# Effect of Annealing on Fracture Behavior of Poly(propylene-*block*-ethylene) Using Essential Work of Fracture Analysis

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**ABSTRACT:** The influence of annealing conditions on the fracture behavior of poly(propylene-*block*-ethylene) sheets was investigated by means of the essential work of fracture method, and was complemented by the study of the effect of annealing on crystal structure, using differential scanning calorimetry. It was shown that both the crystal perfection degree and crystal-linity could be improved substantially as annealing temperature (Ta) increased, while the prolonged annealing time at 80°C mainly resulted in the improvement of crystallinity. The reasons for an increase in the specific essential work of fracture and a decrease in the specific plastic work item as crystal per-

fection degree and crystallinity grew are discussed. The displacement to failure of double edge notched tension specimens decreased gradually with increasing  $T_a$ , and the double-plastic zone could be observed in all specimens. In addition, a novel method to aid the accurate measurement of intense stress-whitening outer plastic zone height by adjustment of illumination conditions is proposed. © 2006 Wiley Periodicals, Inc. J Appl Polym Sci 103: 3438–3446, 2007

**Key words:** polypropylene; annealing; crystal structure; essential work of fracture

## **INTRODUCTION**

Annealing has great effects on the crystal structures and properties of semicrystalline polymers, such as polypropylene; moreover, remarkable structural variations can be obtained for the materials treated under different annealing conditions. Besides effective modification of some properties of materials, the annealing may also occur naturally in the polymeric products because of fluctuations of temperature. Recently, some articles have studied the influence of annealing on the mechanical properties, such as shock resistance, of polypropylene (PP) pieces and have proved that the toughness of both homopolymer and copolymer of PP pieces can be improved substantially.<sup>1–3</sup> However, few studies on fracture toughness together with the deformation behavior of PP films and sheets have been undertaken to our knowledge, probably because the conventional methods of evaluating the fracture properties of ductile sheets and films still present some problems, and it is difficult to find a reliable way to study the fracture toughness of ductile polymer.

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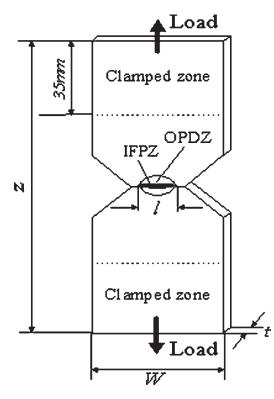
Moreover, it is reported that many deformation mechanisms are involved in the fracture process, which give more information on the structure and property variation in annealing treatment. Fortunately, the development of the Essential Work of Fracture (EWF) procedure based on fracture mechanics gives the opportunity to study the fracture behaviors of polymer films and sheets. Furthermore, attempts have been made to use the EWF method to analyze the effect of annealing on fracture toughness of polymer films. Ferrer-Balas et al.<sup>4</sup> have studied the annealing temperature dependence of fracture properties for castextruded iPP films of 0.09 mm thickness (both homopolymer and copolymer), which were treated for 1 h in a fan-assisted oven at 120 and 140°C.

In this article, the effect of annealing conditions on fracture performance of injected PP sheets of 1.3 mm thickness was studied, using EWF approach, aiming at better understanding of the relationships of crystal structures and fracture properties at different annealing temperatures between 80 and 140°C and for different annealing periods, respectively. Furthermore, it would shed more light on the appropriate application of PP sheets when temperature fluctuated fiercely.

The EWF concept was developed initially by Cotterell and Reddel<sup>5–7</sup> on the basis of Broberg's idea.<sup>8</sup> According to the EWF theory, the total energy required to fracture a notched specimen can be distinguished into two components: the essential work of the fracture ( $W_e$ ), and the nonessential work of the fracture ( $W_e$ ), and the nonessential work of the fracture ( $W_e$ ).

