

Adhesion of semi-crystalline polymers: shear contribution to fracture energy

Antoine Guiu, Martin E.R. Shanahan *

École nationale supérieure des mines de Paris, Centre des matériaux P.M. Fourt, CNRS UMR 7633, BP 87, 91003 Evry cédex, France

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Abstract

A study of the adhesion of two semi-crystalline polymers (EVOH and PEG (grafted polyethylene)) by peel has shown that *local* fracture energy, G_A , is virtually independent of peel angle. Adopting the Dugdale model for energy expenditure, we obtain an estimate of G_A^D of the order of magnitude of G_A . However, observation of fracture fronts suggests that supplementary energy losses occur *after* separation, due to shear stresses reorienting the fibrillar craze material. A simple model is proposed to estimate this shear contribution to fracture energy, G_A^S , suggesting the potential importance of shear effects in overall fracture energy. *To cite this article:* A. Guiu, M.E.R. Shanahan, C. R. Physique 3 (2002) 397–402. © 2002 Académie des sciences/Éditions scientifiques et médicales Elsevier SAS

adhesion / Dugdale model / fracture energy / semi-crystalline polymers / shear

Adhésion de polymères semi-cristallins : contribution du cisaillement à l'énergie de rupture

Résumé

Une étude de l'adhésion par pelage entre deux polymères semi-cristallins (EVOH et PEG (polyéthylène greffé)) montre que l'énergie de rupture locale, G_A , est sensiblement indépendante de l'angle de pelage. En adoptant le modèle de Dugdale pour la dissipation énergétique, nous obtenons une estimation de G_A^D de l'ordre de grandeur de G_A . Cependant l'observation des fronts de rupture suggère que des pertes d'énergie ont lieu en outre, *après* la séparation et que celles-ci sont dues aux contraintes de cisaillement qui orientent le matériau fibrillaire des craquelures. Un modèle simple est proposé afin d'estimer cette contribution en cisaillement à l'énergie de rupture G_A^S , qui suggère l'importance potentielle des effets de cisaillement dans le bilan total de l'énergie de rupture. *Pour citer cet article :* A. Guiu, M.E.R. Shanahan, C. R. Physique 3 (2002) 397–402. © 2002 Académie des sciences/Éditions scientifiques et médicales Elsevier SAS

adhesion / cisaillement / énergie de rupture / modèle de Dugdale / polymères semi-cristallins

Version française abrégée

La séparation à l'interface d'un assemblage polymère/polymère peut être comparée à une fissure au sein d'un matériau homogène. Dans le langage de la mécanique de la rupture, l'énergie de rupture, G ,

* Correspondence and reprints.

E-mail address: martin.shanahan@mat.ensmp.fr (M.E.R. Shanahan).

peut souvent être exprimée par l'équation (1) dans le cas de la rupture d'un système polymère, où σ_0 représente une contrainte en traction (constante) dans la zone cohésive au bout de la fissure, et δ_c est le déplacement critique d'ouverture de fissure. Nous avons étudié l'adhésion d'une interface EVOH/PEg (polyéthylène greffé) en utilisant un essai de pelage, où un bras du système est maintenu plat et le pelage du deuxième membre s'effectue à angle, θ , variable (voir Fig. 1). L'énergie globale de pelage, G_P , ainsi que le rayon de courbure, R_0 , du membre pelé au front de séparation, varient avec θ (Fig. 1), mais après correction tenant compte de la dissipation énergétique associée aux déformations lointaines des polymères, l'énergie d'adhésion locale, G_A , se révèle sensiblement indépendante de θ , et égale à environ $5,3 \text{ kJ}\cdot\text{m}^{-2}$. Nous calculons la valeur de G_A à partir du modèle de Dugdale (équation (1)). Avec des valeurs connues du système, nous obtenons $G_A^D \approx 3,6 \text{ kJ}\cdot\text{m}^{-2}$, où G_A^D représente l'énergie correspondant *uniquement* à la traction perpendiculaire à la fissure. Néanmoins, le modèle de Dugdale ne tient pas compte d'autres mécanismes possibles de dissipation d'énergie. L'observation du front de rupture suggère une contribution supplémentaire à l'énergie de rupture liée au cisaillement des fibrilles formées en traction (craquelures). Cette réorientation du matériau dépend d'une contrainte de cisaillement proche du front de rupture (approximée par l'équation (8)) et l'énergie dissipée, G_A^S , est estimée, de façon simplifiée, par l'équation (9). L'énergie totale de rupture est donc la somme des composantes dues à la traction et au cisaillement (équation (10)). Notre calcul simplifié suggère que G_A^S est de l'ordre de $1 \text{ kJ}\cdot\text{m}^{-2}$, ce qui représente une contribution significative à l'énergie de rupture. Le calcul mérite d'être raffiné. Toutefois, ce premier calcul simple suggère que des effets de cisaillement pourraient contribuer de façon significative aux énergies globales de rupture.

