Heat Sealing of LLDPE: Relationships to Melting and Interdiffusion

C. MUELLER,[1] G. CAPACCIO,[2] A. HILTNER,[1] E. BAER[1]

[1] Department of Macromolecular Science and Center for Applied Polymer Research, Case Western Reserve University, Cleveland, Ohio 44106-7202

[2] B P Chemicals, Ltd., Applied Technology, Grangemouth, FK3 9XH, United Kingdom

ABSTRACT: The effect of heat sealing variables (platen temperature and dwell time) on seal strength of a linear low-density polyethylene (LLDPE) was examined. In order to characterize the development of interfacial strength, blown films were heat-sealed for times from 1 to 100,000 s, much longer than the typical sealing times of less than 1 s. The seal temperature ranged from 100 to 130°C. From the differential scanning calorimetry thermogram, the LLDPE was determined to be completely melted at 130°C. Therefore, the films ranged from partially to fully melted when they were heat-sealed. The seal strength was measured in the T-peel configuration, and the peel fracture surfaces were examined in the scanning electron microscope. A temperature of 115°C or higher was required to form a good seal. The strong effect of seal temperature was related to the heterogeneous composition of the LLDPE studied. At 115°C, the lower-molecular-weight, more highly branched chains easily diffused across the interface. Crystallization upon cooling produced connections across the interface. However, because these chains represented a small fraction of the crystallinity and the molecular weight was low, they contributed much less than the full peel strength. Conversely, chains with less branching represented the main fraction of crystallinity (anchors for tie chains) and the highest molecular weights (more entanglements). Only at temperatures at which the higher-molecular-weight, less branched chains began to melt and diffuse across the interface could high peel strengths be achieved. © 1998 John Wiley & Sons, Inc. J Appl Polym Sci 70: 2021–2030, 1998

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INTRODUCTION

Heat sealing is a method for joining 2 thermoplastic materials and is typically used for sealing packages or forming bags. Although there are many different techniques for heat sealing,[1] the basic sealing methodology is the bonding together of 2 polymer surfaces by bringing them into intimate contact while they are in a partially molten state. To achieve a reasonable bond, the surfaces must be pressed together with adequate pressure for sufficient time so that the polymer chains can diffuse across the interface and form bridges. Increasing seal pressure above a minimum required for good contact is not advantageous.[2,3] The 2 process variables that most strongly affect the heat seal are the interfacial temperature and the heat seal time.

Often, the primary concern is comparison of candidate polymers for film applications.[4–7] Be-

cause very short seal times are a practical necessity, most kinetic studies have also focused on the time scale of seconds or less. However, these times are comparable to the time required for the interface to reach temperature, which can be as much as 0.5 s, depending on conditions, and sealing may not occur under isothermal conditions. To analyze the kinetics of seal formation in terms of established concepts of chain diffusion and entanglement, measurements under isothermal conditions, such as achieved by longer contact times, are required. A time dependence of $t^{1/2}$ is reported for fracture energy of hot tack and welding of amorphous polymers.[8] In these examples, interfacial strength is determined primarily by the number of entangled chains that form connections across the interface. In heat sealing of semicrystalline polymers, the melted chains recrystallize as the seal is cooled to ambient temperature. Rearrangements that occur at the interface during recrystallization must also be considered in evaluating the seal strength.[9]

The seal temperature determines whether the material is partially or fully molten. The residual crystallinity governs the number of chains available for diffusion and the amount of crystalline obstacles to diffusion. The amorphous fraction required to achieve a measurable heat seal appears to be in the range of 75–80%; thereafter, the seal strength increases approximately with the amorphous fraction.[10] Although this relationship applies to various structurally heterogeneous polymers, the empirical approach does not consider the types of melted chains (molecular weight, branch content, or comonomer content). Nevertheless, an approach that relates the melting distribution of the polymer, as determined by differential scanning calorimetry (DSC) measurements, to seal strength appears promising.

In order to address the role of kinetics of chain diffusion and entanglement, the types of diffusing chains, and the extent of melting on formation of a good heat seal, sealing of a particular linear low-density polyethylene (LLDPE) film was investigated over a range of sealing times and temperatures. In this study, times longer than the typical heat seal time were used to elucidate the kinetics under isothermal conditions. The study used a single copolymer of ethylene with 4-methylpentene-1, the comonomer effect is a subject for future study.

