Macromolecules **1998,** *31,* 3075−3080

Welding Behavior of Semicrystalline Polymers. 1. The Effect of Nonequilibrium Chain Conformations on Autoadhesion of UHMWPE

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Received April 22, 1997; Revised Manuscript Received January 13, 1998

ABSTRACT: The effect of the overall crystallinity and the initial crystal morphology on the welding behavior of semicrystalline polymers was investigated by means of T-peel testing above and below the melting point using ultrahigh-molecular-weight polyethylene (UHMWPE) as a model polymer. Different crystal morphologies were generated by either crystallizing UHMWPE from the melt or from dilute solutions. The initial crystal morphology was found to have a large influence on the adhesive fracture energy as measured *above the melting temperature.* In the case of two melt-crystallized films, the adhesive fracture energy above the melting temperature, $G_a^{T>T_m}$, developed only slowly, and did not reach the fracture energy of the bulk material, even after 65 h of welding at 145 °C. However, welding two (completely wetted) solution-cast films above the melting temperature resulted in an almost instantaneous increase of $G_a^{T>T_m}$ to the level of the fracture energy of the bulk material. The adhesive fracture energy *at room temperature* increased almost instantaneously to the fracture energy of the bulk material upon welding above the melting point, irrespective of crystal morphology.

Introduction

The welding behavior of amorphous polymers has been studied extensively, theoretically as well as experimentally.[1−3] It is generally concluded, that complete healing of (amorphous) polymer interfaces involves two stages:[3] wetting and diffusion. Although the time dependences of viscous flow to promote contact and that of interdiffusion are comparable, it is normally assumed, that for amorphous polymers of reasonably high molar mass, the diffusion stage is critical.[1] Due to the strong steric hindrance between the covalent bonded chains, (self) diffusion in polymers proceeds through snakelike motion of the chains,[4] a process called “reptation”. In the case of high molar mass and with plane strain conditions at the crack tip, reptation theory predicts that the adhesive fracture energy G_{Ic} increases proportional to the square root of time (ref 1, Chapter 7), which was confirmed by experiments on monodisperse polystyrene.[5,6]

In the case of amorphous polymers, the random walk configuration in the melt is frozen in upon cooling below the glass transition temperature. Therefore, healing of two symmetric amorphous polymer surfaces involves diffusion of random coiled chains with a random chain-end distribution across the interface. It is normally assumed that a possible nonequilibrium configuration of the chains at the interface has no influence on the diffusion process, an important exception being the case of chain-end segregation at the surface, as occurs in the case of crack healing.[7] Here, it was found that the high concentration of chain ends at the surface enhances diffusion, and, therefore, accelerates the welding process.

In the case of semicrystalline polymers, the crystallization process can lead to chain configurations which, at least locally, are far from the random walk configuration in the melt. Therefore, it is to be expected that the loss of crystalline structure upon melting will locally result in nonequilibrium chain configurations, which initially might lead to strong deviations from “normal” reptation behavior.

This study is concerned with the effect of this “randomization” of the initially ordered chains upon melting, on the welding behavior of semicrystalline polymers. As a model semicrystalline polymer, ultrahigh molecular weight polyethylene is used, due to its ability to crystallize in a wide variety of morphologies, in which the chain dimensions, viz. radius of gyration, differ substantially.

Ultrahigh-molecular-weight polyethylene (UHMWPE) is defined as a linear polyethylene with a weight-averaged molar mass of over 3000 kg/mol.[8] It combines a high abrasion and chemical resistance and is, for example, used as interliner or in highly demanding applications such as artificial hip joints. Due to 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.[8]

Due to its high viscosity, crystallization of an UHMWPE melt results in a semicrystalline material of moderate crystallinity (≈45%), in which the crystalline lamellae have a thickness in the order of a few hundred angstroms. It is normally assumed that, upon crystallization from the melt, an individual chain is incorporated into many different lamellae and amorphous regions. Nevertheless, neutron scattering experiments on HDPE showed that during crystallization the overall chain dimensions, viz. the radius of gyration, do not change much.[9] Also the entanglement density is not really influenced by the crystallization process, as is evident from the, more or less, constant maximum draw ratio (λ_{max}) at higher molar mass, independent from the crystallization conditions.