1. Introduction

Separation of an assembled polymer/polymer interface, be the interfacial bonding physical or chemical, generally involves considerably more energy than that associated with the 'adhesive' properties directly. This is a consequence of dissipative mechanisms related to both local and far-field deformation of the materials constituting the assembly. A similar state of affairs exists for crack propagation within the bulk of a single material. The classic model of Dugdale [1] considers a symmetrical, two-dimensional crack of length $2c$ at the heart of a material, with a cohesive zone of length d at each end, where a (constant) tensile stress, σ_0 , is experienced due to the (distant) application of an overall tensile force perpendicular to the crack. In the framework of linear elastic fracture mechanics (LEFM), the strain energy release rate, or fracture energy, G , may be expressed as

$$G = \int_0^{\delta_c} \sigma(\delta) d\delta = \int_0^{\delta_c} \sigma_0 d\delta = \sigma_0 \delta_c, \quad (1)$$

where δ and δ_c are respectively crack-opening displacement (COD) and its critical value, the latter corresponding to the transition between the cohesive zone and the void (open crack).

Craze regions observed both in amorphous polymers such as PMMA [2], and in semi-crystalline polymers [3,4] appear to correspond to Dugdale zones [5,6]. Thus the validity of Eq. (1) seems to be borne out.

However, in recent work on the adhesion of two semi-crystalline polymers, two interesting findings were obtained. Firstly, the calculated value of local fracture energy, G_A , exceeded expectations pertaining to Eq. (1). Secondly, observation of peel fracture fronts revealed that the energy dissipation mechanisms had *not* ceased abruptly at the transition between cohesive zone and void (at δ_c). The aim of this Note is to suggest a supplementary energy sink during fracture, attributable to *shear*, as opposed to *tensile*, stresses.

