Macromolecules **2007,** *40,* 4322−4326

Understanding the Underlying Physics of the Essential Work of Fracture on the Molecular Level

Haibin Chen and Jingshen Wu*

Center for Engineering Materials and Reliability, Department of Mechanical Engineering, The Hong Kong University of Science and Technology, Clear Water Bay, Kowloon, Hong Kong

Received November 6, 2006; Revised Manuscript Received April 7, 2007

ABSTRACT: The essential work of fracture (EWF) method is widely used in the experimental characterization of fracture toughness of thin polymer films. However, the underlying physics of this method and the EWF parameters are not completely understood. In the present work, we investigated the correlations between the EWF parameters and the molecular structures of amorphous and ductile polymers. Based on our experimental observations, a physical model describing the EWF method on the molecular level was built. With this model, the variations of the EWF parameters with extrinsic and intrinsic factors under a plane stress condition were explained successfully; the theoretical values estimated with some assumptions and approximations of the EWF parameters agree satisfactorily with the experimental ones. This is the first theoretical model in the development history of the EWF method, which gives reliable physical meanings of the EWF parameters. The precise description of the molecular structure and fracture toughness relationships given by this model can also provide guidelines to molecular design of new polymers with high toughness.

Introduction

Fracture toughness is one of the most important material properties for engineering applications. For brittle or semibrittle materials where only small plastic deformation is involved during fracture, fracture toughness can be characterized with well-developed theories including linear elastic fracture mechanics (LEFM) and elastic plastic fracture mechanics (EPFM). For ductile materials, because of the involvement of extensive plastic deformation during fracture, the situation becomes complicated. Both LEFM and EPFM are no longer applicable. The essential work of fracture (EWF) method was then developed, which is to characterize the fracture toughness of ductile materials with extensive plastic deformation involved.[1−5] This method assumes that the total fracture energy can be separated into two components. One is dissipated in the actual fracture process zone (FPZ) to create the fracture surface while the other is dissipated in the outer diffuse plastic deformation zone (PDZ). It is proposed that the former is a surface energy, and the latter is a volumetric energy. The total fracture energy is expressed as $w_f = W_f/lt = w_e + \beta w_p l$, where w_f is the specific total fracture work, w_e is the specific essential work of fracture associated with FPZ, w_p is the specific plastic (or nonessential) work of fracture associated with PDZ, β is the shape factor of the plastic zone, l is the ligament length, and t is the thickness of the test specimen. Because of its simplicity, the EWF method has been widely applied to various ductile materials,[6−10] and it is considered as one of the most promising techniques for toughness determination of ductile and toughened materials. In 1995, the European Structure Integrity Society (ESIS) proposed a protocol specifying test conditions for the EWF test.[11]

Despite its triumph in experimental applications, the underlying physics of the EWF method is however vague. Mathematical modeling was attempted to lay down a theoretical basis for this method but with little success.[12] This is understandable because precise modeling of ductile fracture by the traditional fracture mechanics is extremely difficult, if not impossible, due to the large-scale plastic deformation involved. In the meantime, efforts to understand the EWF method through establishing the correlations between the EWF parameters and the molecular structures of ductile polymers were also made, based on the well-established theories of polymer physics.[6−10] Though these pioneering works did not unveil the physics behind the EWF method, some did suggest the possibility to explore the underlying nature of the EWF by polymer physics. In this work, we established the correlations between the EWF parameters and the molecular structure with a series of tailor-made polymers, which had well-defined molecular structures. With an understanding of our experimental observations from the well-established theories of polymer physics, a model describing the EWF on the molecular level was built and verified with the experimental data of a set of glassy polymers published by other research teams.