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S0024-9297(97)00544-5 CCC: $15.00 © 1998 American Chemical Society
Published on Web 04/17/1998

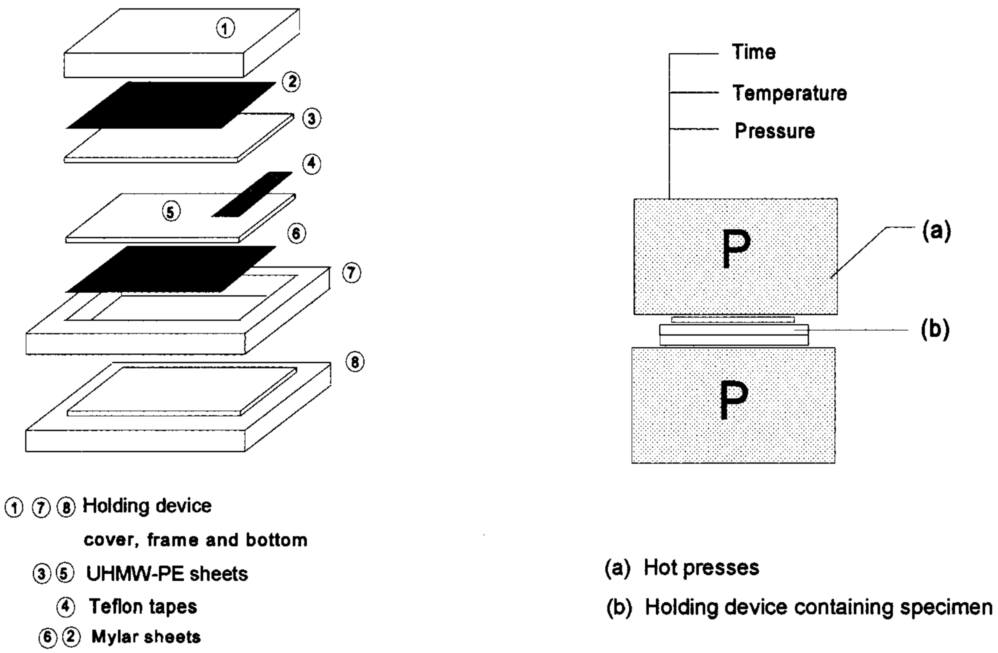


Figure 1. Holding device used to position the UHMWPE films during welding.

In contrast, crystallization of an UHMWPE solution in the limit of extreme dilution results in “single crystal mats”, in which entire polymer chains are confined to one crystal. Compared to the melt, this leads to a large reduction of the radius of gyration and an almost complete loss of entanglements.[9]

Crystallization of a semidilute UHMWPE solution, constrained to a flat surface, results in so-called “solution-cast films”. These films consist of thin lamellae with a thickness of 120 Å, which are regularly stacked, probably due to the combined action of gravity and shrinking forces upon removal of the solvent. The high molecular weight between entanglements, existing in the original solution, is frozen in during crystallization. As a result, the maximum draw ratio in solution cast films depends on the polymer concentration in the original solution and can be as high as $\lambda_{\max} = 200$. The high degree of orientation accompanying these high draw ratios results in favourable mechanical properties[10] and is nowadays used to obtain high performance polyethylene fibers.

