Adhesion of Polyethylene to Metals.
I. Effect of Annealing on Joint Strength

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The formation of an adhesive joint consists of the following three processes: (I) diffusion of adhesive molecules to substrate surface "wetting," (II) adsorption of adhesive molecules onto surface of adherend, and (III) gelation of adhesive. Process I is explainable by the thermodynamic adhesion theory with surface free energy. Process II involves decreasing the adhesive–substrate interfacial energy, according to the orientation of the adhesive molecules (or the hydrogen bond at the adhesive–substrate interface, especially since the thermodynamic adhesion theory could not be used to explain the decrease of interfacial energy by orientation of the polymer molecules). In process III, mechanical strength of the adhesive occurs during evaporation of the solvent, chemical crosslinking, increasing of viscosity on cooling, or crystallization of the polymer. Concomitant with this process there is an occurrence of internal stress due to shrinkage of the adhesive. If the internal stress concentrates at the adhesive–substrate interface, then the adhesive joint strength developed through processes I, II, and III will be decreased sharply, and failure of the adhesive may result.

In the thermodynamic treatment for adhesion between two (equilateral) materials, $\gamma_c \geq \gamma_{LV}$ is a requisite condition, where γ_c and γ_{LV} are the critical surface tension of wetting for the solid and the surface tension of the adhesive, respectively. The wetting depends on the contact time[1] and the contact pressure[2] for constant viscosity of the adhesive. When this condition is satisfied, the diffusion of adhesive into the crevasses or pinholes on the adherend surface will be promoted, and then the effective joint area may increase. Polyethylene melt under the right condition can wet the high surface free energy solids like metals.[1] During the spreading process of the polyethylene melt on the surface of the high energy solid, adsorption of polyethylene molecules occurs at the polymer–solid interface. Therefore, if care is taken in process III (gelation process of polyethylene melt), then it is possible to prepare strong joints between polyethylene and the metal, provided the metal oxide is properly prepared (absence of mechanical weakness).

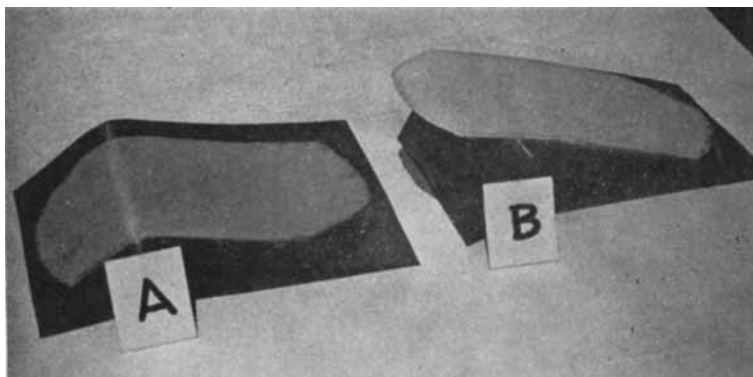Polyethylene used in this study (Sholex 6009 from Showa Denko Co.

Fig. 1. Annealing effect on adhesive joint strength between polyethylene, Sholex 6009, and 0.3-mm iron plate. Molding temperature of polyethylene melt 180°C, for 40 min at 20 kg/cm² initial pressure: (A) annealed sample at 142°C for 60 min; (B) quenched sample at room temperature.

Ltd.) was 0.96 g/cm³ density and 0.9 melt index. Polyethylene sheet, 1 mm, was previously prepared by compression molding between two plates of 3 mm polytetrafluoroethylene (20 × 20 cm²) at 250°C.