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**Figure 1** DENT specimen used for the Essential Work of Fracture tests. A schematic representation of the different zones is shown.

ture or plastic work  $(W_p)$ , respectively.  $W_e$  is essentially a surface energy dissipated in the inner fracture process zone (IFPZ) to generate new crack surface during the fracture of specimen, while  $W_p$  is actually a volume energy dissipated in the outer plastic deformation zone where various types of deformations may take place. For a given thickness,  $W_e$  is proportional to ligament length l and  $W_p$  is proportional to  $l^{2.9}$  Thus, the total fracture energy,  $W_f$ , the integral of force over displacement measured during the tests, can be expressed as

$$W_f = W_e + W_p = w_e t l + \beta w_p t l^2 \tag{1}$$

and the specific work of fracture is given by

$$w_f = W_f / tl = w_e + \beta w_p l \tag{2}$$

where  $w_e$  is the specific essential work of fracture, and  $\beta w_p$  is the specific plastic work item, which is a global parameter that takes into consideration the whole plastic energy consumed.  $\beta$  is a shape factor associated with the plastic zone, which can be obtained from the relationship between the height of the plastic zone and the ligament length,<sup>10</sup> and *t* and *W*, the thickness and width of specimens. The double edge notched tension (DENT) specimen used for the EWF tests, indicating the different energy dissipation zones involved, is presented in Figure 1. For a given thickness,  $w_e$  is a material constant that can

be used to characterize the fracture toughness and has been demonstrated theoretically to be equivalent to  $J_c$ (a critical factor to be used traditionally for fracture evaluation of materials with significant crack tip plasticity in *J*-integral analysis).<sup>11–14</sup> In addition,  $\beta w_p$  can measure the plastic energy density dissipated in the plastic zone.<sup>15,16</sup>  $w_e$  and  $\beta w_p$  can be obtained from the intercept and slope of the regression line of  $w_f - l$  curves, respectively, as suggested in eq. (2). The theoretical background, assumption of analysis, and test procedure of the EWF method have been illustrated in many works mentioned earlier, and hence will not be elaborated here.

# **EXPERIMENTAL**

## Materials

The granular material used in this study was a poly-(propylene-*block*-ethylene) (K8303) with 17.8 mol% of ethylene as determined by Fourier transform infra red spectroscopy, which was tested and supplied by Beijing Yanshan Petrochemical Co. (PRC). The melt flow index of their copolymer sample was 1.39 g/10 min, which was measured at 230°C using a load of 2.16 kg according to the ASTM D 1238-86T standard.

## Sample preparation

The dried PP was injection-molded in the form of DENT specimens ( $Z \times W \times t = 110 \times 40 \times 1.3$  mm) (Fig. 1) using an injection-molding machine PS40E5ASE made in Japan. The sharp precracks of at least 1.2 mm length on both sides of the specimens were made perpendicularly to the tensile direction with a fresh razor blade. The ligament length of the specimens varied between 3.9 and 12.5 mm. Then the specimens were treated in a fan-assisted oven at different annealing conditions (seen in Table I) and were conditioned at room temperature for 48 h before testing. The ligament length and the thickness were measured before the test using a microscope and a Vernier caliper, respectively.

#### Differential scanning calorimetry

A DSC-2C thermal analysis apparatus was used for heat flow measurements. The specimens treated

TABLE I
Nomenclature for Specimens Corresponding to Different
Annealing Conditions

	Annealing temperature (°C)	Annealing time (h)
UA	Unannealed	Unannealed
A80	80	0.5
A110	110	0.5
A140	140	0.5
A80H1.5	80	1.5

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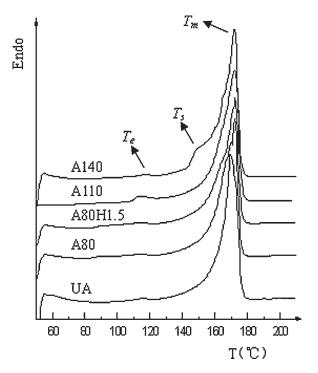


Figure 2 DSC curves of poly(propylene-*block*-ethylene) treated at different annealing conditions, obtained at a heating rate of  $10^{\circ}$ C/min.

under various annealing conditions were studied at a heating rate of  $10^{\circ}$ C/min, from 50 to  $210^{\circ}$ C.