It has been suggested that the low entanglement density, frozen in by crystallization from dilute solution, could pertain for a certain time span upon reheating above the melt temperature. This would then result in an initial lowering of the viscosity, thus offering a time window for melt processing. However, experiments by Lemstra *et al.* on LDPE[11] did not reveal any of these so-called “memory effects” for solution-cast materials. Upon melting solution-cast material, the melt viscosity was immediately equal to the equilibrium melt viscosity. Similarly, one would, perhaps, expect that the maximum draw ratio slowly decreases upon melting and subsequent recrystallization. However, it was found by Bastiaansen *et al.*[12] that indeed the drawability of solution cast material is lost almost instantaneously upon melting. It is as if the polymer chains reentangle on a time scale too short to be observed by macroscopic experiments. This was later confirmed more directly by Barham *et al.*,[9] who performed neutron-scattering experiments on solution-cast high density polyethylene (HDPE) films, which were molten for different periods of time. From these experiments it was evident that, upon melting, the small radius of gyration, characteristic for solution-cast material, increased through very fast “Rouse-like dynamics”[13] to the much larger equilibrium value of the radius of gyration in the melt.

The aim of the current research is to explore the effect of this so-called “chain explosion” on the self adhesion of two UHMWPE surfaces, upon welding above the melting temperature.

Experimental Section

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

Film Preparation. The procedures to prepare solution- and melt crystallized films have been described in detail elsewhere.[10] 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 cupboard, in order to prevent lateral shrinkage of the samples during subsequent removal of the solvent by drying in air for two days and in a vacuum oven at 40 °C, also for 2 days. The melt-crystallized UHMWPE films used in this study were obtained by annealing solution-cast UHMWPE films at 160 °C for 1 h under vacuum.

In order to obtain films with an intimate contact at the interface, so-called “prewetted” laminates were prepared. To this extent, a wet gel at room temperature, obtained from dilute solution as described above, was clamped upon a *dry* solution cast film, after which the films were dried in air for 2 days at room temperature and in a vacuum oven at 40 °C, also for 2 days. It is known that at temperatures close to the melting transition, the lamellar thickness in solution-cast films increases exactly by a factor of 2.[14–16] To prevent this lamellar doubling process to occur across the interface upon melting these prewetted laminates, the starting solution-cast film was first annealed at 125 °C for 15 min.[14] 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 (see Figure 1). 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. Moreover, it was observed that

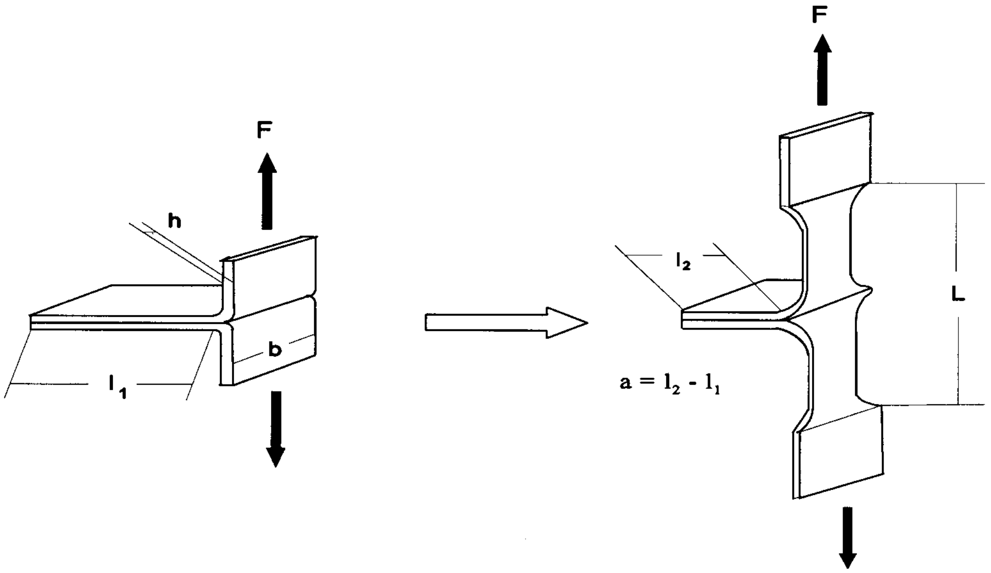


Figure 2. Experimental setup of the T-peel test.

the films could still be separated by hand after the drying procedure.

