

Effects of Thermal History on the Peel Strength of Linear Polyethylene

JOHN P. TORDELLA, *Electrochemicals Department, E. I. du Pont de Nemours and Co., Inc., Experimental Station, Wilmington, Delaware 19898*

Synopsis

Peel strength of linear polyethylene-aluminum bonds is strongly affected by thermal history. Slow cooling from the melt resulted in 10 lb/in. peel strength; quenching, in 50-90 lb/in.; annealing of quenched bonds reduced the peel strength to 30 lb/in. Adhesion to aluminum was obtained by treating the substrates in a solution of vinyl triethoxysilane. Cohesive failure occurred regardless of thermal treatment. The changes in peel strength were not due to changes in strength of the bulk polymer. Rather, the volume of polymer deformed in peeling seemed to correlate with strength. No correlation was found between peel strength and degree of crystallinity or of transcrystalline orientation. Segregation resulting in a weak boundary layer seems to be the probable cause of the dependence of peel strength on cooling rate, and changes in the tie molecule configuration, the cause of loss of strength on annealing.

INTRODUCTION

The structure of linear polyethylene is affected by the manner in which the polymer is crystallized. Quenching from the melt results in reduced density or crystallinity and in transcrystalline orientation in the vicinity of the heat transfer surfaces. The number of intercrystalline links is also increased. Usually, changes in structure affect mechanical performance. The effects of structure changes induced by thermal history on the performance of linear polyethylene when used as an adhesive were investigated. The bulk of the work was done with thin aluminum sheets bonded with polyethylene tested in peel.

MATERIALS AND METHODS

The polyethylene used in the bulk of the work was du Pont's high density, substantially linear, narrow molecular weight distribution Alathon 7030 polyethylene, which has a melt index of 2.8 (ASTM D-1238) and a density of 0.960 (ASTM D-792 in methanol, annealed by slow cooling). This linear polyethylene was treated with cyclohexane in a Soxhlet extractor for 24 hr and dried at 120°C for 16 hr in a vacuum oven with a nitrogen purge prior to use. Limited data were obtained with two branched polyethylenes:

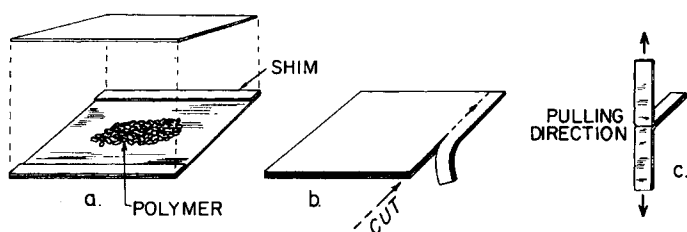


Fig. 1. Sample preparation, cutting, and pulling configuration.

Alathon 14, melt index 1.9, density 0.915, and Alathon 10, melt index 2.1, density 0.923, which were used as received.

One type of peel bond was used principally. It consisted of two 0.005-in.-thick aluminum substrates with an intervening 0.005–0.007-in.-thick polymer layer. The aluminum used was S-1145 H19, commercially pure, fully hardened, smooth (nameplate quality) aluminum. Eight-inch square sheets were vapor degreased in trichlorethylene and subsequently treated with an organosilane. Similar results were obtained with both aminopropyl- and vinyltriethoxysilane (Union Carbide's A-1100 and A-151 silanes). The degreased sheets were immersed in 5 vol-% solution of the silane in 90:10 ethyl alcohol–water mixture for 10 min at 75°C and then air dried 15 min at room temperature. During the latter stages of draining in air, the aluminum dewetted; the remaining solution gathered into droplets and ran down off the sheet, leaving no visible residue on the aluminum substrates.

The silane treatment was necessary to develop adhesion of polyethylene to aluminum under the conditions of preparation used. Without the treatment, very low peel strengths were obtained, of the order of zero to 2 lb/in. width. Failure in such bonds appeared to be adhesive. On the other hand, with silane treatment of the substrates, higher strength bonds were obtained. Failure in this type of bond appeared in all cases to be cohesive and therefore characteristic of the strength properties of the adhesive rather than of the degree of adhesion between the adhesive and the substrate.