Experimental Section

The polymer samples were polyurethanes (PU) and poly(ethylene terephthalate) (PET)-based copolyesters. The PU samples were synthesized in our lab via a two-step polymerization process with a variety of soft segment (SS) to hard segment (HS) ratios (i.e., 1:2, 1:3, 1:4, 1:6, and 1:8). The SS was poly(propylene glycol) (PPG) with an average molecular weight of 1000 g/mol, and the HS was 4,4′-methylene diphenyldiisocyanate (MDI). These samples were named according to the SS/HS ratio. For instance, PU12 indicates the PU sample with a SS/HS ratio of 1:2. To further modify the network structure of the PU samples, a series of PU14, having a SS/HS ratio of 1:4, were irradiated with γ-rays at room temperature with different dosages (i.e., 10, 20, 50, and 100 kGy). All the PU samples were examined by dynamic mechanical analysis (DMA), small-angle X-ray scattering (SAXS), and Fourier transform infrared spectroscopy (FTIR). They were disclosed to have a homogeneous morphology with a single amorphous phase and a network structure.[13] For the nonirradiated PU samples, the network structure was formed with hydrogen-bonded HS clusters, which acted as physical cross-links connecting the SSs. For the PU samples with γ-ray irradiation, chemical cross-links were introduced and the network structure was varied. Through determining the rubbery plateau modulus (G_N^0) by DMA, all the nonirradiated PU samples,

---

* Corresponding author: e-mail mejswu@ust.hk; Tel 852-2358 7200; Fax 852-2358 1543.

10.1021/ma062567r CCC: $37.00

Table 1. Experimental Values of M_c and w_e of the PU Samples with Different Soft-to-Hard Segment Ratios

	PU12	PU13	PU14	PU16	PU18	PU16
T_g [°C]	1	8	22	45	59	45
$T_g - T$ [°C][a]	1	8	2	25	39	5
M_c [kg/mol]	2.08	0.88	0.89	0.92	0.92	0.92
w_e [kJ/m^2]	48.3 ± 1.6	27.3 ± 1.8	26.6 ± 1.9	25.7 ± 1.3	25.2 ± 1.2	26.3 ± 1.9

[a] T_g = glass transition temperature; T = test temperature.

except PU12, were found to have a nearly identical value of M_c (molecular weight between two adjacent cross-links, $G_N^0 = \rho RT/M_c$), independent of the SS/HS ratio. PU12, on the other hand, had a larger value of M_c. The value of M_c of the γ-ray-treated PU14 samples, measured by the method of swelling with a DMF solution, were found to decrease with an increasing irradiation dosage. This decrease was a result of the introducing of chemical cross-links during the irradiation treatment.[13] Three amorphous copolyesters were also tested. They were PET, synthesized from terephthalic acid and ethylene glycol, and two copolyesters based on modified PET, namely PET_C and PET_N. In PET_C, a part of the ethylene glycol group in the PET main chain was replaced by 1,4-cyclohexanedimethylene glycol; in PET_N, it was replaced by neopentyl glycol. The detailed descriptions of these copolyesters were given in ref 14. With the molecular modification, the network characteristics and polymer chain flexibility of the copolyesters vary accordingly.

The EWF tests were carried out with double-edge notched tensile (DENT) specimens on an MTS universal testing machine (Alliance RT/5) with a cross-head speed of 5 mm/min and at temperatures below the glass transition temperature (T_g) of the samples, namely in their glassy state. The specimen width, gauge length, and overall length of the DENT specimens were 40 mm, 50 mm, and 100 mm, respectively. The ligament lengths of the DENT specimens ranged from 5 to 25 mm with an interval of 5 mm and measured with a traveling microscopy before the tests. The initial cracks were notched with fresh blade razors. At each ligament length, at least three specimens were tested. To ensure the tests were under a plane stress condition, the thicknesses of all the samples were less than 0.5 mm. After careful examinations according to the ESIS standard, all the tests were found valid.

Results and Discussion

As shown in Table 1, except PU12, the values of w_e of all the nonirradiated PU samples were virtually identical and independent of the molecular composition. PU12, on the other hand, had a much larger value of w_e. The results suggest that M_c had a direct relationship with w_e, which was further evident by the data obtained with the γ-ray-treated PU14 samples. A linear relationship between M_c and w_e was achieved (cf. Figure 1), suggesting that w_e seems dictated by the properties of the chain segments between cross-links rather than the molecular composition. Moreover, w_e was found nearly insensitive to the test temperature as long as $T < T_g$ (cf. Table 1). In other words, the chain flexibility seemed to have little effect on w_e under this condition.