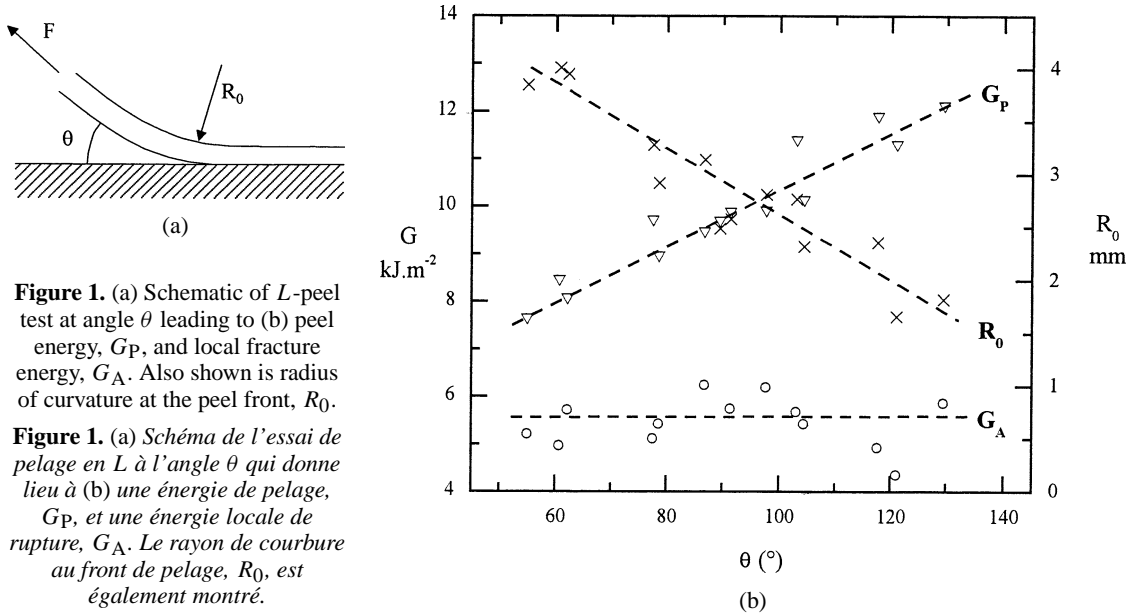


Figure 1. (a) Schematic of *L*-peel test at angle θ leading to (b) peel energy, G_P , and local fracture energy, G_A . Also shown is radius of curvature at the peel front, R_0 .

Figure 1. (a) Schéma de l'essai de pelage en *L* à l'angle θ qui donne lieu à (b) une énergie de pelage, G_P , et une énergie locale de rupture, G_A . Le rayon de courbure au front de pelage, R_0 , est également montré.

2. Experimental system

The adhesion at the interface between a polyethylene–ethylene/vinyl alcohol copolymer (EVOH) and a maleic anhydride grafted linear low-density polyethylene (PEg) has been studied using a so-called *L*-peel test. A five-layer system formed by coextrusion and blow molding at 230 °C, and consisting of two outer layers of high-density polyethylene (HDPE) of thickness ca. 1.2 mm, followed by two inner layers of PEg (the ‘adhesive’) of ca. 100 μm, sandwiching a central layer of EVOH of ca. 150 μm, was loaded in peel. In the case of present interest, an HDPE/PEg bi-layer was peeled at angle θ from the remaining HDPE/PEg/EVOH tri-layer, maintained flat by adhesion to a rigid support (see Fig. 1). Angle θ was varied for a nominal peel rate of 5 mm·min⁻¹, at ambient temperature (ca. 21 °C). Overall peel adhesion energy, G_P , was calculated from

$$G_P = \frac{F}{b}(1 - \cos\theta) \quad (2)$$

where F is peel force and b is peel band width.

As shown in Fig. 1, G_P increased with θ , as may be expected intuitively since the peel band is more flexed at higher angles. This was corroborated by a photographic assessment of the radius of curvature, R_0 , of the peel arm at the peel front, which decreased with angle θ , also shown in Fig. 1. However, after applying an elasto-plastic analysis to the peel results, it was possible to deduct the far-field contribution to G_P and corresponding to bulk energy dissipation in the peel arm, G_F , leaving $G_A (= G_P - G_F)$. G_A may be interpreted as *local* fracture energy, involving only energy-consuming processes in the vicinity of the fracture front. The essential results for present purposes are that $G_A = 5.3 \pm 0.8$ kJ·m⁻² and that this value was found to be virtually *independent* of θ . This (high) value of G_A may be considered to be the practical adhesion energy. A more complete description is given in [4].

3. Evaluation of tensile fracture energy

Initially, we wish to compare $G_A \approx G = \sigma_0 \delta_c$ (Eq. (1)) with the value of 5.3 kJ·m⁻² obtained experimentally. In order to estimate σ_0 and δ_c , we shall use the results of an analysis based on the work of several authors over the years [7–12] but summarised succinctly by Maugis [13]. Taking the peel arm to be

attached to an elastic foundation, an effect of ‘root rotation’ occurs, and an analysis of local displacements and stresses leads to a displacement in the direction perpendicular to the fixed backing:

$$y(x) = \frac{1}{2\lambda^2 R_0} e^{-\lambda x} \left[\left(1 + \frac{R_0 F \sin \theta}{EI\lambda} \right) \cos \lambda x - \sin \lambda x \right], \quad x \geq 0, \quad (3)$$

where [9,14]

$$\lambda = \frac{6^{1/4}}{h} \left(1 + 2 \frac{E h_a}{E_a h} \right)^{-1/4}. \quad (4)$$