#### **Fracture tests**

The EWF tests were performed on an Instron universal testing machine (series IX) equipped with a 10-kN load cell, at room temperature of  $(23 \pm 2)^{\circ}$ C. The crosshead speed was set as 5 mm/min and the length between the grips was 40 mm. The load–displacement curves were recorded and the absorbed energy until failure was calculated by computer integration of the load–displacement curves.

## **RESULTS AND DISCUSSION**

#### **Crystalline structures**

Figure 2 shows the differential scanning calorimetry (DSC) results of PP specimens treated under different annealing conditions. It can be seen in Figure 2 that for each specimen a strong main melting peak ( $\alpha$ -PP) occurs around 170°C and the area of this endothermic peak can approximately represent the crystallinity of the PP sheet. The crystallinity of PP specimen can be calculated by

$$X_c = \Delta H_m / \Delta H_m^0 \times 100\% \tag{3}$$

where  $\Delta H_m$  is the measured value of melting enthalpy and  $\Delta H_m^0$  is the theoretical melting enthalpy of PP with 100% crystal (209 J/g).<sup>17</sup>

The DSC curves in Figure 2 show that for the specimens annealed for 0.5 h between 80 and 140°C, the main melting peak  $(T_m)$  changes very little when compared with those of the unannealed specimens.  $T_m$  of the annealed specimens is about 2°C higher than the unannealed ones, revealing the improvement of crystal perfection and the increase in crystal thickness through the annealing treatment. However, no obvious difference of  $T_m$  for the specimens treated under different annealing temperature can be observed; that is, when annealing temperature  $(T_a)$  increases from 80 to 140°C,  $T_m$  has almost no further changes. Careful observations of DSC curves show that for each specimen, a small endothermic peak  $(T_e)$  at 110–120°C appears, which corresponds to the melting of the crystallites formed by ethylene sequences. The crystalline structures of ethylene sequences are modified because of the annealing treatment; thus the  $T_e$ peak for annealed specimens is more pronounced than that for the unannealed ones. Taking no account of  $T_{e}$ , it can be seen from Figure 2 that there is an endotherm  $(T_s)$ before the main melting peak resulted from annealing treatment, which represents an intermediate state between ordered and amorphous phase (called *sm*-PP). The value of  $T_s$  varies gradually with the annealing temperature. For A80, the platform of crystalline peak in the DSC curve is broader since the  $T_s$  that appeared around 90°C abuts on  $T_{e}$ , whereas a higher endothermic peak is formed because of the almost complete superposition of  $T_s$  and  $T_e$  for A110. When  $T_a$  increases to 140°C, the  $T_s$ moves to around 148°C and overlaps partly with the main melting peak. The smectic endothermic peak,  $T_{sy}$ increases with increasing  $T_{a\nu}$  probably relating to the increase in crystal thickness.<sup>18</sup> The results described earlier agree well with the results presented by Ferrer-Balas about the crystalline structures of PP treated for 1 h at different annealing temperatures.<sup>4</sup> Vittoria<sup>19</sup> and Zanetti et al.<sup>20</sup> suggested that *sm*-PP was stable at room temperature; however, it could transform into a more stable PP phase as the material was heated to temperatures above 70-80°C or applied plastic deformation. Taking into account all these facts, the value of  $T_s$  can be taken as a simple indication of the order perfection of the material (strongly related to the crystal size<sup>18</sup>) at different annealing conditions. The DSC results show that by just annealing for 0.5 h, remarkable variations of the crystalline structures have occurred for the PP copolymer; further-

TABLE II Influence of Annealing on Crystal Structures for Block co-Polypropylene

	$T_s$ (°C)	$T_m$ (°C)	$\Delta H_m (J/g)$	$X_{C}(\%)$
UA	_	169.3	95.3	45.6
A80	87	171.9	96.4	46.1
A110	115	171.9	103.0	49.3
A140	148	171.8	105.6	50.5
A80H1.5	92	172.6	102.9	49.3

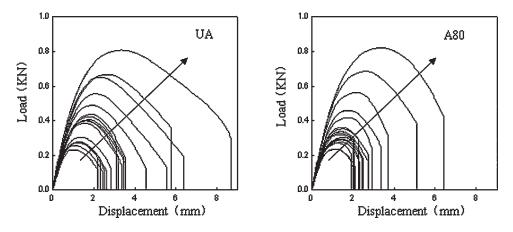


Figure 3 Load-displacement curves obtained with DENT specimens of PP treated at different annealing conditions.