Welding of the UHMWPE Films. The solution cast, melt-crystallized, and “prewetted” UHMWPE films were welded in a hot press, using a holding device as shown in Figure 1. At one end of the UHMWPE films, a Teflon tape was inserted to initiate a crack for the T-peel test. To compensate for the thickness of this Teflon tape, Teflon sheets of the same total thickness were placed between the UHMWPE films and the holding device (see Figure 1). To avoid breaking of the arms during the T-peel test, the total specimen thickness was increased to 3 mm by stacking several UHMWPE films on top of each other. After the welding, the sheets were cut into 10 mm wide T-peel test specimen.

To minimize the thermal equilibrium time during the actual welding, the holding device, containing the T-peel test sample, was preheated at 100 °C. The actual welding was performed at 145 °C, at moderate pressure. After a specific welding time, the holding device was quenched to room temperature, using a cold press. The shortest welding time employed was 3 min.

Tensile Testing. Tensile test experiments were performed on a Zwick 1445 tensile tester at a constant cross-head speed of 5 mm/min, which corresponds to an initial strain rate of $\dot{\epsilon} \approx 10^{-2}$ s^{-1}. The elongation was measured from the displacement of the clamps. The tensile experiments were performed at 20 and 135 °C on a dumbbell-shaped specimen.

T-Peel Testing. The T-peel test is a well-known testing method to determine the adhesive fracture energy G_a. 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, and at two temperatures, 20 and 135 °C, which are below and just above the DSC peak melting temperature of UHMWPE (133 °C), respectively. All data listed in this paper correspond to average values of five measurements.

The T-peel test is shown in Figure 2. In the steady state, two UHMWPE laminates of width b and thickness h are peeled at constant peel force F. At a peeling displacement L, the crack has advanced over a distance a. The extension of the arms is then given by

$$\epsilon = \frac{L - 2a}{2a} \tag{1}$$

During the peel test, the adhesive fracture energy G_a cannot be determined 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. This energy-balance argument[17] leads to the following definition of the adhesive fracture energy G_a:

$$G_a = \frac{1}{b}\left(\frac{dW}{da} - \frac{dU_{arm}}{da} - \frac{dU_b}{da}\right) \tag{2}$$

Here, W is the total power input, $W = \int_0^L F\, dL$, U_{arm} accounts for the stored strain energy and plastic dissipation energy during tensile deformation of the arms, and U_b is the energy dissipated during plastic bending of the arms. The energy stored and dissipated during tensile deformation of the arm, U_{arm}, is equal to

$$U_{arm} = 2bha \int_0^{\epsilon} \sigma\, d\epsilon \tag{3}$$

where $\int_0^{\epsilon} \sigma\, d\epsilon$ can be determined from a tensile test. The plastic bending energy U_b, can not be measured directly, but was estimated as[18]

$$U_b = bha\sigma_y \tag{4}$$

with σ_y the yield stress of UHMWPE in tensile deformation.