I represents the moment of inertia of the peel arm section ($\approx bh^3/12$), h and h_a are respectively HDPE and ‘adhesive’ (PEg) thicknesses, and E and E_a are their corresponding Young’s moduli. Distance x is taken along the (undeformed) intact interface from the crack front. Expression (4) allows for the fact that the peel arm is ‘composite’, consisting of both HDPE and PEg. At the crack opening,

$$y(0) \approx \frac{1}{\lambda^2 R_0} \left(1 + \frac{R_0 F \sin \theta}{EI\lambda} \right). \quad (5)$$

In expression (5), $y(0)$ takes into account both HDPE and PEg displacements. The PEg component is more significant and thus, to a reasonable approximation, $y(0)$ may be identified with δ_c . With the system studied, we then find $\delta_c \approx 180 \mu\text{m}$, which corresponds well with microscopic observation: $R_0 \approx 2.5 \text{ mm}$, $F \approx 140 \text{ N}$, $E \approx 800 \text{ MPa}$, $E_a \approx 170 \text{ MPa}$, $b = 15 \text{ mm}$, $h = 1.2 \text{ mm}$ and $h_a \approx 0.1 \text{ mm}$. Note that the dependence on θ is weak.

The local tensile strains, ε , of the PEg may be estimated simply from $(\delta_c - h_a)/h_a$, and this, in conjunction with data obtained from elasto-plastic extension curves, allows us to estimate the local tensile stress at the crack opening, σ_0 , at ca. 20 MPa. From Eq. (1), we now evaluate G_A^D at ca. $3.6 \text{ kJ}\cdot\text{m}^{-2}$ (where D refers to Dugdale). This value is of the same order of magnitude as the experimentally obtained value of $5.3 \text{ kJ}\cdot\text{m}^{-2}$. However, the Dugdale model does not take into account other possible modes of energy consumption during the fracture process. In particular, microscopic observation of the fracture zone of our system revealed the orientation of fibrillar material *after* separation, i.e. downstream of the crack front. In the following, we propose a tentative first approach to energy dissipation due to such an orientation phenomenon.

4. Shear component to fracture energy

Craze formation has been observed, by both optical and electron microscopy, in the PEg layer near the peel front. For $x > 0$, an apparently fibrillar structure appears with orientation perpendicular to the interface. However, for $x < 0$, instead of an abrupt separation being clear, the fibrils appear to be reorientated as shown schematically in Fig. 2. Simplifying into the two regimes: tension (σ_0) for $x > 0$ and shear (τ_0) for $x < 0$, we attempt to estimate the latter contribution. Kaelble analysed shear stresses in a peel test and showed that shear stresses within an adhesive layer may be expressed as [9,13]

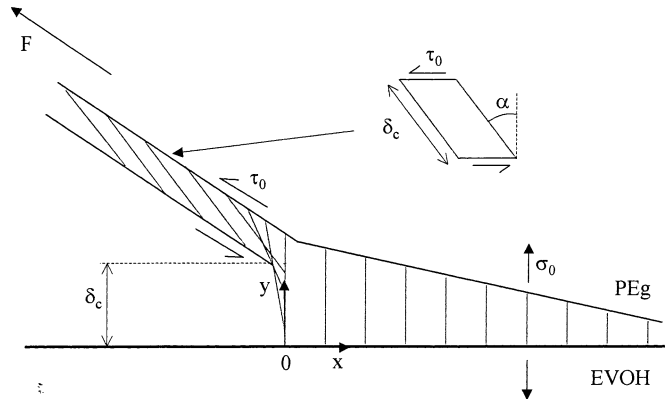
$$\tau(x) = \frac{F \cos \phi}{b} \lambda_T e^{-\lambda_T x}, \quad x \geq 0, \quad (6)$$

where

$$\lambda_T = \left(\frac{\mu_a}{E h h_a} \right)^{1/2}. \quad (7)$$

Figure 2. Schematic of deformation of PEG near peel front. For $x > 0$, deformation is principally in tension; for $x < 0$, principally in shear.