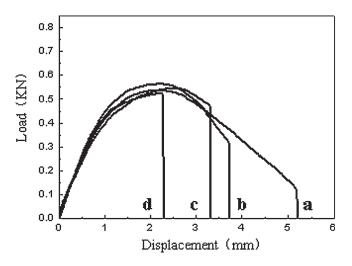
more, the order perfection of the material is improved with increasing  $T_a$ . The results in Table II show that for the specimens annealed for 0.5 h, the value of melting enthalpy increases notably with increasing  $T_a$ , indicating that there is a gradual increase in the crystallinity of PP samples since the crystalline structures show a greater perfection degree and the crystal thickness increases.

On the other hand, it can be seen in Figure 2 that with respect to A80,  $T_s$  shifts slightly to a higher temperature and  $T_m$  shows no significant change for A80H1.5 with increasing annealing time. It is suggested that when  $T_a$  is fixed at 80°C, which is commonly considered as an effective annealing temperature for PP, though the annealing time increases from 0.5 h to 1.5 h,  $T_s$  does not change much even if there is a transition from *sm*-PP to  $\alpha$ -PP or increase in crystal thickness. However, the increase of annealing time from 0.5 to 1.5 h results in a remarkably higher melting enthalpy and crystallinity for the specimens treated at 80°C, the effect of which is similar to that of increasing  $T_a$ . These results show that even at lower annealing temperature (80°C), the influence of prolonged annealing time on the crystal structure and even the fracture behaviors can not be neglected. Hence, it is worth paying more attention to the fracture behaviors of PP products when the temperature fluctuates greatly.

## **Plastic deformation**

The load–displacement curves of unannealed (UA) and annealed PP (A80) specimens with different ligament lengths are exemplified in Figure 3. It can be seen in Figure 3 that at the same annealing conditions, the maximum load, the displacement to failure, and the area below load–displacement curve increase gradually with increasing ligament length and the curves for each group of specimens show excellent self-similarity, indicating that the requirement of selfsimilarity of load–displacement curves for the application of EWF method is always satisfied. The difference of load–displacement curves of DENT specimens with the same ligament length (l = 8 mm) under different annealing temperatures is shown in Figure 4. It can be seen from Figure 4 that the improvement of annealing temperature has little influence on the maximum load, while the displacement to failure decreases gradually with increasing annealing temperature. In spite of the slight fluctuation of the maximum load, the total fracture energy decreases because of the reduction of the displacement to failure. These results demonstrate that the energy consumed in deformation is reduced, because of higher perfection degree and crystallinity of PP specimens through annealing treatment.

Figure 5 exemplifies the development of the precrack tips and the ligament zones of UA and A110 during the tensile test. After crack tip blunts [Fig. 5(a)], more or less simultaneously to that the ligament starts to yield [Fig. 5(b)]. The ligament yielding is followed by the stable crack growth from both sides



**Figure 4** Load–displacement curves of DENT specimens with same ligament length (l = 8 mm) treated at different annealing temperature: a, UA; b, A80; c, A110; d, A140.

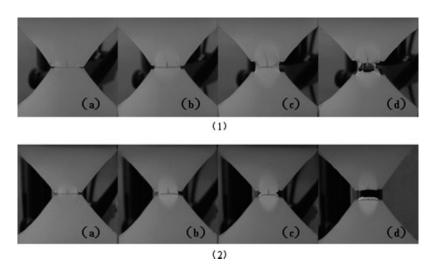
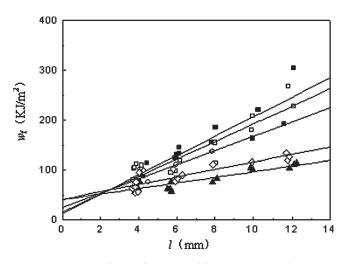


Figure 5 Images taken from the ligament area of the test specimens at the different stages of the fracture test: (1) UA; (2) A110.

