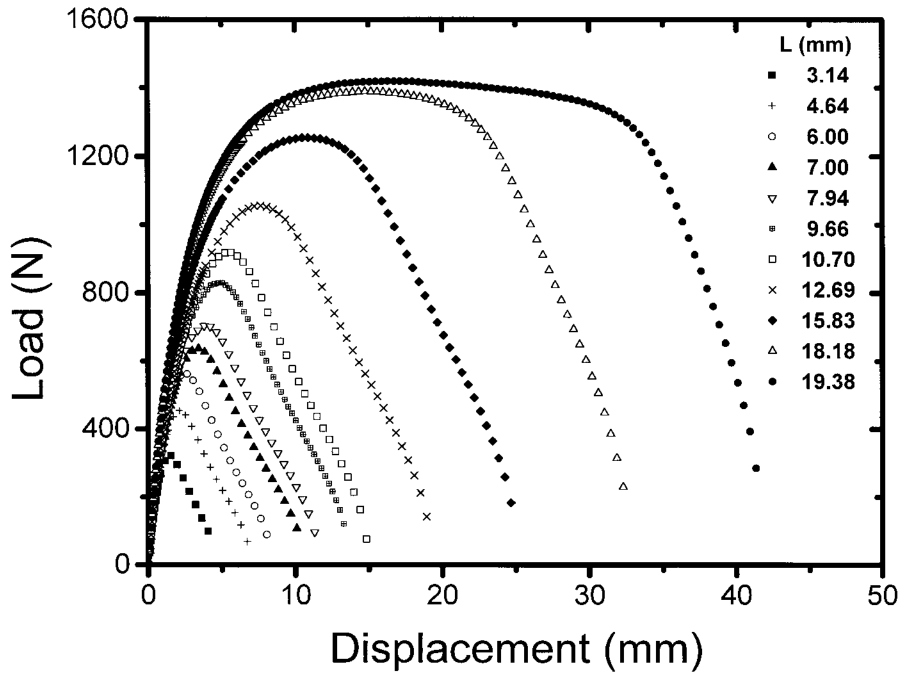

Figure 2 Load–displacement diagrams for DENT specimens at various ligament lengths tested at a crosshead displacement rate of 10 mm/min (B = 25 mm, G = 100 mm).

determined and plotted against the ligament length (L, Figs. 3–8). It is evident from these figures that a linear relationship exists between w_f and L at low values of L. However, an obvious deviation occurs at larger values. Moreover, a linear regression method is used to analyze the linear portion of the data in Figures 3–8, and the results are summarized in Table I. This table also lists the critical ligament value (L_C) in which nonlinearity in each plot begins to occur. Apparently, Table I reveals that L_C tends to increase with increasing tensile rates.

As can be seen, the essential work (w_e) and nonessential work (βw_p) are nearly independent of the tensile rates within a range of 1–30 mm/min. In this tensile rate range employed w_e ranges from 28.45 to 33.62 kJ/m^2. As the tensile rate increases to 50 mm/min and above, the w_e value is reduced considerably. Kocsis and Czi-

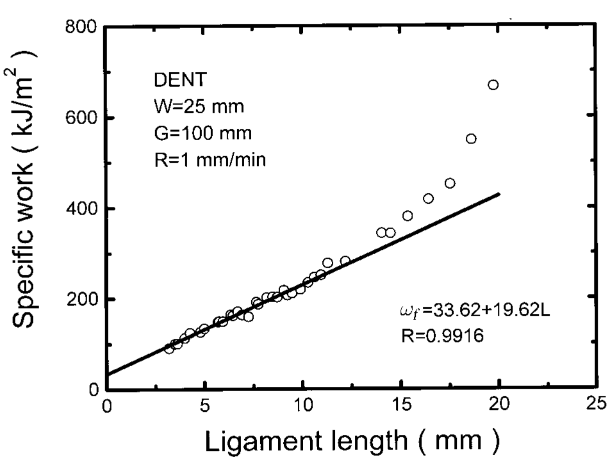

Figure 3 The w_f vs. L for DENT specimens tested at a tensile rate of 1 mm/min (B = 25 mm, G = 100 mm).