Peel samples were prepared in a hydraulic molding press as shown in Figure 1. Two 1-in.-wide, 0.005-in.-thick aluminum shims were placed at opposite edges of a treated substrate. The long axis of these shims was parallel to the faint rolling striations on the substrate. Five grams of polyethylene molding powder were placed thereon. The top substrate was laid on in the same orientation as the lower one and the assembly was placed in the press at 200°C. The platens were closed over about a 30-sec interval to a load of about 13,000 lb and held for 10 min. The peel bond specimen was then ready for thermal treatment.

Cooling rates from 2° to 40°C/min were obtained by cooling the cored press platens with air, water, or both. Very rapid cooling, quenching, was provided by opening the platens, removing the aluminum–polyethylene assembly, and plunging it edgewise into ice water.

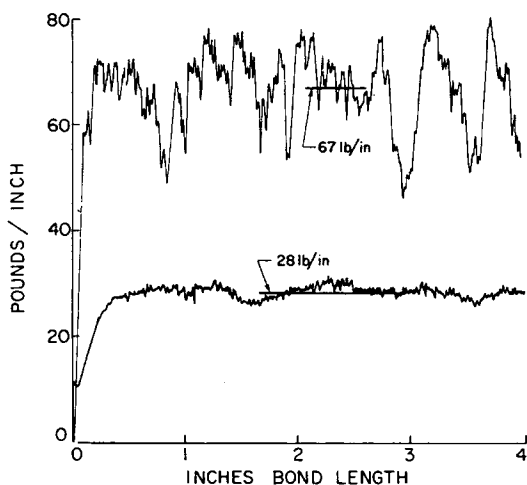


Fig. 2. Specimen force traces for medium and high peel strengths.

The 8-in. square, bonded samples were sheared into $\frac{1}{2}$ -in. strips with the long direction of the strip perpendicular to the sides with the shims (see Fig. 1). The shims provided unbonded tabs to grip in the testing machine. The specimens were pulled in T-peel at a jaw separation rate of 2 in./min, a peeling rate of 1 in./min, unless otherwise stated. The tail of the specimen, which was unsupported, generally assumed an angle different from perpendicular to the tabs by 10–20°. Three to five specimens spaced across the sample were pulled and the average was taken as characteristic. Peel strength is taken as pounds tension per inch of bond width. Testing room conditions were 23°C, 50% relative humidity.

Peeling force versus distance along the peel bond was relatively uniform at low forces and progressively less uniform at higher stresses. Typical medium and high force traces and assigned peeling forces are shown in Figure 2. Peeling usually occurred close to one substrate. It sometimes transferred of its own accord from near one substrate to near the other. This transfer could be induced by bending the unpeeled portion of the bond manually toward the peeled substrate on which was the thicker polymer layer. As the configuration approached 180° peel, the thick layer usually split perpendicular to the peeling direction and peeling then occurred near the surface of the more sharply bent substrate. Peel strength of the standard peel bonds was not significantly different from one side to the other.

Lap-shear data were obtained using specimens made with 0.007 in. of polyethylene between $3 \times 1 \times 0.062$ -in. tabs of aluminum-clad alloy aluminum 7075-T6. The overlap was $\frac{1}{2}$ in. Lap-shear specimens were primed and molded using the same treatment given peel samples.

Tensile data on unsupported film were obtained for polyethylene from peel bonds whose substrates had been removed by acid. Local overheating

was avoided by dissolving the aluminum slowly; 7 part concentrated hydrochloric acid to 13 parts of water removed the 0.005-in. substrates in 10–15 hr.

RESULTS

Effect of Cooling Rate

Peel strength of linear polyethylene–aluminum peel bonds varied from about 10 lb/in. for specimens cooled at low rates to 50–90 lb/in. for quenched specimens. Representative data are given in Table I, along with an orientation index, the significance of which will be discussed later.