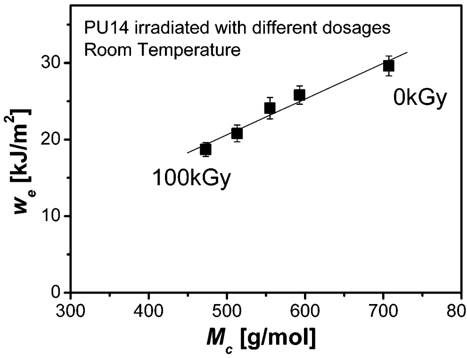

Figure 1. Experimental values of w_e of γ-ray-irradiated PU samples as a function of M_c.

The evaluation of w_p was mostly focused on the copolyesters because the samples exhibited a well-defined plastic zone, enabling the determination of the shape factor of the plastic zone. The value of w_p of the copolyesters decreased with an increasing temperature, which was in the same trend as the yield stress (σ_y). Most importantly, the w_p/σ_y ratio for a given copolyester was found virtually a constant, but it was evidently dependent on the molecular structure (cf. Figure 2). This observation suggests that w_p may be associated with the yield stress by $w_p = m\sigma_y$, where m is a material constant. To understand this relationship and the physical meaning of m, the deformation and fracture process in the plastic zone has to be understood.

The major deformation mechanism in the plastic zone for the tested materials was shear yielding via network stretching. This was proven by the fact that when the fractured specimens were heated at a temperature higher than the T_g of the polymer, the plastically deformed zone was recovered completely. The deformation mechanism of network stretching is well-known and widely accepted.[15] The entanglements in the molecular network can be assumed to be permanent chemical cross-links within the time scale as long as disentanglement does not take place. The detailed stretching process is as follows. After reaching the yield point, the network starts to be stretched plastically up to a strain limit, beyond which the network is locked and no further viscoplastic flow is allowed; after the locking point, the network becomes rigid and elastic deformation takes place via stretching the backbone bonds of the entangled chains; as a consequence, the stiffness increases dramatically; finally, the chains rupture at a certain chemical bond. Evidently, two energy components are involved during the network stretching and breaking process. One is the plastic work dissipated in the plastic stretching of the network until the locking point. The other is the elastic work stored during the covalent bonds stretching and released as heat at the breaking of the bonds of the network.[16] Obviously, the plastic work is temperature-dependent while the elastic one is insensitive to temperature; the plastic stretching takes place in the entire plastic zone while the elastic stretching occurs only near the fracture plane due to the stress concentration ahead of the crack tip.

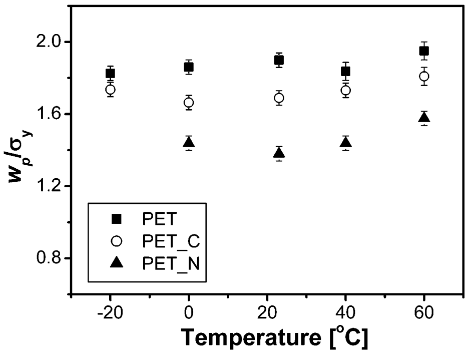

Figure 2. w_p/σ_y ratios of copolyesters as a function of temperature.

Table 2. Theoretical Values of E_{plastic} and Experimental Value of w_{p} of a Set of Glassy Polymers at Room Temperature[20–26]

polymer[a]	σ_y [MPa]	C_∞	E_{plastic} [MJ/m^3]	w_{p} [MJ/m^3]
PC	58	2.4	68	45
PEEK	63	3.7	107	79
PET	52	4.2	97	99
PETG	45	4.9	94	77
PEN	65	5.4	146	111

[a] PC = polycarbonate; PEEK = poly(ether ether ketone); PET = poly(ethylene terephthalate); PETG = poly(ethylene terephthalate) glycol; PEN = poly(ethylene 2,6-naphthalate).

Given the definitions of w_{e} and w_{p} in the EWF theory and our experimental findings, it can be expected that w_{e} is most likely a function of the elastic work while w_{p} is closely related to the plastic work. The following context is to verify this proposition.