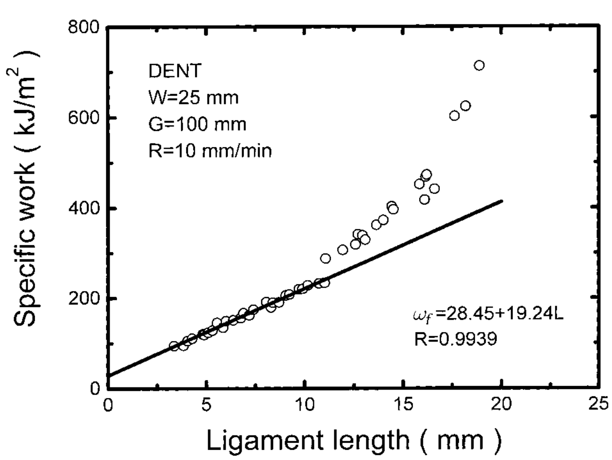

Figure 4 The w_f vs. L for DENT specimens tested at a tensile rate of 10 mm/min (B = 25 mm, G = 100 mm).

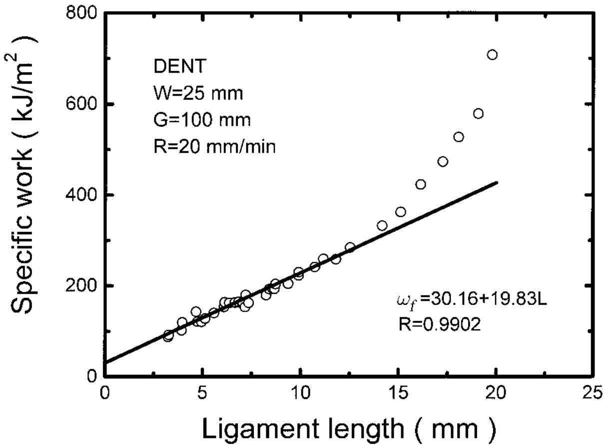

Figure 5 The w_f vs. L for DENT specimens tested at a tensile rate of 20 mm/min (B = 25 mm, G = 100 mm).

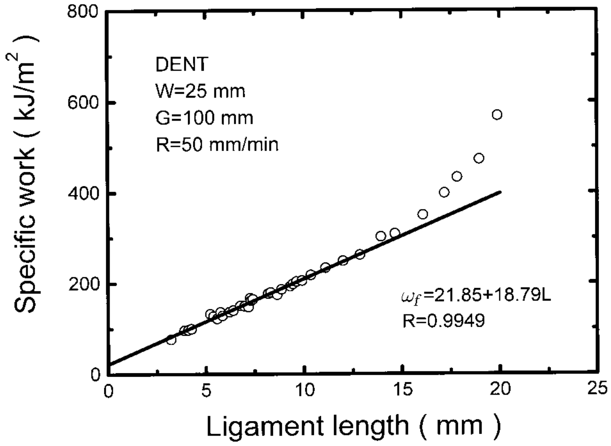

Figure 7 The w_f vs. L for DENT specimens tested at a tensile rate of 50 mm/min (B = 25 mm, G = 100 mm).

gany[7] and Hashemi[22] studied the effect of the tensile rate on w_e. They concluded that increasing the crosshead speed had no effect on w_e but markedly increased the slope of the regression line (i.e., βw_p). It is well known that the toughness of polymers deteriorates (or remains unchanged) when the tensile rate increases. Furthermore, a ductile to brittle transition generally occurs with increasing tensile rates for many polymer materials. Therefore, the fracture work should decrease or remain unchanged when the tensile rate is increased. Consider the case where w_e is independent of the tensile rate while βw_p is increased: the fracture work should increase with an increasing tensile rate for the sample with a given L because w_f is composed of w_e and $\beta w_p L$. This obviously contradicts the general experimental results.

Effect of Gauge Length

The effect of the specimen gauge length (G) on the work of fracture was evaluated using DENT specimens under a tensile rate of 10 mm/min. Figures 9–11 show the plots of w_f versus ligament length at various gauge lengths, and the results from these plots are summarized in Table II. Figure 9 shows that the specimen gauge length employed is 25 mm, and such a length is identical to the width of the sample. In this case the data points are more scattered or dispersed than those with larger G values, and the correlation coefficient is only 0.8908. This implies that a linear relationship between w_f and L may not hold when the gauge length is close to or less than the width of the sample. Moreover, it can be seen in Table II