TABLE I
Effect of Cooling Rate

Cooling rate, °C/min	Average peel strength, lb/in.	Orientation index (020/200 ratio)
0.18	9	—
1.5	8	0.12
4	10	0.13
8	11	0.13
16	14	0.14
40	27	0.14
Ice quench, perhaps 500°–1000°C/min	67	1.3

The appearance of the peeled surfaces varied with cooling rate, as shown in Figure 3. Cohesive failure occurred for all cooling rates. The surfaces shown in the figure are those near which peeling occurred. The amount of polymer remaining varied from quite thin layers for slowly cooled samples to fairly thick layers consisting of small peaks for samples cooled at 40°C/min or quenched. The peaks are the result of formation of strands extending from one substrate to the other during peel and subsequent breaking. The strands tended to break toward their centers leaving peeled surfaces which were mirror images. Even in the case of heavy strand formation, the failure plane was always quite close to one or the other interface; 5%, to 10% of the polymer remained on the one substrate, 90% to 95% on the other.

No effect of testing rate on peel strength was observed for peeling rates over the range 0.04 to 10 in./min. Any rate dependence was within the uncertainty of the data of perhaps $\pm 10\%$ to 30%.

Peel strength of any given sample was alterable by thermal treatment. A high-strength, quenched bond changed to a low-strength bond if remelted and cooled slowly. The reverse was also true. Thus, cooling rate was the significant variable rather than some adventitious variable, such as the total time in the melt.

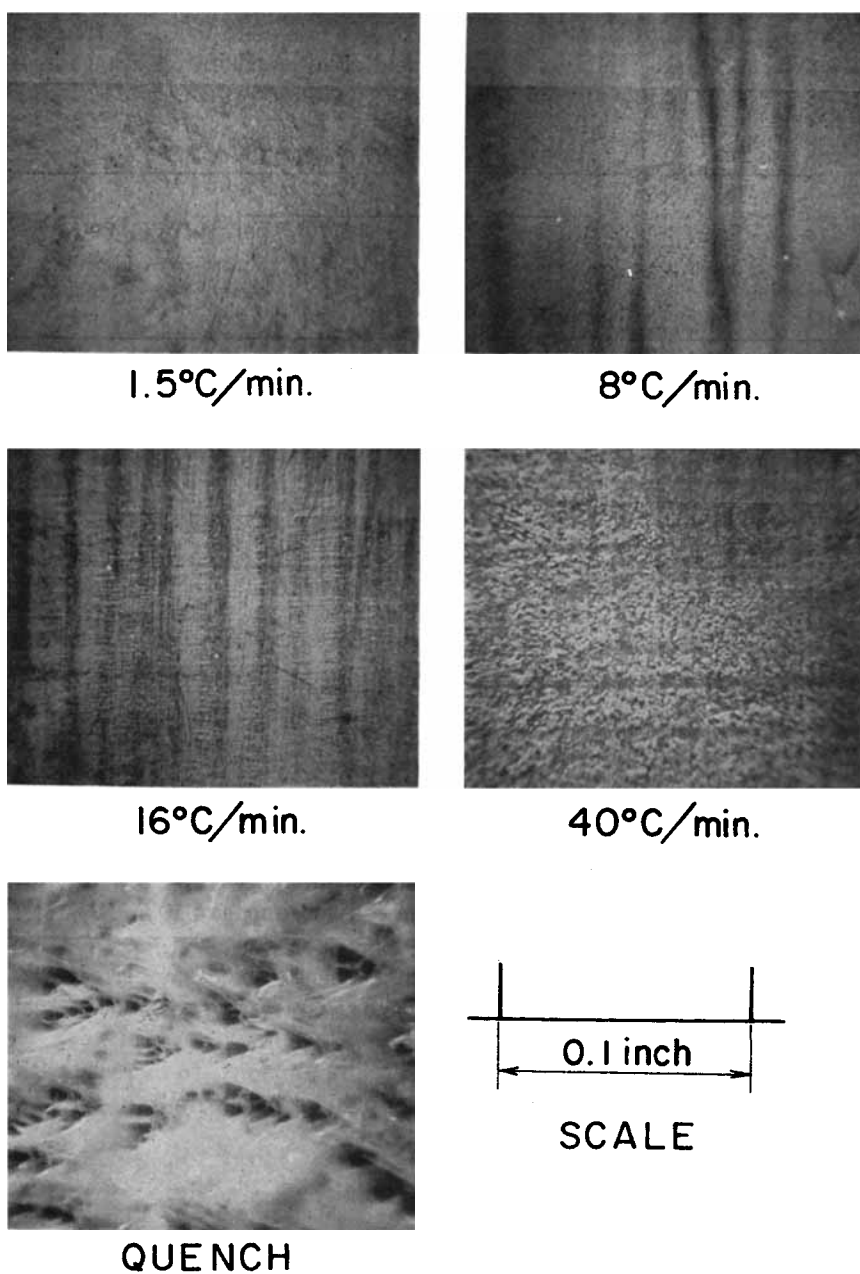


Fig. 3. Effect of cooling rate on appearance of peeled bonds.