[Fig. 5(c)]. Finally, the specimen fails by tearing as both cracks meet one another at the center of the ligament [Fig. 5(d)]. A fine necking can be observed in Figure 5(b) for both UA and A110 specimens; moreover, it still exists in skin layer for UA specimen, though the crack propagates in the core layer in Figure 5(c). It may be caused by the structure discrepancy, such as orientation between layers, which resulted from injection molding. On the contrary, the necking phenomenon disappeared after annealing because the structure discrepancy can be removed through thermal treatment. In addition, it can be clearly observed that the fracture surface of UA is less regular than that of A110. These results reveal that higher crystallinity and crystal perfection degree due to the annealing treatment restrain the plastic deformation of material, which may be related to a decrease



**Figure 6** Plots of specific work of fracture versus ligament length for block copolypropylene sheets at different annealing conditions.  $\blacksquare$ , UA;  $\square$ , A80;  $\bigcirc$ , A110;  $\blacktriangle$ , A140;  $\square$ , A80H1.5.

in chain flexibility with increased packing and decreased free volume.

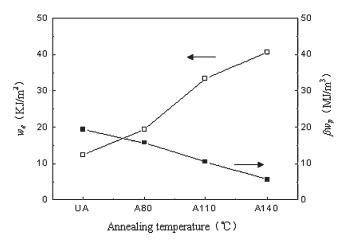
# $w_e$ and $\beta w_p$

The plots of  $w_{fr}$  the specific fracture work obtained from the integral of load–displacement curves, *versus* ligament length l are shown in Figure 6. Though the slight brittleness and necking for all the specimens as discussed previously can not agree well with the prerequisite required by the EWF method,  $w_f - l$  diagrams take on good linearity for all the specimens in Figure 6. According to the intercept and slope of the regression line of  $w_f - l$  curves,  $w_e$  and  $\beta w_p$  can be calculated, respectively, and the results are listed in Table III.

It can be seen in Table III that as the annealing time is fixed at 0.5 h, and  $T_a$  varies from 80 to 140°C gradually, the values of  $w_e$  and  $\beta w_p$  change markedly when compared with those UA specimens, indicating that the annealing treatment has great effect on EWF parameters of PP copolymer, even in a short period of annealing time. Figure 7 shows the dependence of fracture properties, as represented by  $w_e$  and  $\beta w_p$ , on annealing temperature. It is shown that  $w_e$  increases and  $\beta w_p$  decreases as  $T_a$  increases, indicating that the fracture toughness is improved while the total plastic

TABLE III Influence of Annealing on the EWF Parameters

	$\frac{w_e}{(\text{kJ/m}^2)}$	$\beta w_p$ (MJ/m <sup>3</sup> )	$R^2$ (for $w_f - l$ )	β	$\frac{w_p}{(MJ/m^3)}$
UA	12.37	19.43	0.8445	0.45	43.2
A80	19.33	15.71	0.8113	0.73	21.5
A110	33.45	10.49	0.7514	0.71	14.7
A140	40.60	5.61	0.8059	0.51	11.0
A80H1.5	41.40	7.49	0.8172	0.65	11.5



**Figure 7** Evolution of EWF fracture parameters with annealing temperature:  $\Box$ ,  $w_{e^*} \blacksquare$ ,  $\beta w_p$ .

energy dissipation is reduced. This clearly reflects the different natures of the two energy parameters, and thus the whole fracture process can hardly be described by a single parameter, as has also been suggested in the literature.<sup>21</sup> Karger-Kocsis<sup>22,23</sup> has concluded that both  $w_e$  and  $\beta w_v$  can hardly be improved or depressed simultaneously based on the results of EWF parameter determination from some specific rubber-toughened, fiber-reinforced, and particle-filled polymer systems. Obviously, this is in agreement with what has been obtained in the present study.  $w_e$  is the energy to create two new fracture surfaces, which is essentially the work to break the specimen, whereas  $\beta w_p$  involves all plastic deformation processes outside the fracture process zone and surrounding the fracture path. It can be seen from Table III that the square of the correlation coefficient for linear regression analysis  $(R^2)$  of annealed specimens are close to that of UA specimen.