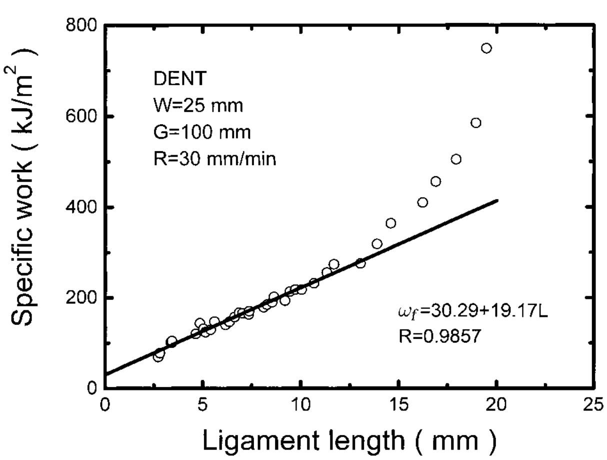

Figure 6 The w_f vs. L for DENT specimens tested at a tensile rate of 30 mm/min (B = 25 mm, G = 100 mm).

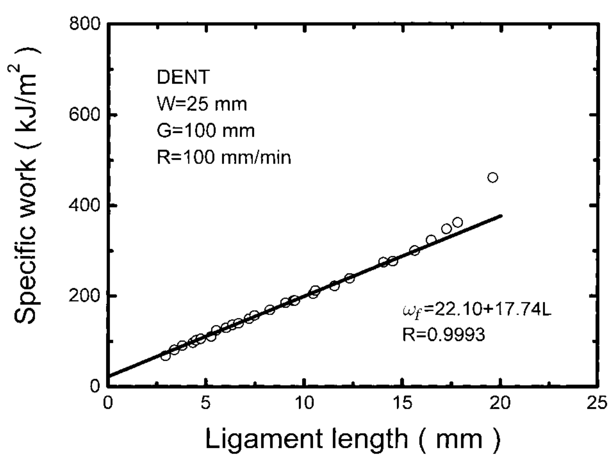

Figure 8 The w_f vs. L for DENT specimens tested at a tensile rate of 100 mm/min (B = 25 mm, G = 100 mm).

Table I Effect of Tensile Rate on Fracture Work of PS/HDPE/SEBS 10/80/10 Blend

R (mm/min)	Regression Equation	ω_l (kJ/m^2)	$\beta\omega_p$ (kJ/m^2)	r	L_C (mm)
1	$\omega_f = 33.62 + 19.62L$	33.62	19.62	0.9916	11.0
10	$\omega_f = 28.45 + 19.24L$	28.45	19.24	0.9939	11.0
20	$\omega_f = 30.16 + 19.83L$	30.16	19.83	0.9902	12.5
30	$\omega_f = 30.29 + 19.17L$	30.29	19.17	0.9857	13.0
50	$\omega_f = 21.85 + 18.79L$	21.85	18.79	0.9949	13.0
100	$\omega_f = 22.10 + 17.74L$	22.10	17.74	0.9993	15.6

R, tensile rate; ω_l, essential work; $\beta\omega_p$, nonessential work; r, correlation coefficient; L_C, critical ligament length; ω_f, total work of fracture.

that the w_e shows little variation for the specimens with G ranging from 50 to 100 mm. On the other hand, the specimen gauge length has little effect on βw_p when the gauge length is larger than the sample width. It is worth pointing out that the relationship between βw_p and G is rather complicated. Paton and Hashemi[3] reported that βw_p was independent of the gauge length G for polycarbonate (PC). However, Hashemi indicated that the βw_p decreases with increasing G for the poly(butylene terephthalate) (PBT)/PC blend,[22] and he attributed the increase in βw_p to a greater stability of the specimens with longer gauge lengths during loading.

Effect of Specimen Geometry

Figure 12 shows the plot of w_f versus L for SENT specimens (100-mm gauge length, 25-mm width) tested at a crosshead speed of 10 mm/min. Apparently, the w_f varies linearly with the L within the tensile rates studied. Table III tabulates the results determined from the plots of Figures 4 and 12. It is evident that the W_e and βw_p for SENT are 58.43 and 30.97 kJ/m^2, respectively, which are much higher than those of DENT specimens. Paton and Hashemi[3,22] also studied the effect of sample geometry on the w_e and βw_p of PC and PBT/PC samples. They reported that the w_e is independent of the geometry of the test piece.[3] This is in contradiction with our results above. The difference may arise from the polymeric materials used and from the smaller sample thickness employed by Paton and Hashemi. Although they claimed that there is little variation in w_e with the geometry of the test specimen of PBT/PC,[22] we noted that the w_e for SENT is generally higher than that for DENT with the exception of the sample with a thickness of 0.25 mm (table II of ref. 22).