MATERIALS AND METHODS

Materials

The LLDPE was supplied by BP Chemicals, Ltd. in the form of blown film 40 μm-thick and as pellets. The comonomer was 4-methylpentene-1. The polymer had an average branch density of 20/1000C, M_w of 132,000, M_n of 26,000, and PDI of 5.1, as indicated by the manufacturer. The density of the pellets was measured with an isopropanol–water density gradient column; 5 specimens gave an average density of 0.9176 $\pm$ 0.0001 g/cc.

Thermal Analysis

Thermal analysis was performed with a Perkin–Elmer Model 7 DSC. Annealing experiments to determine the crystal population were performed following the procedures described previously.[11] The specimen was quenched from the melt to -50°C, heated to the annealing temperature (T_a) at a rate of 40°C/min, held at temperature for 1 h, and quenched to -50°C. The heating thermogram was recorded from -50 to 190°C using a heating rate of 10°C/min. The experiment was repeated with other annealing temperatures to create a family of thermograms with T_a ranging from 0 to 130°C. A heat of fusion of 290 J/g for the perfect polyethylene crystal was used to calculate the crystallinity.[12]

Heat Sealing

Sections measuring 6 × 6 cm cut from the blown film were sandwiched between Mylar sheets with the inside surfaces of the blown film tube contacting each other. To create a notch, the 2 pieces of film were separated at 1 edge by a strip of Mylar to prevent sealing. The sandwich was placed between the platens of a preheated press, as shown in Figure 1(a), and a pressure of 3.4 MPa was applied. The seal time was varied from 1 to 100,000 s, and the seal temperature was varied from 100 to 130°C. Temperature control on the press was ±1°C. After sealing, the sandwich was removed from the press and cooled under ambient conditions.

The film temperature was measured by inserting a 12.5-μm-thick copper–constantan type T thermocouple from Omega Engineering, Inc., between the films, as indicated in Figure 1(a). The interfacial temperature was recorded with a sampling rate of 100 data points per second to obtain

(a)

(b)

Figure 1   (a) Schematic of the sandwich construction used to create the heat seal; (b) interfacial temperature during heating and cooling.

the heating curve in Figure 1(b). The films reached the platen temperature within 0.4 s. The interfacial temperature was also recorded during cooling; the cooling curve in Figure 1(b) shows the initial rapid cooling rate to be essentially a quench condition.

Peel Strength

Specimens 1 cm wide were cut from the sealed films and tested in the T-peel configuration in an Instron mechanical testing machine. The peel rate was 5 mm/min unless otherwise specified. Peel strength was taken as the average plateau peel strength (N/cm) of 5 specimens taken from 1 heat-sealed film. Specimens were cut parallel to the machine direction of the blown film and backed with sealing tape to prevent deformation of the arms. Experiments were carried out to determine whether the bending moment of the backing tape affected the peel measurement. Add-

ing up to 4 layers of backing did not affect the measured peel strength. Other experiments tested for plastic deformation in the arms. A strip of film was taken to loads typically encountered in the peel test, and the hysteresis recorded during repeated loading and unloading. Minimal plastic deformation indicated that the energy spent during peeling went to propagating the crack.

Peeled surfaces were prepared for examination in the scanning electron microscope (SEM) by coating with 90Å of gold. They were viewed in a JEOL 840A SEM with the stage tilted to a 40° angle. The crack tip of an interrupted peel test was examined in the SEM by mounting a specimen in a stage designed to hold the specimen in the T-peel configuration. A 90Å gold coating was applied, and the crack tip was examined by viewing directly into the crack. In this case, the acceleration voltage was 2 keV to minimize charging.

RESULTS

Effect of Peel Rate on Peel Strength

Films were heat sealed for times from 1 to 100,000 s, much longer than the typical sealing times of less than 1 s. The sealing temperatures ranged from 100 to 130°C. The LLDPE was determined to be completely melted at 130°C from the DSC thermogram. Therefore, the films ranged from partially to fully melted when they were heat sealed. When the sealed films were tested in the T-peel configuration, a crack usually initiated and propagated along the heat seal at a relatively constant load. An example in Figure 2 shows the

Figure 2   Peel curves of a specimen sealed at 115°C for 1000 s and loaded at progressively higher rates.