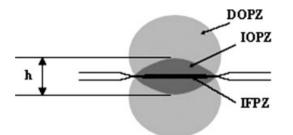
Ferrer-Balas et al.<sup>4</sup> studied the relationship between crystalline structures and fracture properties of PP copolymer films with lower ethylene content which were annealed for 1 h at 120 and 140°C. Their results showed that with increasing  $T_a$ ,  $w_e$  decreased, while  $\beta w_p$  slightly increased ( $\beta w_p$  increased appreciably below 120°C, whereas it became stable above 120°C with a little reduction for PP copolymer, and it was worthwhile noting that  $\beta w_p$  for PP homopolymer always increased). A possible explanation for these differences between trends in fracture work was presented by Karger-Kocsis,<sup>21</sup> who suggested that the dependence of toughness on crystalline structure relied on two facts: on one hand, as the crystal perfection degree, crystallinity, molecular arrangement, lamellar size, etc., increased, the toughness in the bulk crystals increased because destroying this structure implied a strong energy consumption; on the other hand, an increase in the crystal perfection degree could be obtained by reducing the number of tie molecules,

which acted as stress-transfer units between the crystalline regions. Hence the reduction of the number of tie molecules was harmful to the fracture toughness of PP. These assumptions were confirmed by the observations of Alberola et al.,<sup>24</sup> who claimed that a clear loss in the degree of entanglement between amorphous and crystalline phase occurred as the iPP quenched films were annealed. Thus, a crystallinity threshold may exist, and below it, the toughness increased with higher crystal perfection degree, while above it, a decrease in toughness appeared due to the lack of tie molecules. In this article, block copolypropylene (K8303) with higher ethylene content may have lower crystal perfection degree and more tie molecules; thus it is more difficult to reach the crystallinity threshold. In other words, in a short period of annealing time (0.5 h), though the crystal perfection degree of annealed material can be improved, the number of tie molecules is still enough to act as stresstransfer units. Furthermore, it is worthwhile paying more attention to the difference in thickness between the specimens, which is more than an order of magnitude higher in the present article than other article,<sup>4</sup> since it is commonly suggested that the specific EWF depends on the thickness of the specimen. The variation of  $\beta w_p$  with increasing  $T_a$  is similar to that of the displacement to failure, which coincides with the development of crack tip and plastic zone, all reflecting the depressed plastic deformability resulted from the higher crystal perfection degree and crystallinity.

It also can be seen in Table III that when  $T_a$  is 80°C and annealing time increases from 0.5 to 1.5 h,  $w_e$  increases remarkably while  $\beta w_p$  decreases sharply, which are also similar to that the variation of EWF parameters when  $T_a$  increases. These results demonstrate that even at relative low annealing temperature (80°C), the increase of annealing time can definitely improve the crystal perfection degree of PP, thus greatly varies the fracture properties.

## $\beta$ and $w_p$

The stress-whitening zone surrounding the ligament is generally caused by the cavitation and crazing of matrix. Careful observation of the stress-whitening zone shows that it can be divided into an intense and a diffuse stress-whitening outer plastic zone (IOPZ and DOPZ, respectively), according to the different extent of transparency (Fig. 5). The two zones form in different stages of the fracture process and are related to strictly different deformation stages. The schematic drawing of double plastic zone is shown in Figure 8 Ferrer-Balas et al.<sup>25</sup> claimed that the stress-whitening effect is due to the appearance of a large number of holes (1  $\mu$ m diameter) in the bulk material. Previous works showed that double plastic zone phenomenon was not visible for all materials and it was only



**Figure 8** Schematic drawing of double plastic zone, indicating the different zones (IFPZ, inner fracture process zone; IOPZ, intense outer plastic zone; DOPZ, diffuse outer plastic zone).

reported in studies on the fracture behaviors of block copolypropylene<sup>25,26</sup> and blend of iPP/EPR.<sup>27</sup> The value of  $\beta$  can be determined by the ratio of *h* (height of plastic zone) to *l*, as recommended in the first EWF protocol version.<sup>10</sup> It is worth noting that the value of  $\beta$  should be determined by the height of DOPZ or IOPZ. Generally, the IOPZ always appears during the whole fracture process and is strongly related to the distinct deformation of ligament, which involves the deformation occurring in the stage of yielding and necking initially, and subsequently during crack propagation. Moreover, the energy consumed in the DOPZ is far less than that in the IOPZ. Therefore, the value of  $\beta$  should be determined by the relationship between the height of IOPZ and *l*.