Validity of Test Results

For a valid determination of w_e one has to consider the following conditions.[14,23] First, the liga-

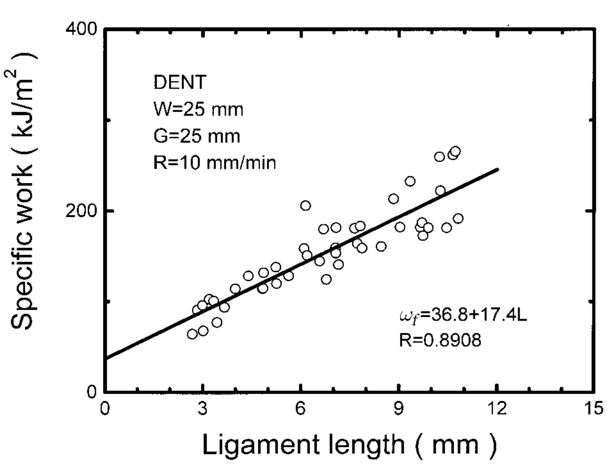

Figure 9 The w_f vs. L for DENT specimens with a gauge length of 25 mm (B = 25 mm, R = 10 mm/min).

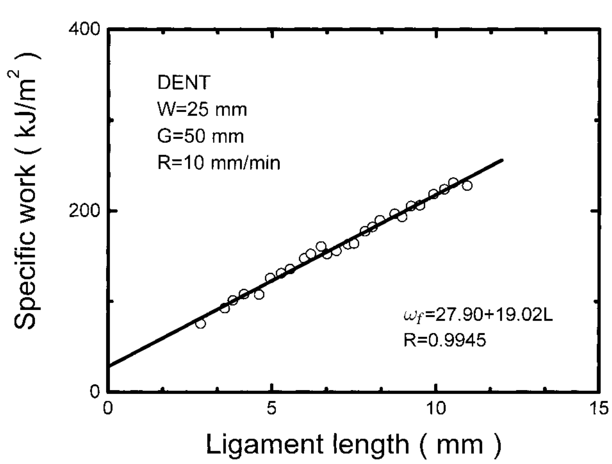

Figure 10 The w_f vs. L for DENT specimens with a gauge length of 50 mm (B = 25 mm, R = 10 mm/min).

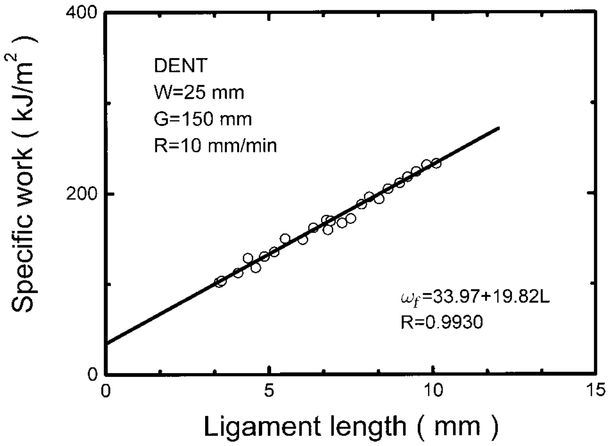

Figure 11 The w_f vs. L for DENT specimens with a gauge length of 150 mm (B = 25 mm, R = 10 mm/min).

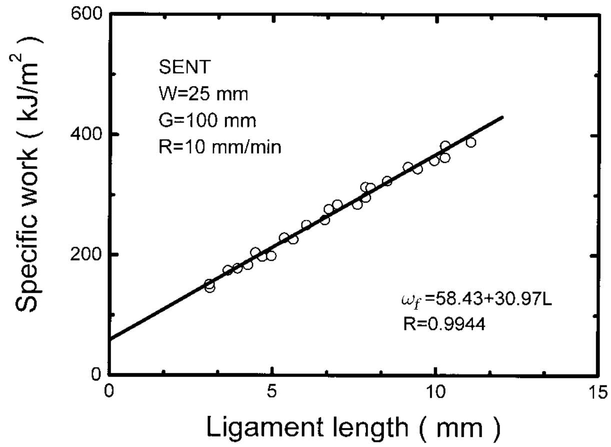

Figure 12 The w_f vs. L for SENT specimens with a gauge length of 100 mm (B = 25 mm, R = 10 mm/min).

ment lengths used for the extrapolation must be much larger than the specimen thickness to ensure that the material is under a state of plane stress. Second, the plastic zones at the crack tips should overlap to ensure the ligament is fully yielded before the cracks start to grow, thereby maintaining the proportionality of W_f with L^2. Thus, the ligament length should be smaller than twice the plastic zone radius (r_p) around a single crack tip. Third, the specimen width should be much larger than 3 times the ligament length so that yielding does not spread to the lateral boundary of the specimen (i.e., $L < W/3$).

