Welding Behavior of Semicrystalline Polymers. 2. Effect of Cocrystallization on Autoadhesion

Y.-Q. Xue,[†] T. A. Tervoort,*[,‡] S. Rastogi,[†] and P. J. Lemstra[†]

Eindhoven Polymer Laboratories, Eindhoven University of Technology, P.O. Box 513,
5600 MB Eindhoven, The Netherlands, and ETH Zürich, Materials Department,
Institute for Polymers, ETH Zentrum, UNO C 15, Universitätstrasse 41, CH-8092 Zürich, Switzerland

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ABSTRACT: The effect of cocrystallization on the welding behavior of semicrystalline polymers was studied by means of T-peel testing at room temperature, using ultrahigh-molecular-weight polyethylene (UHMWPE) as a model polymer. Solution-cast films of UHMWPE have a very special morphology, consisting of regularly stacked, 107 Å thick lamellae, which exactly double in thickness upon annealing for 15 min below the melting point at 125 °C. This lamellar doubling process was used to introduce a well-defined amount of cocrystallization across the interface, by annealing two stacked, completely wetted solution-cast films. It was found that doubling of the lamellae across the interface enhances the peel energy to such a level that the films could not be separated anymore. By contrast, reference samples, in which cocrystallization across the interface was prohibited by "preannealing" one side of the film, could still be separated easily. Therefore, it is concluded that cocrystallization across the interface is extremely efficient in enhancing the adhesive fracture energy.

Introduction

The welding behavior of amorphous polymers has been studied extensively, theoretically as well as experimentally.[1−3] It is generally accepted that the adhesive fracture energy depends to a large extent on the size of the local plastic zone behind the crack tip, which in turn is determined by the formation of entanglements upon diffusion. It is, therefore, well recognized that there exists a strong analogy between the molecular weight dependence of the fracture toughness of amorphous polymers and the development of adhesive strength at the interface.[1,4]

The welding behavior of semicrystalline polymers has received much less attention. First of all, in contrast to amorphous polymers, the crystalline phase can give rise to extensive plastic deformation, often prohibiting the use of *linear* fracture mechanics. If the plastic zone behind the crack tip compares to the sample dimensions, it becomes increasingly difficult, both experimentally and theoretically, to define a geometry-independent parameter that characterizes the welding behavior (ref 5, Chapter 9).

In addition, little is known about the molecular weight dependence of the fracture behavior of semicrystalline polymers. Unlike amorphous polymers, the morphology of semicrystalline polymers is dependent on the molar mass, which in its turn can have a large effect on the fracture energy.[6] Huang and Brown determined the effect of molar mass[7,8] and the density of short-chain branches[9] on slow crack growth in polyethylene. Recently, the critical molecular weight for resisting slow crack growth in an ethylene−hexene copolymer was determined.[10] Finally, crystallization also can lead to compact chain-folded crystals, which upon melting can give rise to anomalous diffusion behavior.[11] This, again, has no equivalent in amorphous polymers.

It is, therefore, not surprising that the welding characteristics of semicrystalline polymers can be quite different from amorphous polymers and are far from being understood. In the previous paper of this series,[11] the effect of nonequilibrium chain configurations and the resulting anomalous diffusion behavior on welding was discussed. It was concluded that the rapid transition from a compact folded chain to a random walk configuration upon melting can have a large influence on the welding characteristics measured *above* the melting point. It was also found that the adhesive fracture energy measured *below* the melting point (at room temperature) increased rapidly (within a few minutes) to the fracture energy of the bulk material upon welding. This last result was also observed on cross-linked polyethylene by Gent et al.,[12] who attributed this unusual quick healing to cocrystallization across the interface.

The aim of the current research is to study the effect of cocrystallization on welding of semicrystalline polymers in more detail, again using ultrahigh-molecular-weight polyethylene as a model polymer. Ultrahigh-molecular-weight polyethylene (UHMWPE) is defined as a linear polyethylene with a molar mass over 3000 kg/mol. It combines a high abrasion and chemical resistance and is, for example, used as coating inside pipes or as hip prosthesis. Because of its high molar mass, UHMWPE can be regarded as an intractable polymer for which conventional melt processing is not possible. Instead, application of UHMWPE typically involves processing routes which strongly rely on full recovery of interfaces, like welding of skived films, ram extrusion, and powder sintering.[13]

Crystallization of a semidilute UHMWPE solution, constrained to a flat surface, results in a so-called "solution-cast film". These films consist of thin lamellae with a thickness of 107 Å,[14] which are regularly stacked, probably due to the combined action of gravity and shrinking forces upon removal of the solvent. It was recently found[14,15] that, upon annealing these solution-

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[†] Eindhoven University of Technology.
[‡] ETH Zürich.
* To whom correspondence should be addressed.