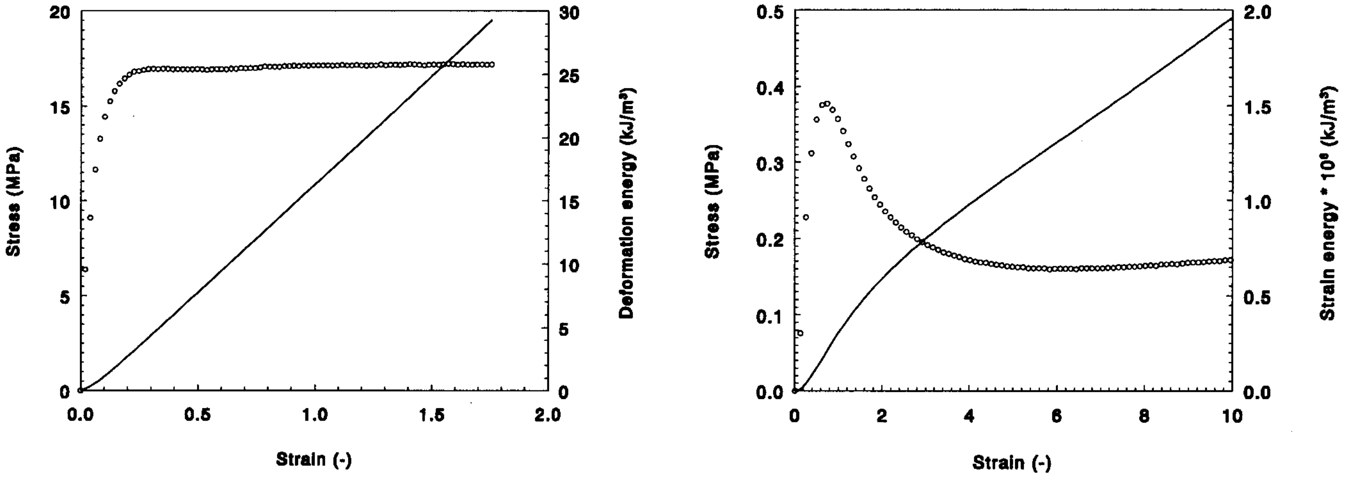
The adhesive fracture energy G_a at constant peel force F in terms of experimental observable quantities then follows from the strain definition eq 1, the energy balance eq 2, and eqs 3 and 4

$$G_a = \frac{2}{b}F(1 + \epsilon) - 2h \int_0^{\epsilon} \sigma\, d\epsilon - \sigma_y h \tag{5}$$

Results and Discussion

Tensile Testing of UHMWPE. Tensile stress–strain curves of UHMWPE at 20 and 135 °C are depicted in parts a and b of Figure 3. At 20 °C, the yield stress equals $\sigma_y = 17$ MPa. At 135 °C, UHMWPE is above the DSC peak melting temperature, and consequently, the (apparent) “yield stress” is virtually zero ($\sigma_y = 0.4$ MPa). Also included in Figures 3a and b, is the deformation energy per unit volume $\int_0^{\epsilon} \sigma\, d\epsilon$

T-Peel Testing at 20 °C. The solution-cast, melt-crystallized, and prewetted films were welded at 145 °C and subsequently tested at 20 °C. For all films it was observed that, already after 3 min of welding at 145 °C, failure occurred in the arms during the T-peel tests. This indicates, that, during this short welding period, the adhesive fracture energy at 20 °C, G_a^{20}, has advanced toward the fracture energy of the bulk mate-



(a) (b)

Figure 3. Stress–strain curves (○) and the corresponding deformation energy $\int_0^{\epsilon}\sigma\, d\epsilon$ (solid line) of UHMWPE at (a) 20 °C and at (b) 135 °C.

rial. Three minutes is the shortest welding time that could be achieved experimentally. Although no steady state could be achieved during the peel test, a lower bound for the adhesive fracture energy was estimated by substitution of the strain at failure, ϵ_f into eq 5:

$$G_a^{20} \geq \frac{2}{b}F(1 + \epsilon_f) - 2h\int_0^{\epsilon_f}\sigma\, d\epsilon - \sigma_y h \qquad (6)$$

In this way, for all films, a lower bound of the adhesive fracture energy at 20 °C was estimated as: $G_a^{20} \geq 30$ kJ/m^2.

The fast increase in adhesion after cooling to room temperature, observed for all films, has also been observed in the case of cross-linked polyethylene[19] and was attributed to co-crystallization across the interface. Apparently, this mechanism only requires local segment diffusion across the interface, which occurs on a time scale shorter than the shortest welding time employed in this study. The effect of crystallinity on autoadhesion was already recognized by Epstein,[20] who observed a sharp decrease of the shear strength of the interface above the melting point, for a number of polymers.