According to the first EWF protocol version,<sup>10</sup> the plastic zone shape can be classified as circle, diamond, or ellipse. However, the IOPZ usually has an intermediate shape between elliptical and diamond (Fig. 8), and so the value of  $\beta$  can be determined by

$$h = k \beta l \tag{4}$$

where *h* is the height of the IOPZ, and *k* is a constant set as the value of 1.5, between 2 (for diamond-shape) and 1.27 (for ellipse-shape).

Generally, it is difficult to distinguish the IOPZ and the DOPZ because of the obscure borderline. Through repeated tests and comparison, we find it is easier to observe the distinct borderline between the IOPZ and the DOPZ from the other side, when the specimen is placed under an intense light source. This increases the accuracy of the measured values of the height of IOPZ greatly. Once the IOPZ height is found, the plots of *h* versus *l* can be completed, as shown in Figure 9. From Figure 9 it can be seen that the curves of *h* versus *l* also have good linearity, as proved by the square of the correlation coefficient for linear regression analysis  $(R^2)$  being in most cases higher than 0.90. Thus,  $\beta$  can be determined from the slope of the regression line for h - l plots (Fig. 9), according to eq. (4); then the value of  $w_p$  can be easily deduced. The results of  $\beta$  and  $w_p$ are listed in Table III.

Table III shows that the  $\beta$  values of annealed specimens are higher than those of unannealed. While the variation of  $w_p$  for both the annealed and unannealed specimens is approximately similar to that of  $\beta w_p$ , for the specimens annealed for 0.5 h,  $w_p$  decreases with increasing  $T_a$  on the whole. However, the decrement of  $w_p$  for annealed specimens is more pronounced with respect to the unannealed one. Even at the  $T_a$  of 80°C, the reduction of  $w_p$  is nearly 50%. The results show that when crystal perfection and crystallinity of block copolypropylene are improved by annealing treatment, not only does the specific plastic work item  $\beta w_p$  decrease, but the specific energy absorption per unit volume  $w_p$  also shows a remarkable decrease.

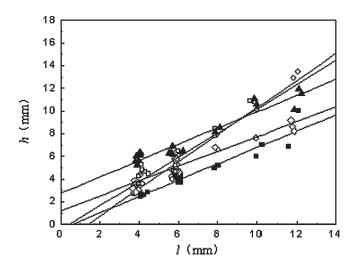
In addition, the results in Table III show that when  $T_a$  is 80°C,  $w_p$  also decreases with increasing annealing time. It is obvious that the properties of PP sheets can be influenced either by increasing  $T_a$  or by prolonging annealing time.

### Crack opening displacement

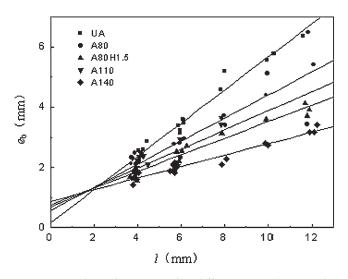
Recently, determination of crack opening displacement (COD) through EWF method<sup>28–31</sup> has gained more attention. Figure 10 shows the plots of the displacement to failure  $e_b$  versus the ligament length l for DENT specimens, where it can be seen that the values of the displacement to failure increase linearly with ligament length. The observed linearity between  $e_b$ and l can be expressed as

$$e_b = e_0 + e_p l \tag{5}$$

where  $e_0$  is the intercept of the regression line of  $e_b - l$  curve, which can also be regarded as the displacement to failure at zero ligament length, and  $e_p$  is the rate of



**Figure 9** Plots of *h* against *l* for the determination of  $\beta$  (**I**, UA;  $\Box$ , A80;  $\bigcirc$ , A110;  $\blacktriangle$ , A140;  $\Box$ , A80H1.5).