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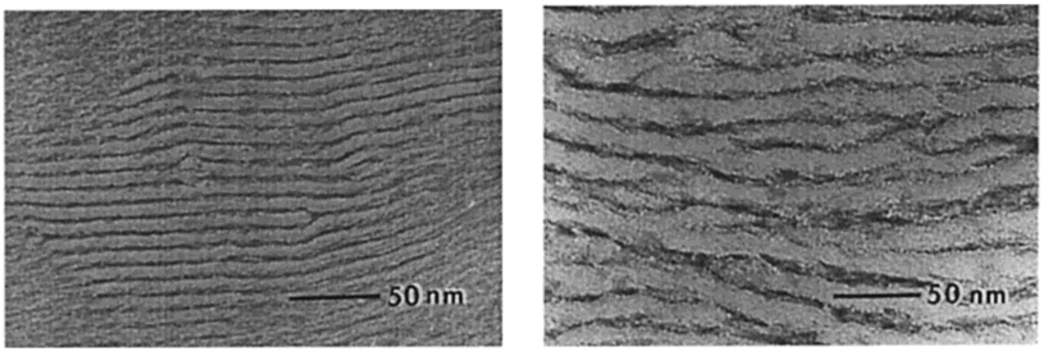

(a) (b)

Figure 1. Transmission electron micrographs showing the lamellar doubling in solution-cast UHMWPE films upon annealing: (a) not annealed, (b) after 15 min annealing at 125 °C.

cast films close to the melting temperature, the lamellar thickness doubles from 107 to 209 Å (see Figure 1). It was concluded that the thickening occurs through sliding diffusion of the chain segments in the direction of the chain axis, i.e., not through melting and subsequent recrystallization.

In the current research, this lamellar doubling effect will be used to introduce a well-defined amount of cocrystallization across the interface by annealing two stacked, completely wetted, solution-cast films. Subsequently, the effect of this cocrystallization on the welding behavior will be determined by T-peel testing at room temperature.

Experimental Section

Materials. The material used was Gur 2122 UHMWPE powder, kindly supplied by Hoechst, with a weight-averaged molar mass $M_w = 4.4 \times 10^6$ g/mol.

Film Preparation. The procedures to prepare solution- and melt-crystallized films have been described in detail elsewhere.[16] Solution-crystallized films were prepared by pouring a 1 wt % UHMWPE solution in xylene containing 0.5 wt % stabilizer (based on polymer content), in an aluminum tray at room temperature. After crystallization, the wet gel was clamped to a cardboard, to prevent lateral shrinkage of the samples during subsequent removal of the solvent by drying in a vacuum oven at 40 °C for 2 days.

To obtain films with an intimate contact at the interface, a wet gel at room temperature, obtained from dilute solution as described above, was clamped upon a *dry* solution cast film, after which the solvent was removed in a vacuum oven at 40 °C for 2 days. To initiate a crack in these so-called "prewetted films", a Teflon tape was inserted at one side between the wet gel and the dry film. As the polymer chains in the gel are largely immobilized by the crystallization process and, moreover, the dry film will not dissolve in xylene at room temperature, no large-scale diffusion is to be expected. The films could still be separated by hand at room temperature after the drying procedure, in agreement with the absence of large-scale diffusion. The total thickness of the films was 0.2 mm.

Welding of the UHMWPE Films. The prewetted films (completely dried) were subsequently welded by annealing for 15 min in a silicon oil bath at different temperatures, using aluminum foil for protection. A schematic representation of the effect of annealing at the molecular level is depicted in Figure 2.[15] A reference sample was obtained by first annealing a (dry) solution-cast film at 125 °C to induce the lamellar doubling and then using this film to make a "prewetted film" as described in the Materials section. Upon annealing these reference samples, lamellar doubling is expected *not* to occur across the interface, since in one part of the film the doubling process process has already been completed (see Figure 2).

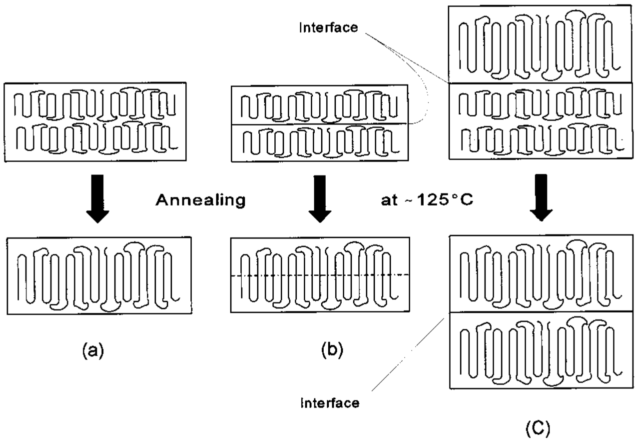

Figure 2. Schematic drawing of (a) the lamellar doubling process upon annealing at 125 °C, (b) cocrystallization across the interface due to the lamellar doubling process, and (c) the reference sample in which cocrystallization across the interface is prohibited by preannealing one side of the sample.