The plastic work required to extend the molecular network of a glassy polymer to its locking point can be estimated by $E_{\mathrm{plastic}} = \sigma_y(\lambda_{\max} - 1)$, where $\lambda_{\max}$ is the maximum extension ratio of an entanglement chain segment (the molecular strand between two adjacent entanglements). The assumption here is that the entire network stretching takes place under the same stress, that is, the yield stress of the material. This assumption would bring an estimation error of the plastic work because in reality during plastic deformation strain softening, followed by strain hardening, always takes place after reaching the yield point. The error introduced is however reasonably acceptable. For instance, for the polycarbonate reported in ref 17, the difference between the actual plastic work calculated using the stress−strain curve and the estimated one using the above assumption is less than 5%. $\lambda_{\max}$ can be estimated with a simple model if the entanglements are assumed to be permanent cross-links as proposed by ref 18, $\lambda_{\max} = L_{\mathrm{e}}/d$, where L_{e} is the contour length of an entanglement chain segment with a fully extended conformation and d is the root-mean-square end-to-end distance of a chain with a molecular weight of M_{e}, the entanglement molecular weight. L_{e} and d are determined by $L_{\mathrm{e}} = N_{\mathrm{v}}l_{\mathrm{v}}\cos(\theta/2)$ and $d = \sqrt{C_\infty N_{\mathrm{v}} l_{\mathrm{v}}^2}$, respectively, where N_{v} is the number of real and/or virtual skeletal bonds in an entanglement chain segment, l_{v} is the average length of a real or virtual skeletal bond, θ is the angle between two skeletal bonds, and C_∞ is the characteristic ratio of the polymer.[19] Further, the relationship between N_{v} and C_∞ was proposed as $N_{\mathrm{v}} = 3C_\infty^2$, which has been verified with a variety of glassy polymers.[20] The plastic work can then be estimated by

$$E_{\mathrm{plastic}} = \sigma_{\mathrm{y}}[\cos(\theta/2)\sqrt{3C_\infty} - 1] \tag{1}$$

Equation 1 suggests that the ratio between the plastic work and the yield stress, $[\cos(\theta/2)\sqrt{3C_\infty} - 1]$, is a temperature-insensitive constant, but this ratio depends on the molecular structure of the polymer because C_∞ reflects the flexibility and rigidity of a coiled chain. This E_{plastic}−σ_{y} relationship is the same as that of w_{p}−σ_{y}, suggesting that w_{p} may be a function of E_{plastic}. To quantitatively correlate these two parameters, a set of glassy polymers were selected for further study. Table 2 lists the molecular characteristics of the polymers, and the value of E_{plastic} calculated with eq 1 in which θ is taken to be 68° (the bond angle for polyethylene is 68°). Evidently, the calculated value of E_{plastic} is very close to the experimentally determined value of w_{p}. The good agreement suggests strongly that $w_p \equiv E_{\mathrm{plastic}}$. The minor discrepancy between the two is expected and understandable because of the nonequal length of the chain segments between entanglements in real situations. With different chain lengths, some of the segments cannot be fully extended in the loading direction when the shorter ones are fully stretched. Therefore, the actual extension ratio (λ_{a}) must be lower than the theoretical maximum one ($\lambda_{\max}$). Using our experimental data, the $\lambda_{\mathrm{a}}/\lambda_{\max}$ ratio was found to be about 0.85, which is in the range reported by Donald et al.[18]

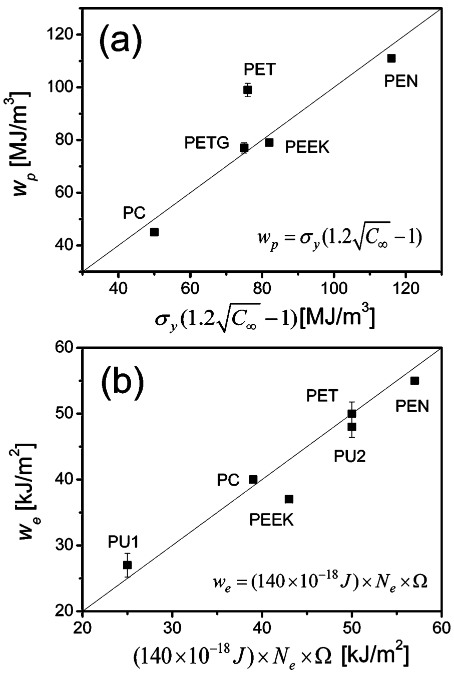

Figure 3. Correlations between the experimental data of w_{e} and w_{p} and their theoretical values: (a) w_{p}; (b) w_{e}.