**Figure 10** Plots of  $e_b$  against *l* at different annealing conditions.

change of displacement to failure with ligament length. The value of  $e_0$  was taken as another measurement of the fracture toughness, by Arkhireyeva and Hashemi,<sup>32</sup> which was called critical COD. Moreover, it has been used to estimate the value of  $w_e$  successfully,<sup>29–31</sup> as eq. (6) shows:

$$w_e = e_0 \sigma_n \tag{6}$$

where  $\sigma_n$  is net-section stress, which can be calculated from the maximum load ( $P_{\text{max}}$ ) of each sample.<sup>33,34</sup> Though studies of the physical concept of  $e_p$  have been rare, Cotterell et al.<sup>35</sup> regarded it as the crack tip opening angle. The results of  $e_0$ ,  $e_p$ , and the estimated values of  $w_e$  through COD method for all specimens are listed in Table IV.

The results in Table IV show that for the specimens annealed for 0.5 h, the value of  $e_0$  increases gradually with increasing  $T_a$ , which is similar to the evolution of fracture toughness ( $w_e$ ) when crystal perfection degree and crystallinity are improved. Though the estimated values of  $w_e$  are not completely identical with the directly measured values of  $w_e$ , their evolution with increasing  $T_a$  is similar. As can be seen from Table IV, the evolution of  $e_p$  also shows some good regularity. It decreases gradually with increasing  $T_a$ , which is consistent with the evolution of  $\beta w_p$ . Whether or not a certain close corresponding relationship exists between  $e_p$ and  $\beta w_p$  requires further investigation. Furthermore, the difference between  $R^2$  values of  $e_b - l$  diagram for the specimens before and after annealing treatment showed that  $R^2$  for UA is higher than that of the annealed ones, indicating that the higher scattering of fracture data resulted from increasing brittleness.

In addition, Table IV also shows that when  $T_a$  is 80°C, the evolutions of  $e_0$  and  $e_p$  with increasing annealing time are similar to that with increasing  $T_a$ .

## CONCLUSIONS

- 1. The  $T_m$  for the specimens annealed for 0.5 h from 80 to 140°C increases definitely when compared with that of the unannealed ones.  $T_s$  and melting enthalpy increase with increasing  $T_a$ , which indicate that crystal perfection degree and crystallinity can be improved as  $T_a$  increases. At lower  $T_a$  (80°C), the increase of annealing time mainly works on the improvement of crystallinity.
- 2. With increasing  $T_a$ , the displacement to failure of DENT specimen decreases, indicating that the modification of crystal structures due to annealing treatment results in the reduction of energy consumed in deformation process.
- 3. With increasing  $T_a$ ,  $w_e$  and  $e_0$  increase gradually, whereas  $\beta w_p$  and  $w_p$  decrease. The increase of  $w_e$ and  $e_0$  may be caused by the improvement of crystal perfection degree without the excessive reduction of the tie molecules number, which results in higher fracture toughness. Otherwise, the decrease of  $\beta w_p$  and  $w_p$  may be related to the depressed plastic deformability.
- 4. Increasing the annealing time at a fixed  $T_a$  (80°C) has almost the same effect as does increasing  $T_a$  on the fracture properties of PP sheets.
- A novel method to aid the accurate measurement of IOPZ height (and hence obtain reliable values of plastic zone shape factor) by adjustment of illumination conditions is proposed.

TABLE IV
COD Parameters and the Comparison between Estimated and Directly Measured $w_e$

	e <sub>0</sub> (mm)	e <sub>p</sub> (mm)	Estimated values of $w_e$	Directly measured values of $w_e$	$R^2$ (for $e_b - l$ )
UA	0.1518	0.5515	7.82	12.37	0.9727
A80	0.5643	0.3839	27.63	19.33	0.7754
A110	0.6893	0.3192	34.83	33.45	0.5852
A140	0.8762	0.1912	39.85	40.60	0.9457
A80H1.5	0.7571	0.2764	35.11	41.40	0.9483

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