Small-Angle X-ray Scattering (SAXS). Small-angle X-ray scattering experiments were performed on a Philips X-ray generator, operated at 40 mA and 20 kV and equipped with a Cu target. Sample strips, having a thickness of 0.4 mm, were fixed perpendicular in the sample holder, with the cross section facing the X-ray beam. The SAXS intensity contours $I(2\theta)$ were recorded by a Rigaku small-angle scattering goniometer (CN2203E5) at sampling intervals of 0.002° and a scan speed of 0.002°/min from 0.13° to 2.5°. The receiving slit was 0.1 mm, and the sample-to-detector distance was about 227 mm.

Tensile Testing. Tensile test experiments were performed on strips of 0.3 mm thick, 50 mm length, and 10 mm width, using a Zwick 1445 tensile tester at a constant cross-head speed of 5 mm/min, which corresponds to an initial strain rate of $\dot{\epsilon} \approx 3 \times 10^{-3}$ s^{-1}. The elongation was measured from the displacement of the clamps (initial clamp distance 28 mm). The tensile experiments were performed at 20 °C.

T-Peel Testing. The T-peel test is a well-known testing method to determine the adhesive fracture energy. The T-peel experiments were performed according to ASTM D1876-72, on a Zwick 1445 tensile tester, at a constant speed of 5 mm/min, at 20 °C. In steady state, two UHMWPE laminates of width $b = 10$ mm and thickness $h = 0.1$ mm are peeled at constant peel force F. At a peeling displacement L, the crack has advanced over a distance a. The elongation in the arms was always small; therefore, $L = 2a$. In this study, the so-called "peel energy" W, defined as

$$W = \frac{1}{ab}\int_0^L F \, \mathrm{d}L = \frac{2F}{b} \qquad (1)$$

was used as a measure of adhesion. The peel energy is not

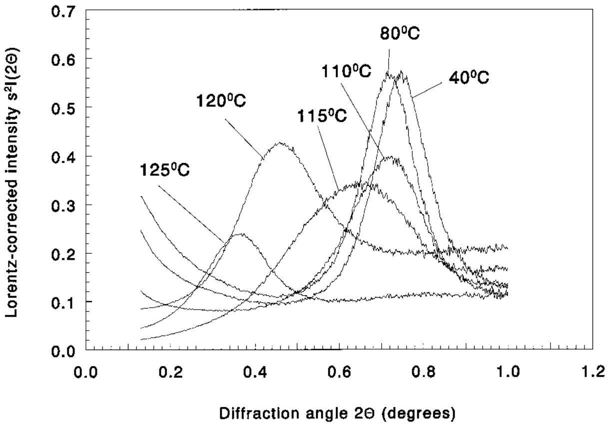

Figure 3. Lorentz-corrected SAXS intensity curves of solution cast films as a function of annealing temperature. The annealing time for each sample was 15 min.

equal to the adhesive fracture energy directly, since not all the external work is available for debonding the laminates. Tensile deformation of the arms will lead to stored strain energy and plastic (or viscoelastic) energy dissipation in the peeling arms. Furthermore, part of the work will be dissipated due to plastic bending of the arms. All data listed in this paper correspond to average values of five measurements.

Results and Discussion

Lorentz-corrected SAXS intensity curves of solution-cast UHMWPE tapes, annealed at different temperatures for 15 min, are depicted in Figure 3. The corresponding average lamellar thickness values are listed in Table 1, as well as the yield stress data, the melting temperatures, and melting enthalpies. The average lamellar thickness values l were determined from the peak positions, using Bragg's law:

$$l = \frac{\lambda}{2\sin(\theta)} \tag{2}$$

with the X-ray wavelength λ and the diffraction angle θ.

It is normally assumed that welding involves two stages: wetting and diffusion.[3] In this particular case of welding through annealing at 125 °C, diffusion of chains across the interface can only result from the lamellar doubling process. It is, however, very unlikely that merging of the lamellae will occur across a *non-wetted* surface. Therefore, to circumvent the wetting stage, wet solution-cast gels were clamped upon dry solution-crystallized films at room temperature, *after* crystallization but *before* removal of the solvent, resulting in so-called "prewetted" films (see Experimental Section). After removal of the solvent, these "prewetted" films could still be separated by hand, indicating that large-scale segmental diffusion across the interface is prohibited since the dry film will not dissolve in xylene at room temperature. Moreover, due to crystallization, even in the presence of solvent, the polymer chains in the gel are "locked" in the crystals.