The effects observed are not unique to Alathon 7030 polyethylene resin. Similar results were obtained with Alathon 7050 (17.5 melt index, 0.962 density) and with Marlex 6050 (5.0 melt index, 0.964 density).

Strength characteristics of Alathon 7030 as 0.005- to 0.007-in. film are given in Table II. Initial modulus, yield stress, and initial draw stress

TABLE II
Tensile and Lap-Shear Data

Cooling condition	Tensile data ^a			
	Initial modulus, psi	Yield stress, psi	Initial draw stress, ^b psi	Lap-shear strength, psi
2°C/min	2.1×10^6	4,200	2,800	—
5°C/min	—	—	—	1,300
40°C/min	1.8×10^6	3,600	2,300	—
Quenched	1.1×10^6	2,800	1,800	1,150
Quenched, 10 min, anneal at 80°C	1.2×10^6	2,800	1,800	—
Quenched, 10 min, anneal at 100°C	1.4×10^6	3,200	1,900	—

^a Determined according to procedure in ASTM Standard Method of Test D-638 with the following exceptions: microtensile specimen (ASTM D-1798), 0.876 in. gauge length, 0.05 in./min pulling rate for initial modulus measurement, and 0.5 in./min pulling rate for yield and draw stress.

^b Minimum stress after yielding at beginning of drawing.

were relatively unaffected by cooling rate up to 40°C/min. Quenching lowered these values about 40%. Elongations at yield were 5% to 8%; those at the initial cold drawing, 60% to 100%. Strength at failure, about 5000 psi, is unaffected by cooling condition; complete structural reorganization must occur in the drawing process, which involves about 1000% elongation. Lap shear strength of quenched specimens is 10%–15% less than that of slow-cooled specimens.

The tensile properties of quenched versus slow cooled samples do not seem sufficiently different to account for the several fold variations of peel strength with cooling rate.

The amount of material deformed in peeling appeared to increase with increasing cooling rate. This is especially evident in Figure 3 for the two higher rates.

Degree of Crystallinity

The crystallinity of linear polyethylene is a function of the rate at which it is cooled through its freezing point. Degrees of crystallinity were calculated from heats of fusion taking 70 cal/g as the heat of fusion of completely crystalline polymer.¹ Heat of fusion and degree of crystallinity for quenched Alathon 7030 were 37 cal/g and 54%, respectively; for polymer cooled at 1.6°C/min, 55 cal/g and 80%, respectively. The significance of this variation in the degree of crystallinity relative to the peel strength was investigated in two ways as follows.

If the low crystallinity of the quenched polymer were responsible for its high peel strength, then the peel strength of low-density, branched polyethylene would be expected to be even higher. Heats of fusion, derived crystallinities, and peel strengths for two branched polyethylenes are given in Table III for both quenched and slow-cooled bonds. The level of peel

TABLE III
Effect of Cooling Rate with Branched Polyethylenes

Material	Cooling rate, °C/min	Heat of fusion, cal/g	Crystallinity, %	Peel strength, lb/in.
Alathon 10	2.3	20	28.5	2
	ice quench	18	25.7	11
Alathon 14	2.3	19	27.2	7
	ice quench	18	25.7	20-40

strength is not greater than that of quenched linear polymer. Further, peel strength changes fivefold as a function of cooling rate with only a small change in crystallinity. This experiment does not support the hypothesis that peel strength increases with decreasing degree of crystallinity.

The second way the effect of degree of crystallinity was investigated involved special, thick peel bonds. The polyethylene layer was 0.05 rather than 0.005 in. thick. (In peeling these bonds, it was necessary to bend the unpeeled tail to about 90° by hand to obtain a "T" peel geometry.) Normally prepared bonds of this type had strengths comparable to those of standard thin bonds (see Table IV).