Figure 3 Effect of peel rate on the measured peel strength of 1000-s heat seals.

peel curve of a heat-sealed film that was loaded at progressively higher rates. If the crack followed the heat seal, the average plateau load for 5 peel tests is reported as the peel strength. However, if the strength of the heat seal exceeded the yield strength of the films, the arms started to neck and tear. The highest peel strength recorded without yielding of the arms, 335 N/m, constituted the upper limit of the measurable seal strength in these tests.

The effect of peel rate on the measured peel strength is illustrated in Figure 3 for films sealed for 1000 s at several temperatures. For each peel rate, a rapid increase in the peel strength with increasing seal temperature was recorded. However, there was also a strong dependence of the measured peel strength on peel rate. The effect was most pronounced in the temperature range at which the seals attained significant peel strength. For example, seals made at 115°C were determined to be very weak if peeled slowly, but very strong if peeled rapidly. Even for the weakest seals, which were those made at 110°C, the measured seal strength increased from 20 to 85 N/m with a factor of 100 increase in the peel rate. The intermediate peel rate of 5 mm/min was chosen for all subsequent experiments.

A view into the crack tip of a partially peeled heat seal showed a craze zone ahead of the crack (Fig. 4). Profuse cavitation in the craze created the three-dimensional cellular structure. Highly stretched and presumably biaxially oriented material constituted the thin walls of the cavities. Subsequent crack propagation through the craze left numerous fractured craze fibrils on the matching surfaces.

Micrographs of the peel surfaces revealed changes in the craze morphology with peel rate.

Numerous small, fractured craze fibrils characterized the fracture surface peeled at the slowest rate, 0.05 mm/min, in Figure 5(a). The fibril diameter and length increased, and, correspondingly, the fibril density decreased, as the peel rate increased [Fig. 5(b)]. At the highest peel rate, the micrograph showed a porous texture consisting of much thicker and longer fractured fibrils and thick, membrane-like connections between fibrils. Although craze fibrils recoil and change dimensions upon fracture, the micrographs clearly showed that as the peel rate increased, the diameter of the fibrils increased, and the fibril density decreased. Lower strain rates increase the contributions of chain disentanglement and creep in craze fibrils. Loss of entanglements is equated with reduced effective surface energy and thinner fibrils.[13] Furthermore, as the creep component in fibril rupture increases, the stable length of the craze fibril decreases.

Effect of Seal Time

The increase in peel strength as a function of sealing time for 3 representative sealing temperatures is shown in Figure 6. At 120°C, a seal time of 100 s was required to create a full strength seal, that is, the peel crack did not follow the seal; instead, the arms necked and tore. At 115°C, this time increased to 5000 s, and at 110°C, the peel strength gradually increased with sealing time but did not reach full strength even after 100,000 s (more than 1 day).

Figure 4 An SEM view into the crack tip of a partially peeled heat seal. The film was sealed at 125°C for 1 s and peeled at 5 mm/min. The peel strength was 206 N/m.

Figure 5   SEM micrographs of peel surfaces from a film sealed at 115°C for 1000 s. The peel rate is indicated.

The 115°C results typified the gradual development of the heat seal with time. Increasing peel strength was manifest in the changing craze mor-

phology at the crack tip, as revealed by the peel surfaces. Visually, the peel surfaces of specimens exhibited some whitening, which was more apparent in specimens with high peel strengths. When examined in the SEM, broken craze fibrils were visible on all the peel surfaces (Fig. 7). Surfaces from the weakest seals (1 and 2 s) contained isolated fractured fibrils, which were less than 1 μm in diameter. These characteristics suggested that the craze consisted of isolated fibrils rather than the cellular morphology of a good heat seal, as illustrated in Figure 4. On peel surfaces from somewhat longer times (10 and 100 s), some evidence of membrane-like connections between fibrils suggested the beginning of a three-dimensional cellular structure. Nevertheless, the peel strength of these seals was also quite low (40 and 50 N/m, respectively). The broken fibrils on the fracture surface were noticeably longer and thicker after the seal time was increased to 1000 s, and even more so after 3500 s seal time. Simultaneously, the fibril density declined, and the membrane-like connections became more prominant. The changes in craze morphology and the significant increase in peel strength (170 and 273 N/m) were consistent with the increasing number of chain entanglements.