Through the above discussion, we may propose that w_{p} of the EWF theory under a plane stress condition reflects the plastic work dissipated during the fracture of a polymer thin film via plastically deforming the molecular network up to its locking point. This fracture parameter is therefore mostly dependent on the test temperature and the molecular structure. For a given polymer sample, as long as its yield stress and molecular structure are provided, w_{p} may be predicted with the following equation, which is achieved by the best fitting of the experimental data of a set of glassy polymers as shown in Figure 3a.

$$w_{\mathrm{p}} = \sigma_{\mathrm{y}}(1.2\sqrt{C_\infty} - 1) \tag{2}$$

Now we consider the energy stored in the elastic stretching of fully extended networks, which is finally released as heat at the breaking of the networks. At this stage, the molecular chains near the fracture plane are highly orientated, and no further plastic flow is allowed. The conformations of these molecular chains are schematized as Figure 4. The nodes linking the molecular chains are entanglements or cross-links. This network structure is comparable with the structure proposed by Brown where crazing was considered and between the nodes there were crazing fibrils.[27,28] Assuming that the chains in Figure 4 are straight and the force is transmitted primarily by the entanglements or cross-links, all the backbone bonds between two adjacent junctions are subject to the same force.[29,30] An entanglement chain segment can therefore be treated as a unique point. This treatment bridges the gap between the discrete microstructure of glassy polymers and the continuum constitutive model of the continuum mechanics, which enables the estimation of the total elastic energy stored around the crack tip before the chains break. To calculate this elastic energy, the number of the chain segments in which the elastic stretching takes place and their corresponding energy state should be

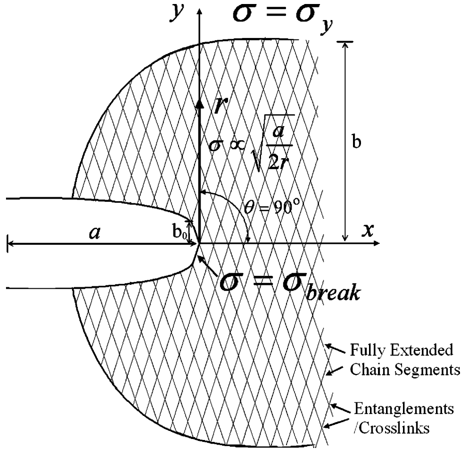

Figure 4. Conformation of highly orientated molecular chains around a crack tip.

determined. According to the continuum fracture mechanics, the stress in the loading direction ahead of a crack tip can be expressed as $\sigma \propto \sqrt{a/2r}$ when assuming the crack is sharp, where a is the crack length and r is the distance away from the crack tip.[31] Because of the different stress level, the stretching extents of the chains around the crack tip are varied. There are two characteristic stresses at the boundary of the elastic stretching zone. The maximum stress is at the crack tip, which reaches the chain breaking stress (σ_{break}) when fracture occurs. The stress at the outside boundary is taken to be σ_y since the chains within the zone must have been deformed plastically when fracture occurs. The half-width of the elastic stretching zone can thereby be expressed as $b = b_0(\sigma_{\mathrm{break}}/\sigma_y)^2$, where b_0 is the distance between the crack tip and the nearest chain segment orientated in the direction 90° to the fracture plane, which can be treated approximately to be the length of a chain segment between two entanglements. Given the force to break a single C−C bond is 2.0−13.4 nN[32] and the chain density across a unit area is about $5 \times 10^{18}/\mathrm{m}^2$,[16] σ_{break} is in the range of 10−67 GPa. The σ_{y} of the present polymers is about 10−50 MPa. Then, $b \approx (0.2-7) \times 10^6 b_0$. In other words, in each side of the fracture plane along the loading direction, namely the y-direction in Figure 4, there are about $(0.2-7) \times 10^6$ chain segments being elastically stretched. The stored elastic energy in these segments is different, varying with the distance away from the crack tip, that is, $E \propto \sigma^2 \propto 1/n$ (assuming the elastic deformation via bond stretching is linear), where n is from 1 to $(0.2-7) \times 10^6$, corresponding to the distance of the chains away from the crack tip. Nominating the maximum elastic energy stored in the chain segment at the crack tip before it breaks as E_{chain}, the elastic energy stored in other chains is $E_n = E_{\mathrm{chain}}/n$. Then, the maximum elastic energy stored in the chains perpendicular to a unit fracture area on both sides of the fracture plane is $E_{\mathrm{elastic}} = 2\Omega\sum_{n=1}^{(0.2-7)\times10^6}(E_{\mathrm{chain}}/n) = (26-32)\Omega E_{\mathrm{chain}}$, where Ω is the chain density across the fracture plane. Since all the backbone bonds in an entanglement chain segment are stressed to the breaking point when rupture occurs,[29,30] the activation energy for breaking a fully stretched chain segment is $E_{\mathrm{chain}} = N_{\mathrm{e}}E_{\mathrm{bond}}$, where E_{bond} is the activation energy to break a covalent bond and N_{e} is the number of the backbone bonds in an entanglement chain segment. Finally