The peel energy of these prewetted films, annealed for 15 min at different temperatures, is depicted in Figure 4. From this figure it is clear that, after annealing at 125 °C where doubling of the lamellae occurs, the films cannot be separated anymore. The peel energy, however, is not equivalent to the adhesive fracture energy alone but also includes energy stored and dissipated during deformation and bending of the arms, of which the latter depends on the yield stress. Since the yield stress also increases upon lamellar doubling (see Table 1), it is not a priori clear that the increase in peel energy can be attributed to an increase in adhesive fracture energy alone. Therefore, reference samples were prepared consisting of prewetted films of which one side was "preannealed" at 125 °C, before wetting and final annealing. In this case, the final annealing step is expected *not* to result in cocrystallization across the interface, since the doubling process on one side of the film is already completed (see Figure 2). Nevertheless, the yield stress in these reference films will be the same as in the normal films, and so will be the contribution of the dissipated energy in the arms to the peel energy. Comparing the peel energy of these reference sample and the annealed prewetted films, it is clear that cocrystallization across the interface due to the lamellar doubling process indeed results in a large increase of the adhesive fracture energy. Since chain diffusion during the doubling process is limited, it must be concluded that, in the solid state, large-scale chain diffusion is not a prerequisite for good welding performance. Apparently, cocrystallization across the interface is extremely efficient in raising the adhesive fracture energy.

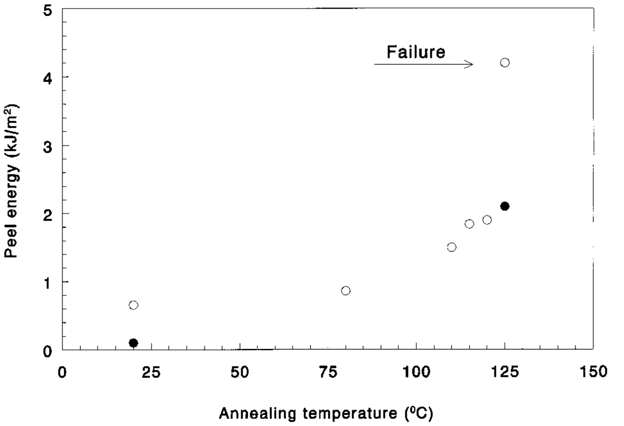

Figure 4. Peel energy of prewetted films annealed for 15 min at different temperatures (○). The two dots (●) refer to prewetted films of which one side was "preannealed" before wetting and final annealing, so that cocrystallization across the interface is prohibited (see text).

Table 1. Average Lamellar Thickness and Yield Stress as a Function of Annealing Temperature (Annealing for 15 min)

annealing temp (°C)	av lamellar thickness (Å)	yield stress (MPa)
20	118.1	12
110	125.1	17
115	137.1	19
120	192.9	28
125	236.2	35

Conclusions

This study is concerned with the effect of cocrystallization across the interface on the welding behavior of semicrystalline polymers, using ultrahigh-molecular-weight polyethylene as a model polymer. Crystallization of a semidilute UHMWPE solution, constrained to a flat surface, followed by evaporation of the solvent, results in so-called "solution-cast films". These films consist of regularly stacked, 107 Å thick lamellae, which exactly double their thickness upon 15 min annealing at 125 °C.[14] To obtain two stacked films with an intimate contact at the interface (to circumvent the wetting stage), wet solution-cast gels were clamped upon dry solution-crystallized films at room temperature, *after* crystallization but *before* removal of the solvent. The combination of completely wetted films, consisting of regularly stacked lamellae which double upon annealing below the melting temperature, offers a unique way to introduce a well-defined amount of cocrystallization across the interface.

It was found that doubling of the lamellae across the interface enhances the peel energy to a level such that the films could not be separated anymore. By contrast, reference samples, in which cocrystallization across the interface was prohibited by "preannealing" one side of the film, could still be separated easily. Therefore, it can be concluded that the limited amount of chain diffusion across the interface, as it occurs during doubling of the lamellae, is extremely efficient in raising the adhesive fracture energy.

In the case of amorphous polymers, the buildup of adhesive fracture energy during autoadhesion is due to the formation of entanglements upon diffusion. This requires, in general, large-scale chain diffusion and, especially at high molar mass, long welding times (ref 1, Chapter 8). The results obtained in this study indicate that large-scale chain diffusion is not a prerequisite for good welding performance in the case of semicrystalline polymers. Apparently, local plastic yielding in crystalline domains,[17] formed by cocrystallization across the interface, induces substantial energy dissipation and results in high levels of adhesive fracture energy which can be obtained in relatively short welding times.[12]

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