To examine the time dependence of peel strength, it is assumed that peel strength is determined by the number of bridges that span the interface. To form a bridge that is capable of transmitting forces across the plane, a chain segment needs to cross the interface several times. It has been suggested that in the melt this number is 3.[14] Several approaches give the

Figure 6   Effect of seal time on peel strength measured at a rate of 5 mm/min.

Figure 7   SEM micrographs of peel surfaces from films sealed at 115°C. The seal time and the peel strength are indicated.

result that the number of bridges in a noncrystalline polymer should be proportional to $t^{1/2}$.[15–17] The situation may be modified for a semicrystalline polymer, in which a molecule can create a bridge by diffusing across the interface in the melt and crystallizing into crystalline anchors on either side of the interface upon cooling, thus becoming a tie molecule. Nevertheless, the peel strength conformed reasonably well to the $t^{1/2}$ dependence, as shown in Figure 8. A strong temperature effect on the seal rate was noted with a transition at about 115°C between lower temperature seals that formed very slowly without achieving full seal strength and higher temperature seals that achieved full strength very rapidly.

Figure 8   Peel strength plotted as $t^{1/2}$ for various seal temperatures.

Figure 9 Effect of seal temperature on peel strength measured at a rate of 5 mm/min.

Effect of Seal Temperature

The large effect of seal temperature on seal formation is shown in Figure 9 for films sealed for 1 and 1000 s at temperatures from 100 to 125°C. A 1-s seal time produced a very low strength seal until the seal temperature reached 115°C; then the peel strength increased rapidly between 115 and 125°C. Increasing the seal time shifted the peel strength curve to lower temperatures; for example, the rapid increase in peel strength occurred between 110 and 115°C with a seal time of 1000 s.

The changes in craze morphology with increasing seal temperature (Fig. 10) were analogous to those observed with increasing seal time (Fig. 7). Surfaces of the 100, 105, and 110°C seals all contained small, isolated fractured fibrils. The 115°C

Figure 10 SEM micrographs of peel surfaces from films sealed for 1 s. The seal temperature and the peel strength are indicated.

Figure 11   Thermograms of annealed specimens. The annealing temperature T_a is indicated.

seal surface exhibited some evidence of the membrane-like connections between fibrils that suggested the beginning of a three-dimensional cellular structure, although the peel strength was quite low (35 N/m). The broken fibrils on the fracture surface were noticeably thicker and longer after the seal temperature was increased to 120 and 125°C. Simultaneously, the fibril density declined and the membrane-like connections became more prominent. The increasing density of chain entanglements indicated by these changes in the craze morphology resulted in significantly higher peel strengths (100 and 206 N/m, respectively).

Melting Behavior

The DSC thermogram of this LLDPE revealed a very broad melting range with a long tail on the low temperature side of the 130°C melting peak. To minimize ambiguities in the thermogram from melting and recrystallization during heating, the temperature dependence of the crystallinity was determined by isothermally annealing the polymer within the melting range. The subsequent heating thermograms are illustrated in Figure

11. The broad endothermic peak below the annealing temperature T_a was interpreted as melting of crystallizable chains that were in the melt at the annealing temperature and that were subsequently crystallized when the specimen was cooled from the annealing temperature. Endotherms above T_a represented melting of crystals that were present at the annealing temperature.

The total enthalpy of melting (130 J/g) did not vary with the annealing temperature. Therefore, the melting thermograms were divided into 2 parts: the heat of melting for the part below the annealing temperature was assigned to melting of crystallizable chains with melting temperatures below the annealing temperature, and the heat of melting for the other part represented melting of crystallizable chains with melting temperatures above the annealing temperature. The latter was normalized to the heat of fusion of the perfect crystal to obtain the temperature dependence of the residual crystallinity, which is plotted in Figure 12. A gradual decrease in the residual crystallinity below 115°C accounted for melting of about 50% of the crystallizable chain segments. Nevertheless, melting of these chain segments did not produce a full strength heat seal. A strong heat seal only formed between 115 and 125°C, at which the remaining crystallizable chain segments melted.