$$E_{\mathrm{elastic}} = (26-32)\Omega N_{\mathrm{e}}E_{\mathrm{bond}} \tag{3}$$

Evidently, this specific elastic energy is independent of the specimen geometry and ligament length, insensitive to the test temperature, and mostly determined by N_{e}, which is a function of the entanglement molecular weight (M_{e}). These dependences are in good agreement with our experimental observations of w_{e}, suggesting that w_{e} may be a function of E_{elastic}. Quantitatively correlating these two parameters was also made with a set of glassy polymers as follows. E_{bond} is mainly composed of the energy for bond stretching and bond bending.[16] The former is to elongate the chemical bond from the equilibrium distance to the critical value where the chemical bond fails. For a C−C bond, this dissociation energy is about 350 kJ/mol.[16] The latter is to open the equilibrium angle between two bonds to a larger one. For C−C bonds, the maximum energy for this bond angle opening is about 400 kJ/mol with an assumption that the angle is opened to 180°.[33] Therefore, the activation energy for breaking a C−C bond is about 750 kJ/mol, namely, 1.3×10^{-18} J/bond. This value may be larger than the actual one since the bond angle is impossible to be opened to 180° before the bond breaks. Since the activation energy for breaking a C−O or C═C bond is much larger than that for breaking a C−C bond, we can suppose that the rupture of a chain occurs at C−C bonds and take 1.3×10^{-18} J/bond as E_{bond}. Then

$$E_{\mathrm{elastic}} = [(34-42) \times 10^{-18}\mathrm{J}]N_{\mathrm{e}}\Omega \tag{4}$$

Table 3. Theoretical Values of E_{elastic} and Experimental Values of w_{e} of a Set of Glassy Polymers[20−26]

polymer[a]	M_{e} [g/mol]	N_{e}	Ω[b] [$10^{-18}/\mathrm{m}^2$]	E_{elastic} [kJ/m²]	w_{e} [kJ/m²]
PC	1780	90	3.1	10−12	40
PEEK	1350	70	4.4	11−13	37
PET	1680	76	4.6	12−15	50
PEN	1810	89	4.5	14−17	55
PU12	900	47	3.5	6−7	27
PU13	2080	109	3.5	13−16	48

[a] PC = polycarbonate; PEEK = poly(ether ether ketone); PET = poly(ethylene terephthalate); PEN = poly(ethylene 2,6-naphthalate); PU = polyurethane. [b] Estimated by Ω = (sample density × length of repeat unit)/(weight of repeat unit).[34]