TABLE IV
Peel Strength Data for Special 0.05-in. Bonds

Cooling condition	Average peel strength, lb/in.	Orientation index (020/200 ratio)
3°C/min	15	—
40°C/min	36	—
ice quench	50	—
5 1/4°C/min (25°C gradient*)		
cool side	50	0.42
warm side	~3	0.21

* Heat of fusion 50 cal/g, 71% crystallinity.

A special bond was prepared by holding a 25°C gradient across the thickness during freezing at a cooling rate of 5 1/4°C/min. (In later discussion, this type of bond is referred to as the "thick, gradient-cooled bond.") This bond had two markedly different peel strengths, 50 and 3 lb/in. The high strength was measured between the substrate at which nucleation initiated and the 0.05-in.-thick polyethylene layer. The low strength was measured between the polymer layer and substrate which was the hotter

during the cooling. The higher strength is the one which concerns us at this moment, since in normal peel bonds we are concerned with interfaces at which nucleation initiates. High strength at this interface was attained by cooling slowly in an imposed thermal gradient and at a relatively high crystallinity, 71%. Thus, in two different experiments degree of crystallinity was shown not to be the dominant factor in the variation of peel strength with thermal history.

Transcrystalline Orientation

One of the consequences of rapid cooling of linear polyethylene is a type of orientation called transcrystalline.²⁻⁴ Many nuclei form adjacent to the heat transfer surface. Growth of the nuclei parallel to the surface is impeded by adjoining nuclei. Growth toward the interior is unimpeded. The result is that the *b* axes of the unit cell of the polyethylene crystallites tend to lie normal to the plane of the substrate.³ The significance of transcrystalline orientation relative to peel strength was tested.

The amount of transcrystalline orientation may be assessed with an x-ray diffractometer from the integrated intensities of the 200 and 020 crystallographic reflections. The 020/200 intensity ratio, referred to as the orientation index in the tables, is a positive function of the degree of orientation. (Substrates were removed prior to measurement by dilute acid.)

Correlation between the orientation index and peel strength was poor for samples cooled at various rates (see Table I). Orientation index remained unchanged at about 0.12, while peel strength increased from 9 to 27 lb/in. for samples cooled up to 40°C/min. Quenched samples had high peel strength and high orientation index. The slow-cooled, thick, gradient-cooled bond (see Table IV) had intermediate orientation and both high and low peel strength.

Annealing affected the peel strength of quenched bonds but not the orientation index. Substantiating data are given in Table V. Peel

TABLE V
Effect of Annealing^a of Quenched Bonds

Annealing temp, °C	Average peel strength lb/in.	Orientation index (020/200 ratio)
Control	67	1.3
40	56	1.3
50	51	—
60	48	1.6
70	46	—
80	42	1.5
90	41	—
100	38	0.903
110	36	—
120	32	1.35
130	29	—

^a Ten-minute anneal followed by ice quench.