Based on the above restrictions on ligament length, the validity range of the essential work approach is generally given by[7,18,19,24]

$$(3\text{–}5)B \leq L \leq \min\left(\frac{W}{3} \quad \text{or} \quad 2r_p\right) \tag{7}$$

where $2r_p$ is the size of the plastic zone, which can be determined from the following equation:

$$2r_p = \frac{1}{\pi} \cdot \frac{Ew_e}{\sigma_Y^2} \tag{8}$$

where E is the elastic modulus and σ_Y is the yield strength. Therefore, the $2r_p$ of the PS/HDPE/SEBS 10/80/10 blend can be estimated from the following average mechanical data is $2r_p \approx 20$ mm: E = 1193 MPa, σ_Y = 24.1 MPa, and w_e = 30 kJ/m^2. We apparently have $L \leq 2r_p$ for the blend specimens we investigated.

Based on the similarity in shape of the load–displacement curves for the ligament range up to L = 15 mm, we can claim that the criterion of $W/3$ is too conservative for the PS/HDPE/SEBS 10/80/10 blend. Similarly, the lower ligament threshold value of ($3B$–$5B$) is also too conservative here. Note that all of the specimens with various L values exhibit ductile failure with gross yielding and necking and the specimen surfaces are contracted in the tensile process, which demonstrates the presence of the plane-stress deformation. In addition, it must be pointed out that

Table II Effect of Gauge Length on Fracture Work of PS/HDPE/SEBS 10/80/10 Blend

G (mm)	Regression Equation	w_l (kJ/m^2)	βw_p (kJ/m^2)	r
25	w_f = 36.80 + 17.40L	36.80	17.40	0.8908
50	w_f = 27.90 + 19.02L	27.90	19.02	0.9945
100	w_f = 28.45 + 19.24L	28.45	19.24	0.9939
150	w_f = 33.97 + 19.82L	33.97	19.82	0.9944

G, gauge length; ω_l, essential work; $\beta\omega_p$, nonessential work; r, correlation coefficient; w_f, total work of fracture; L, ligament length.

Table III Effect of Sample Geometry on Fracture Work of PS/HDPE/SEBS 10/80/10 Blend

Geometry	Regression Equation	w_l (kJ/m^2)	βw_p (kJ/m^2)	r
DENT	$w_f = 28.45 + 19.24L$	28.45	19.24	0.9939
SENT	$w_f = 58.43 + 30.97L$	58.43	30.97	0.9944

ω_l, essential work; $\beta\omega_p$, nonessential work; r, correlation efficient; ω_f, total work of fracture; L, ligament length.

the linearity of w_f with L can be maintained for $R = 10$ mm/min, provided that the ligament does not exceed 11 mm (Fig. 4), although the self-similarity of the load–displacement curves is observed up to $L = 15$ mm (Fig. 2). This means that the self-similarity of the load–displacement is a necessary but not a sufficient prerequisite for the validity of a linear relation between w_f and L. Finally, L_c increases with an increasing tensile rate (Table I), indicating that the validity range of the essential work approach depends on the experiment conditions.

CONCLUSIONS

It is shown that the essential work concept can be used to characterize the ductile fracture behavior of a PS/HDPE/SEBS 10/80/10 blend. From the above results, the following conclusions can be drawn:

1. The essential work (w_e) is independent of the tensile rate range of 1–30 mm/min. However, w_e decreases considerably when the tensile rate is increased to 50 mm/min and above.
2. The w_e is independent of the gauge length (G), provided that G is greater than the width of the specimen.
3. The w_e of SENT specimens is much higher than that of DENT specimens.
4. The specific nonessential work of fracture (βw_p) is nearly independent of the tensile rate. Moreover, βw_p is also independent of the gauge length of the specimens, and the βw_p of DENT specimens is much lower than that of SENT specimens.
5. The lower ligament threshold value ($3B$–$5B$) and higher ligament threshold value of $W/3$ are too conservative to estimate the validity range for the ligament length.

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