Specimens A and B shown in Figure 1 were prepared as follows: polyethylene films were molded at 180°C for 40 min at 20 kg/cm² between 0.3-mm iron plate (low carbon content steel, carbon content 0.30%) and 3-mm polytetrafluoroethylene (PTFE). The iron plate was polished with sand paper and degreased with trichloroethylene prior to application of the polyethylene. After cooling the composite, the PTFE was easily removed. All iron substrates in this paper were prepared as above unless stated otherwise. After application of polyethylene melt at 180°C, one sample (sample A in Fig. 1) was annealed for 60 min in an air-circulating oven which was controlled at 142°C, then cooled to room temperature (25°C). The other sample (sample B in Fig. 1) after application of polyethylene melt was immediately cooled to room temperature. There was no postcure for this specimen. The thickness of the polyethylene was maintained at 1.3 mm with the use of appropriate aluminum spacers. As shown by sample B in Figure 1, the adhesive joint strength of the specimen which was quenched was low since it failed in the first 90° bending test. The annealed specimen (sample A in Fig. 1), however, did not break during many 90° bending tests.

Figure 2 indicates the adhesive joint strength for specimen A which was prepared by melting polyethylene between 3-mm iron plate (same as in Fig. 1) and 3-mm PTFE at 180°C for 30 min under 20 kg/cm² initial pressure. The specimen was annealed in a 142°C air-circulating oven for 30 min and cooled to room temperature slowly, then the PTFE was removed. Specimen B was prepared under the same conditions, except that it was immediately cooled to room temperature. Annealed sample A (Fig. 2) shows a strong joint strength when pealed; the polyethylene film

(1.3-mm thickness) failed during the test.   However, quenched sampled B was easily pealed (peal strength <1 kg/in.).   From these results we assert that in the adhesion of polyethylene to metals, the gelation process strongly affects the joint strength.

To discuss the joint strength in detail, the tensile shear strength of joints consisting of iron–polyethylene–iron composites were investigated.   Poly-
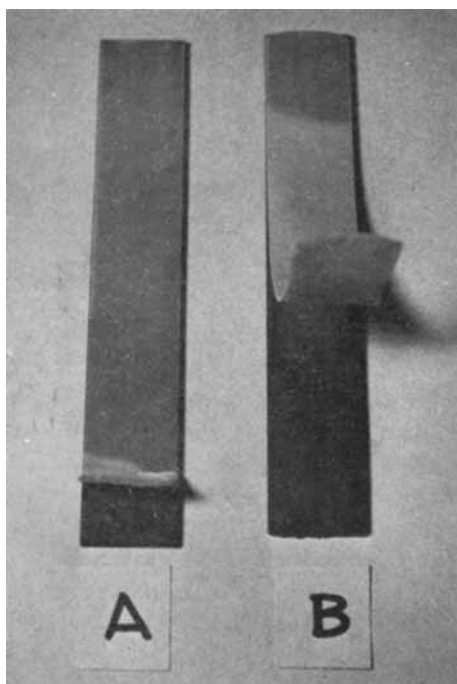

Fig. 2. Annealing effect on adhesive joint strength between polyethylene, Sholex 6009, and 3-mm iron plate. Molding temperature of polyethylene melt 180°C, for 30 min at 20 kg/cm² initial pressure: (A) annealed sample at 142°C for 30 min; (B) quenched sample at room temperature.
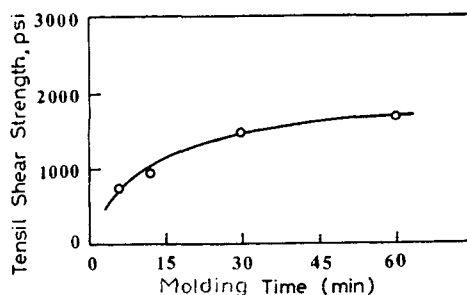

Fig. 3. Tensile shear strength of the composite iron–polyethylene–iron plotted as a function of annealing time at 142°C. Molding temperature 300°C for 6 min at 20 kg/cm² initial pressure.
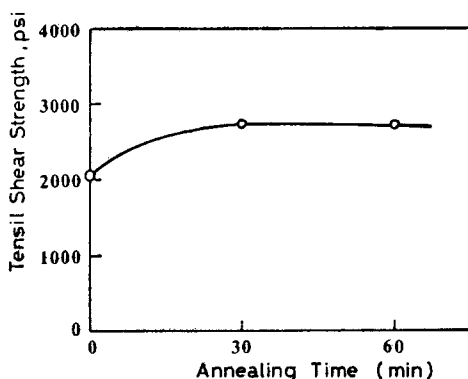
Fig. 4. Tensile shear strength of the composite iron–polyethylene–iron plotted as function of molding time at 180°C. Annealing temperature 142°C, 60 min annealing time at 20 kg/cm² initial pressure.