DISCUSSION

The effect of seal temperature is presented in Figure 13 by plotting the time required at each

Figure 12   Residual crystallinity as a function of annealing temperature.

Figure 13 Seal time required to reach a peel strength of 200 N/m as a function of seal temperature.

temperature to reach a peel strength of 200 N/m. For the LLDPE under investigation, a temperature of 115°C or higher is required to form a good seal. Several factors could be responsible for this feature. A good heat seal requires chains in crystals to melt, diffuse across the interface, form entanglements, and recrystallize. The temperature dependence of the diffusion coefficient determines whether the seal time is sufficient for the chains to diffuse across the interface. Over the temperature range at which heat sealing is achieved (100 to 125°C), the peel strength changes by several orders of magnitude. However, assuming a reasonable activation energy (30 kcal/mol), the diffusion coefficient increases by only a factor of 2. Furthermore, the seal times used in the study were always larger than the characteristic diffusion time, even for the shortest seal times. Therefore, arguments based on the temperature dependence of the diffusion coefficient do not explain the seal behavior. Another factor is the temperature dependence of the amorphous fraction, for it has been suggested that formation of a heat seal requires an amorphous fraction of 75–80%,[10] and the amorphous fraction at 115°C is in this range. However, in the temperature range at which the seal behavior changes most dramatically, between 113 and 117°C, the amorphous fraction increases only slightly from 70 to 75%, based on the melting enthalpy (Fig. 12), so the change in amorphous content alone does not account for the seal behavior. It appears that the amount of amorphous polymer is less important than the type of chains that are melted and able to diffuse across the interface.

The peel strength depends on the strength of the craze fibrils at the crack tip. The structural origin of craze fibril strength resides in the interlamellar tie molecules. Upon loading, the tie molecules stretch as they take up the applied stress and form taut links between crystals. Crystals shear when the local stresses generated by the taut molecular links induce local yielding and microvoiding and, as the voids expand, drawing of the material into highly oriented craze fibrils. The strength of the craze fibrils that span the heat seal is determined by the density of tie molecules and the rate at which interlamellar ties are lost by chain pullout. Both are determined by molecular weight and branch content of the molecules that diffuse across the interface. As molecular weight increases, more tie chains form, and more time is required to disconnect a tie chain from a crystal anchor. Long linear chain segments form large, well-ordered crystals that provide strong anchors for the tie molecules and hence determine the density of intercrystalline links. Chain branches dramatically improve the fibril toughness by acting as protrusions along the chain to hamper chain disentanglement and restrict a chain in sliding through a crystal. This results in a considerable increase in the disentanglement time.

Therefore, it is necessary to consider the types of chains that are mobile and can diffuse across the interface. The composition of the LLDPE studied here is highly heterogeneous with the branches concentrated in the lower molecular weight part of the distribution (Fig. 14). Both Figure 14 and the DSC results in Figure 12 suggest that this LLDPE is composed, broadly, of 2 types of chains, as follows: higher-molecular-

Figure 14 Molecular weight and SCB distributions of LLDPE. Data provided by the manufacturer.

weight chains with low branch content that melt above 115°C, and lower-molecular-weight chains that are more branched and melt below 115°C. From the published relationship between melting temperature and SCB content, chains that melt at 115°C have approximately 15SCB/1000C.[18] Data in Figure 14 suggest that chains with SCB content at least this high constitute a significant fraction on a weight basis, although they represent a smaller fraction of the crystallinity.

At 115°C, the lower-molecular-weight, high SCB chains easily diffuse across the interface. Crystallization upon cooling produces connections across the interface. However, these chains represent a small fraction of the crystallinity, and because the crystallizable chain segments are short the crystals that do form, possibly fringed micellar crystals,[11] make weak anchors. Furthermore, the low-molecular-weight molecules produce few interlamellar ties. For these reasons, the low-molecular-weight chains contribute much less than the full peel strength. The relative ease with which the entanglements are pulled out is evident in the large rate dependence of the peel strength of 115°C seals. Conversely, the low SCB chains represent the main fraction of crystallinity (anchors for tie chains) and the highest molecular weights (more entanglements). Only at temperatures at which the higher-molecular-weight, low SCB chains begin to melt and diffuse across the interface can high peel strengths be achieved.

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