As shown in Table 3, the calculated value of E_{elastic} is lower than the experimentally determined value of w_{e} of the glassy polymers. The theoretical value of E_{elastic} would be even lower if we consider that the energy for bond angle opening cannot reach as high as 400 kJ/mol. The disagreement between E_{elastic} and w_{e} is believed to be mostly a result of the assumption of a sharp crack made in the model. In real situations, the crack tip should be severely blunted because of the large-scale plastic deformation involved in front of the crack. With a blunted crack tip, the half-width of the elastic stretching zone (b) will be much larger, which means that the $E_{\mathrm{elastic}}/(N_{\mathrm{e}}\Omega)$ ratio in eq 4 should be larger than $(34-42) \times 10^{-18}$ J. A more accurate estimation of E_{elastic} needs precise modeling of the stress distribution in front of a severely blunted crack tip. However, the difficulty is obvious, and it will involve other assumptions. Moreover, one may notice that in our model different treatments of stress distribution only affect the prefactors in eqs 3 and 4, which means that the basic relationship between the total elastic work and the molecular characteristics, $E_{\mathrm{elastic}} \propto (N_{\mathrm{e}} \times \Omega)$, is always valid, regardless of stress distribution used.

When best fitting the experimental data, as illustrated in Figure 3b, a linear relationship between w_{e} and $N_{\mathrm{e}}\Omega$ was achieved as eq 5.

$$w_{\mathrm{e}} = (140 \times 10^{-18}\ \mathrm{J})N_{\mathrm{e}}\Omega \tag{5}$$

The good linearity of the fitting curve implies strongly that $w_e \propto (N_e\Omega)$. With a comparison between eqs 4 and 5, we may propose that $E_{elastic}$ is most likely the dominant energy component dedicated to w_e. The difference of the prefactor in the two equations (the prefactor in eq 4 is lower than the prefactor in eq 5) is mostly owing to the assumption of a sharp crack made in our model, as discussed previously. Similar to the case of w_p, the value of w_e of a given polymer may be predicted from its molecular characteristics with eq 5.

Finally, we wish to address that the model was established with glassy polymers deforming via network stretching under a plane stress condition. Some assumptions are as follows: (1) The physical entanglements are taken to be permanent cross-links, which is valid only when $T < T_g$. When temperature is high or the molecular weight of the polymer is very low, disentanglement or chain pull-out must be considered. (2) The deformation mechanism in the plastic zone is shear yielding, which is valid only for the polymers with flexible chains. For those with crazing mechanism, the model needs to be modified. (3) The entanglement chains are fully extended before rupture occurs, which can only be achieved when the deformation rate is low enough so that the stress can be transmitted efficiently in the entire zone ahead of the crack tip. When the deformation rate is high, the rate dependence of deformation needs to be considered, which will lower both the plastic and elastic energy terms. Moreover, because of the lack of theoretical and experimental data, some other approximations were also made during quantitatively correlating the plastic and elastic work to the EWF parameters. Obviously, there are still rooms for the improvement of the current model.

Conclusion

In summary, a model that can describe the EWF method on the molecular level was built with some assumptions and simplifications. This is the first theoretical model in the EWF development history. The physical meanings of the EWF parameters for glassy polymers were proposed and tested. w_p is proposed to be the energy for fully plastic extending of the networks in the plastic zone, and w_e is proposed to be the energy for elastic stretching and breaking of the backbone bonds of the extended chain segments near the fracture plane. With this model, some of the previous experimental observations of w_p and w_e were successfully explained. For instance, w_p is temperature and molecular structure dependent and has a direct relationship with σ_y; w_e is geometry-independent for thin films and temperature-insensitive at $T < T_g$. Use of this model, the toughness in terms of EWF parameters for a given polymer may be predicted from its molecular characteristics, and meanwhile, molecular structures of new polymers with desired fracture toughness may be designed according to the model, too.

Acknowledgment. This work was supported by Hong Kong Research Grant Council through the project HKUST 6020/01E. We thank Dr. Chenxi Zhang of Bayer Ltd. Shanghai for raw PU monomer supply and invaluable discussion on sample preparation.