ethylene films used for hot application were the same films mentioned above. Iron adherends were 3 mm thick, 25.4 mm wide, 150 mm long. The tensile shear strength specimens were prepared by molding polyethylene film between preheated metal plates in a hot press maintained at 300°C (Fig. 3) or 180°C (Fig. 4) for a period of 6 to 60 min under an initial pressure of 20 kg/cm². The bonding area was 1 in.². The thickness of the polyethylene layer was 0.34 mm maintained by aluminum spacers. After the application of the polyethylene melt, the specimens were immediately annealed in the 142°C air oven for a predetermined time and cooled to room temperature and tested. Using a Schopper tensile tester, the tensile shear strengths were measured; the jaw separation rate was 30 mm/min.

The relation between the tensile shear strength and annealing time at 142°C is shown in Figure 3. From the results shown in Figure 3 we cannot find a difference between the 30-min and 60-min annealing time samples and the sample prepared at the shortest annealing time, which has a high joint strength. The condition for annealing is dependent upon the thickness of the polymer film and the heat capacity of the specimen. For thin film sandwiched with 3-mm iron plates, the shrinkage stresses which occur during gelation may not concentrate at the polymer–substrate interface and/or boundary layer.

The melt application time dependence of joint strength was investigated. In Figure 4 the relation between the tensile shear strength and the molding time at 180°C is shown. The initial pressure applied was 20 kg/cm². All the specimens were annealed at 142°C for 60 min. As can be seen in Figure 4, the joint strength increases with increase of molding time. This involves process I, which is related to the wetting of the polyethylene melt onto the metal surface. Surface tension of the polyethylene melt at 180°, 250°, and 300°C is 24.3, 19.0, and 15.2 dynes/cm, respectively.[3] The molding time dependence of the joint strength is attributed to the time

dependence of the wetting process. This is due to the high viscosity of polyethylene melt.[7] The progress of spreading of a polymer melt into pinholes or crevasses on the surface of a substrate is dependent on the time at a particular temperature; maximizing the effective contact area between the polymer melt and the substrate will result in a stronger joint strength.

In the adhesion of polyethylene to metal, especially in iron, a consideration of both the molding temperature and time can satisfy the condition of wetting as proposed in process I. When the polymer melt has spread on the substrate, the existence of polar sites on the substrate surface may promote strong adsorption and orientation of the polymer molecules. The adsorption of polymer chain depends on the kind of crystal lattice of a solid surface.[4] Considering the decrease of the interface free energy by the orientation of polymer chain, Yong-Dupre's equation for spreading,

$$e_A = 2e_{LV}$$

where e_A and e_{LV} are the energy of adhesion and the surface free energy of adhesive, respectively, must be rewritten as

$$e_A = 2e_{LV} + e'$$

where e' corresponds to the energy value decreased by the orientation of adhesive molecules. In the other adhesive joint systems, e' will be produced by a hydrogen bond or a covalent bond. If there is orientation of a polymer chain to a solid surface at the interface, then the adhesion may exceed the cohesive strength of polymer.

In the step of the melt application of a polyethylene onto a metal surface, strong adhesion must be built through process I and process II. However, if we disregard process III, the gelation of the polyethylene melt, the internal stress due to shrinkage stress on cooling will concentrate at polymer–substrate interface and adhesive joint strength will decline. If there are weak boundary layers in the interfacial region of polymer or substrate, the adhesive joint strength may be affected by this internal stress concentration. In this report, a new method for preventing the concentration of internal stress at the polyethylene–substrate interphase on cooling is shown, that is, annealing. We contend that if care is taken in the preparation of adhesive joints to prevent any stress concentration at the interface, then it may be possible to prepare strong adhesive joints for other systems. Our experimental results suggest that polyethylene is an effective adhesive for metals when no mechanical weakness exists in the metal oxide.

References

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