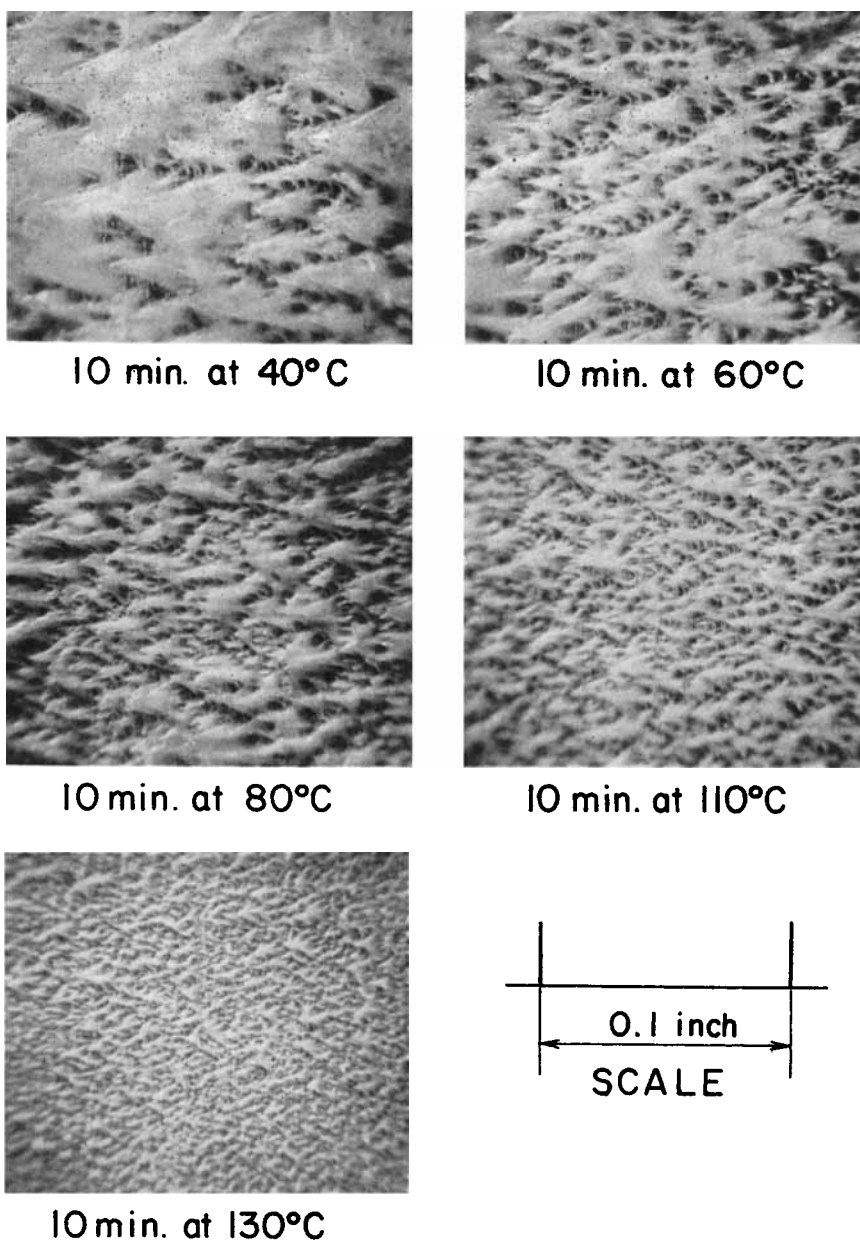


Fig. 4. Effect of annealing on appearance of peeled, quenched bonds.

strength fell linearly with annealing temperature from 67 to 29 lb /in., but orientation was substantially unchanged.

Photomicrographs of annealed peeled specimens are shown in Figure 4. The texture became finer with increasing temperature of treatment. The

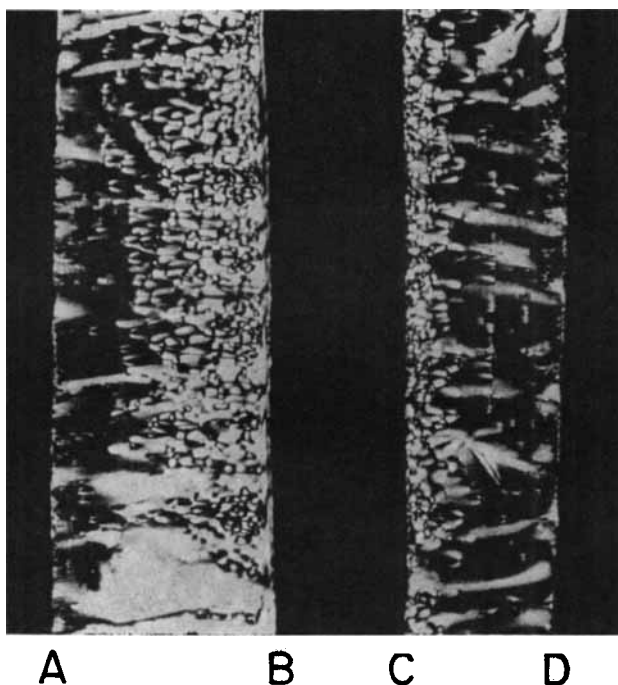


Fig. 5. Photomicrographs through crossed polarizers of cross section of quenched "club sandwich" bond: (A-B) and (C-D) polyethylene interlayers; dark boundaries at left, center, and right are aluminum substrate.

group of annealed specimens had textures and peel strengths intermediate between those of quenched samples and those cooled at 40°C/min.

Annealing did not affect peel strength of specimens cooled at 5 and 40°C/min.