Figure 2. Schéma de la déformation du PEG près du front de pelage. Pour $x > 0$, la déformation est principalement en traction; pour $x < 0$, principalement en cisaillement.



μ_a represents the shear modulus of the ‘adhesive’ layer (PEG), ϕ is the local peel angle near the crack front, and other symbols have their previous meaning. Clearly, in the purely elastic case, we have:

$$\tau_0 \approx \frac{F \cos \phi}{b} \lambda_T \quad (8)$$

with an exponential decay as x increases. An abrupt cut-off is assumed for $x < 0$, but our observation has shown the effect of shear in this region for the system studied. A rigorous analysis of shear for $x < 0$ has not been undertaken (and, we suggest, may well be complex due to the partially plastic nature of the system!), but we tentatively propose that shear stress along the HDPE/PEG will remain essentially constant, corresponding to a plastic reorientation of the PEG, while the angle of orientation of the craze structure, α , (see Fig. 2) evolves from ca. 0 to its final value, $\alpha_f \approx \pi/2$. Admittedly, use of Eq. (8), stemming from elastic analysis, will introduce some errors for our elasto-plastic system, but microscopic observation confirmed the physics of this approach. No significant further *extension* of the fibrillar zone beyond δ_c is taken into account. Thus, following the Dugdale scheme, and ignoring a pre-factor which may well be difficult to evaluate (being related to the decay of $\tau(x)$ for $x < 0$), we may define a shear contribution to effective fracture energy:

$$G_A^S \approx \int_0^{\alpha_f} \tau(x) \delta_c d(\sin \alpha) \approx \int_0^{\alpha_f} \tau_0 \delta_c d(\sin \alpha) \approx \frac{F \cos \phi}{b} \lambda_T \delta_c. \quad (9)$$

With $\lambda_T \approx 0.8 \text{ mm}^{-1}$ (taking $\mu_a \approx 60 \text{ MPa}$ and $h_a \approx 100 \text{ }\mu\text{m}$), $\phi \approx \pi/4$ (from observation) and $\delta_c \approx 180 \text{ }\mu\text{m}$, we obtain $G_A^S \approx 1 \text{ kJ}\cdot\text{m}^{-2}$. We cannot attach any great significance to the actual numerical value obtained for G_A^S but, it is of the same order of magnitude as G_A^D , and thus may help explain, at least partially, the difference between values of G_A obtained from experimental and analytical approaches. Clearly, various (over)simplifications have been adopted in calculating G_A^S , but results and observations of fracture fronts suggest that shear deformation may significantly contribute to fracture energies.

5. Conclusions

The adhesion of two semi-crystalline polymers has been studied using peel tests at various angles. Once bulk polymer contributions to fracture energy have been allowed for, the intrinsic local energy of adhesion, G_A , is virtually independent of peel angle, but rather high. Application of the Dugdale model explains a part, G_A^D , but not all, of the local adhesion energy. Observation of post-separation fibrillar structures suggests that part of the ‘missing’ energy, G_A^S , may be attributed to shear-induced orientation of the zone crazed during (tensile) peel. We may thus write, ignoring pre-factors, an expression for adhesion energy of

the form:

$$G_A \approx G_A^D + G_A^S \sim \sigma_0 \delta_c + \tau_0 \delta_c \quad (10)$$

where δ_c is a critical crack opening displacements, and σ_0 and τ_0 are tensile and shear stresses occurring near the peel front.

Work is required to elucidate the precise nature of the proposed shear contribution to fracture energy, but this preliminary study points to the fact that energy dissipation, and therefore increased fracture toughness, may be associated with a mode of polymer deformation in which volume change is not implicit.

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