References and Notes

(1) Cotterell, B.; Mai, Y. W. In *Advances in Fracture Research*; Francois, D., Ed.; Pergamon: Oxford, 1981; pp 1683−1695.
(2) Mai, Y. W.; Cotterell, B. *Eng. Fract. Mech.* **1985**, *21*, 123−128.
(3) Mai, Y. W. *Inter. J. Mech. Sci.* **1993**, *35*, 995−1005.
(4) Wu, J. S.; Mai, Y. W.; Cotterell, B. *J. Mater. Sci.* **1993**, *28*, 3373−3384.
(5) Wu, J. S.; Mai, Y. W. *Polym. Eng. Sci.* **1996**, *36*, 2275−2288.
(6) Chan, W. Y. F.; Williams, J. G. *Polymer* **1994**, *35*, 1666−1972.
(7) Karger-Kocsis, J.; Czigany, T.; Moskala, E. J. *Polymer* **1998**, *39*, 3939−3944.
(8) Hashemi, S. *Polym. Eng. Sci.* **2000**, *40*, 1435−1446.
(9) Ferrer-Balas, D.; Maspoch, M. L.; Martinez, A. B.; Santana, O. O. *Polymer* **2001**, *42*, 1697−1705.
(10) Lach, R.; Weidisch, R.; Janke, A.; Knoll, K. *Macromol. Rapid Commun.* **2004**, *25*, 2019−2024.
(11) ESIS, *Testing Proposal for Essential Work of Fracture*, European Structural Integrity Society 1995, 1998.
(12) Pardoen, T.; Hachez, F.; Marchioni, B.; Blyth, P. H.; Atkins, A. G. *J. Mech. Phys. Solid* **2004**, *52*, 423−452.
(13) Chen, H. B.; Wu, J. S. *J. Polym. Sci., Part B: Polym. Phys.* **2007**, *45*, 1418−1424.
(14) Chen, H. B.; Karger-Kocsis, J.; Wu, J. S. *Polymer* **2004**, *45*, 6375−6382.
(15) Basu, S.; Mahajan, D. K.; Van der Giessen, E. *Polymer* **2005**, *46*, 7504−7518.
(16) Sperling, L. H. *Introduction to Physical Polymer Science*, 3rd ed.; John Wiley & Sons: New York, 2001.
(17) Boyce, M. C.; Arruda, E. M.; Jayachandran, R. *Polym. Eng. Sci.* **1994**, *34*, 716−725.
(18) Donald, A. M.; Kramer, E. J. *Polymer* **1982**, *23*, 1183−1188.
(19) Rubinstein, M.; Colby, R. *Polymer Physics*; Oxford University Press: New York, 2003.
(20) Wu, S. *J. Polym. Sci., Part B: Polym. Phys.* **1989**, *27*, 723−741.
(21) Hashemi, S.; Williams, J. G. *Plast. Rubber Compos.* **2000**, *29*, 294−302.
(22) Medellin-Rodriguez, F. J.; Phillips, P. J.; Lin, J. S. *Macromolecules* **1995**, *28*, 7744−7755.
(23) Arkhieyeva, A.; Hashemi, S. *Eng. Fract. Mech.* **2004**, *71*, 789−804.
(24) Tonelli, A. E. *Polymer* **2002**, *43*, 637−642.
(25) Fetters, L. J.; Lohse, D. J.; Colby, R. H. In *Physical Properties of Polymers Handbook*; Mark, J. E., Ed.; Springer: New York, 2006; pp 445−452.
(26) Youk, J. H.; Jo, W. H.; Yoo, D. I. *Polym. Bull. (Berlin)* **1997**, *39*, 257−263.
(27) Brown, H. R. *Macromolecules* **1991**, *24*, 2752−2756.
(28) Creton, C.; Kramer, E. J.; Brown, H. R.; Hui, C. Y. *Adv. Polym. Sci.* **2001**, *156*, 53−136.
(29) Lake, G. J.; Thomas, A. G. *Proc. R. Soc. London, Ser. A* **1967**, *300*, 108−119.
(30) Lake, G. J. *Rubber Chem. Technol.* **2003**, *76*, 567−591.
(31) Hertzberg, R. W. *Deformation and Fracture Mechanics of Engineering Materials*; John Wiley & Sons: New York, 1995.
(32) Grandbois, M.; Beyer, M.; Rief, M.; Clausen-Schaumann, H.; Gaub, H. E. *Science* **1999**, *283*, 1727−1730.
(33) Hedenqvist, M. S.; Bharadwaj, R.; Boyd, R. H. *Macromolecules* **1998**, *31*, 1556−1564.
(34) Vincent, P. I. *Polymer* **1972**, *13*, 558−560.

MA062567R