The significance of transcrystalline orientation was further tested using a special three-substrate, two-interlayer, "club sandwich" type of bond. (Pre-molded film was used in the preparation of this type of bond.) Peel strength of such a bond which had been quenched in ice water was high, about 60 lb/in., at all four interfaces, A, B, C, and D in Figure 5. Peeling against the various surfaces was controlled by gripping two substrates together in one grip, the third in the other. Peeling at one surface versus the other was controlled by bending the unpeeled tail as described earlier. Figure 5 is a photomicrograph through crossed polarizers of a cross section of a quenched "club sandwich" bond. The two light bands between A and B and C and D are the polyethylene interlayers to which the aluminum is still attached. Transcrystalline orientation is present in the vicinity of the A and D interfaces through which the heat was abstracted on cooling. It dies out $\frac{1}{3}$ to $\frac{2}{3}$ of the way toward the inner aluminum substrate, B-C, with the appearance of resolvable, randomly oriented spherulites. Since high strength was obtained at all interfaces with or without transcrystalline orientation, transcrystalline orientation is not a prerequisite for high

strength. Further, crystallization toward a cold interface does not necessarily result in a weak bond as in the case of the thick, gradient-cooled bond.

Fractionation and Tie Molecule Configuration

Two other effects which may be relevant to the effect of thermal history on peel strength are fractionation and tie molecule configuration.

Molecular weight fractionation occurs in spherulite growth; the lower molecular weight species tend to concentrate in the outer regions of the spherulite.⁵ The degree of segregation would be expected to vary inversely with cooling rate. Concentration of low molecular weight species in the layer near an interface would be expected to reduce strength. In quenched bonds, both normal and "club sandwich" bonds, cooling is apparently too rapid for segregation to occur. Strength is high even at last-frozen interfaces. In the thick, gradient-cooled bond cooled at $5\frac{1}{4}^{\circ}\text{C}/\text{min}$, the first-frozen interface was strong; the low molecular weight fraction was pushed away therefrom. At the low cooling rate, low molecular material apparently concentrated at the last-frozen interface, resulting in low strength.

Fractionation may explain the inverse relation between strength and cooling rate for bonds cooled in the press with no thermal gradient between the platens at rates of $40^{\circ}\text{C}/\text{min}$ and less. At these cooling rates, the thermal gradient within the adhesive was probably not large enough to restrict nucleation to the substrate-adhesive interfaces. Nucleation may have occurred in regions somewhat removed from the interface in amounts inversely related to cooling rate or to the thermal gradient. Under such conditions, some crystallization toward the interface could occur and fractionation would then result in some low molecular weight species at the interface and reduced peel strength. This point of view is consistent with the data for thick, gradient-cooled bonds cooled at the low rate of $5\frac{1}{4}^{\circ}\text{C}/\text{min}$. The thermal gradient imposed by the temperature difference between the platens presumably limited nucleation to the first-frozen interface. The resulting exclusion of the low molecular weight species from the interface resulted in the observed high strength.

Neither mechanical relaxations nor lamellar thickness of solution-grown crystals of polyethylene is affected by annealing at temperatures below 100°C .⁶ Some reorganization in the disordered part of the structure seems more likely. Perhaps sufficient mobility is introduced during annealing that crystallization tightens the tie molecule network, molecules which are crystallized in two or more domains.⁷ Resulting increased local stress could reduce peel strength of annealed quenched bonds.

Tie molecule configuration may also be involved in the dependence of peel strength on cooling rate. Segregation may be dominant at low rates and tie molecule configuration at high cooling rates, e.g., $40^{\circ}\text{C}/\text{min}$ and higher. This point of view is consistent with the observation that annealing does not affect the strength of bonds cooled at 5 and $40^{\circ}\text{C}/\text{min}$.

Reference to tie molecule configuration to explain performance of crystalline polymers is not without precedent. Large changes in sorption of

tetrachloroethylene by linear polyethylene which did not correlate with degree of crystallinity were ascribed to strain differences in tie molecules.⁸

In summary, the peel strength of linear polyethylene depends strongly on thermal history. Neither bulk strength nor the degree of crystallinity, nor the degree of transcrystalline orientation are responsible. Rather, the effects may be due to segregation resulting in weak boundary layers and to details of the configuration of the tie molecule network.

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