T-Peel Testing at 135 °C. To eliminate the effect of cocrystallization and to reveal the contribution of chain diffusion across the interface on adhesion, T-peel testing was also conducted at 135 °C, above the melting point of UHMWPE. At 135 °C, the "yield stress" of UHMWPE is only 0.4 MPa (see Figure 3b). According to Gent,[18] the energy, dissipated during plastic bending of the arms (U_b), should be proportional to the film thickness h and the yield stress (eq 4). An extra advantage of peeling at 135 °C, therefore, is that the plastic bending term U_b, which can not be measured directly, will be small. Consequently, the adhesive fracture energy at 135 °C, G_a^{135}, is mainly determined by the total external work, $W = \int_0^L F\, dL$, and the sum of stored and dissipated energy in the arms U_{arm} (eq 3). This was verified experimentally, by T-peel testing of melt-crystallized films, welded at 145 °C for 15 min, at different film thickness. The adhesive fracture energy G_a^{135}, calculated according to eq 5, is depicted in Figure 4. It can be seen that G_a^{135} is independent of film thickness and, thus, can be used to characterize the bond strength of the interface.

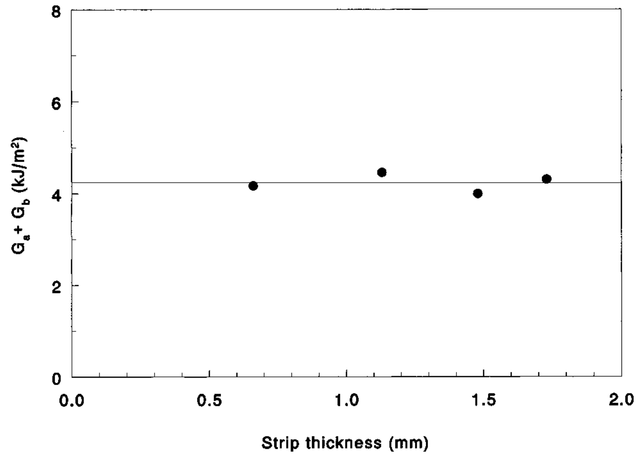


Figure 4. The adhesive fracture energy G_a at 135 °C, as a function of thickness h, after welding at 145 °C for 15 min.

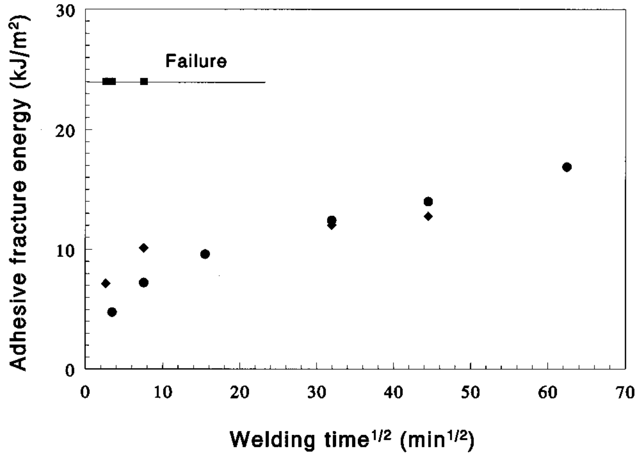


Figure 5. The adhesive fracture energy G_a as a function of welding time, for melt-crystallized (●), solution-cast (◆), and prewetted films (■).

The adhesive fracture energy G_a^{135} for two melt-crystallized films, as a function of welding time, is depicted in Figure 5. Evidently, the buildup of adhesive fracture energy at 135 °C upon welding at 145 °C is a slow process, extending over many hours. This is not surprising, since the increase in G_a^{135} is expected to involve large scale self-diffusion (formation of “entanglements”), which, due to the ultrahigh molar mass of UHMWPE, is a slow process. From rheological experiments, the longest relaxation times of UHMWPE, which correspond to the time scale for main-chain self-diffusion, were shown to be several hours long.[12]

The increase in adhesive fracture energy at 135 °C as a function of time, for two solution-cast films, is also depicted in Figure 5. Surprisingly, the buildup of adhesive fracture energy of two solution-cast films at 135 °C is identical to the development of G_a^{135} of two melt-crystallized films. This is unexpected at first sight, since solution-cast films exhibit the so-called “chain explosion”, a very fast increase of the radius of gyration upon melting (see the Introduction), which should accelerate the welding process. However, from welding experiments on amorphous polymers, it is known that the development of adhesive fracture energy normally involves two stages. The first stage is related to complete *wetting* of the surface, i.e., the removal of air inclusions and contaminants. During the second stage, chain diffusion results in the formation of “entanglements”, which finally raises the adhesive fracture energy to the equilibrium value of the fracture energy of the bulk material. From the welding experiments on the solution-cast films (Figure 5) it is evident that the “chain explosion” upon melting does not occur across a *nonwetted* surface. The “chain-explosion” is a fast reorganization of the chains, but will hardly result in chains “jumping” out of the surface. If, therefore, on a microscopic level, surface roughness prevents an intimate contact between the films, it is to be expected that the chain-explosion process has been completed before wetting enables chains to cross the surface. In this case, at the moment wetting is complete, and chain diffusion will commence, melt- and solution-cast films are more or less indistinguishable, and the increase in surface bond strength will proceed at equal pass.

In order 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 the 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 development of adhesive fracture energy of these prewetted films at 135 °C as a function of welding time finally exhibits the expected sudden increase due to the chain explosion, as is depicted in Figure 5. Analogous to the T-peel tests at room temperature, the prewetted films cannot be separated anymore. Already after 3 min of welding, the arms break before the crack can advance, and only a lower bound for the adhesive fracture energy can be estimated, using eq 6.

Conclusions

Upon melting of a semicrystalline polymer, the chain transforms from the rather compact, more or less ordered folded-chain conformation to the sparse equilibrium random walk conformation. This study is concerned with the effect of this transition on the welding behavior of semicrystalline polymers. Ultra high molecular weight polyethylene was used as a model polymer due to its ability to crystallize in a wide variety of morphologies, in which the chain dimensions can differ substantially. Two morphologies were selected: melt-crystallized films, in which the overall chain dimensions (viz. the radius of gyration) are essentially equal to the random walk values in the melt, and solution-crystallized films, which have a much more compact configuration. The adhesive fracture energy was determined by T-peel testing above and below the melting point.

It was found, that the adhesive fracture energy *at room temperature* became comparable to the fracture energy of the bulk material on a time scale shorter than the shortest welding time employed in this study (3 min), *irrespective* of the initial morphology.

By contrast, the initial crystal morphology was found to have a large influence on the adhesive fracture energy measured *above the melting temperature*. In the case of two melt-crystallized films, the adhesive fracture energy above the melting temperature, $G_a^{T>T\mathrm{m}}$, developed only slowly, and did not reach the fracture energy of the bulk material, even after 65 h of welding at 145 °C. This is not surprising, since, in the melt, the increase in adhesive fracture energy can only be due to the formation of “entanglements” through self-diffusion, which, due to the ultrahigh molar mass of UHMWPE, is a slow process. However, welding two *fully wetted* solution-cast films above the melting temperature, resulted in an almost instantaneous increase of $G_a^{T>T\mathrm{m}}$ to the level of the fracture energy of the bulk material. This dramatic decrease in welding time necessary for complete recovery of the fracture energy above the melting temperature, is in accordance with the observed “instantaneous” increase of the radius of gyration upon melting of solution-cast high-density polyethylene films, as observed by neutron scattering experiments by Barham and Sadler (1991).[9] It was observed that this so-called “chain explosion” did not accelerate diffusion across a *nonwetted* surface. Apparently, the time scale for the “chain explosion” to occur is shorter than the time scale for complete wetting.

Although the “chain explosion” has only been observed directly (by neutron scattering) for HDPE,[9] the absence of memory effects for solution-cast LDPE[12] suggests that this phenomena is of general importance for semicrystalline polymers (of high molar mass).

Acknowledgment. The authors acknowledge many helpful discussions with Dr. C. Bastiaansen and Dr. S. Rastogi.

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