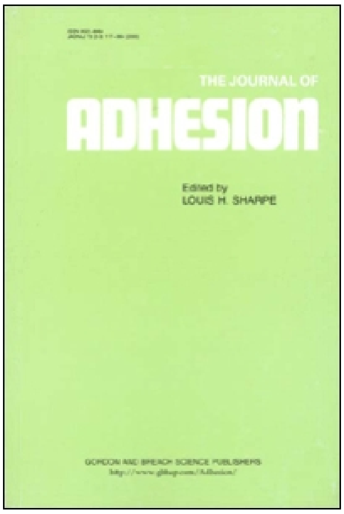

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Relationship Between Bond Strength and Crystallinity of High Polymers—Polyethylene, Polyethyleneterephthalate, and Nylon[†]

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The effect of crystallinity of polyethylene on the peel strength of aluminum plate-polyethylene-aluminum foil laminate was investigated. The 180° peel strength increased by rapid cooling with water, ice water, or liquid nitrogen after bonding with hot-melt polyethylene compared with slow cooling with air at room temperature. It was concluded that the increase of peel strength by rapid cooling was due to the decrease of modulus by the microcrystallization of polyethylene.

The tensile bond strength of steel-polyethyleneterephthalate (PET)-steel composite was investigated. The tensile bond strength increased about 10 times by rapid cooling of the composite bonded with hot-melt PET compared with slow cooling. On annealing the rapidly cooled composite over 100°C, the tensile bond strength decreased rapidly. It was concluded that the tensile bond strength decreases with the development of PET spherulite. Also in the case of Nylon 12, the tensile bond strength increased about 2 times by rapid cooling compared with slow cooling. In the case of Nylon 12, however, the tensile bond strengths of the both rapidly and slowly cooled specimens increased by annealing at high temperature.

INTRODUCTION

When crystalline polymers are used as hot-melt adhesives, and matrices or fibers in the composite materials, or are bonded with adhesives, the following are especially interesting subjects for consideration: weak boundary layer

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[†] This paper was presented at the *Symposium on Recent Advances in Adhesion* during the 162nd National American Chemical Society Meeting, September 1971.

(WBL), surface morphology (transcrystal, epitaxial growth, orientation of lamella, and others), bulk morphology (number, size, and distribution of spherulites), overall crystallinity, density, melting point, crystallizing point, tacticity, expansion and shrinking, and so on. In addition, as well as amorphous polymers, the following subjects should be considered: surface geometry, surface tension or surface free energy, visco-elastic behavior (modulus and viscosity), degradation, generation of new polar groups, chemical reaction, crosslinking, molecular weight, and so on. However, the relationships between bond strength and these subjects for crystalline polymers have not been fully established. We have studied the relationship between bond strength and crystallinity of several high polymers for about ten years. In this paper, the main results of our study are reported.

EXPERIMENTAL

Materials

Polyethylene—Hizex 3,000P (Mitsui Petroleum Chemical Co.), high density, powder. Polyethyleneterephthalate—Mitsubishi Resin Co., film. Nylon 12—XF-5,000 (Toray Co.), powder. Aluminum foil and plate—½H, high purity, Toyo Aluminum Co. Steel—Middle steel (JIS: SPC-1). The steel specimens were polished by No. 400 emery paper, degreased in distilled trichloroethylene by the use of an ultrasonic cleaner and finally dried under vacuum at 100°C for 4 hrs.

Measurement of Bond Strength

180° Peel strength—ASTM 903-49, T-Peel strength—ASTM D1876-61T, Tensile bond strength—ASTM D1344-54T. (The crosshead speed was 2 mm/min.) All bond strengths were measured under 65% RH at 23°C using Instron or Autograph tensile tester.

RESULTS AND DISCUSSION

Polyethylene

According to Bikerman[1] and Kaelble,[2,3] peel strength decreases with increasing modulus of adhesive. By quenching PE from melt, a microcrystalline structure having lower modulus is obtained. On the contrary, by slow cooling of PE from melt or annealing, a spherulite structure having higher modulus is obtained. In addition, according to Bikerman[4] and Schonhorn,[5] the low bond strength of PE is due to the failure of WBL formed at PE surface. The formation of WBL at PE surface is expected to be prevented by quenching, but accelerated by slow cooling from melt or annealing. For these reasons, the peel strength of Al/PE/Al laminate should increase by quenching, but decrease by slow cooling or annealing. In order to confirm the consideration, we investigated the peel strength of Al/PE/Al laminate. After degreasing with trichloroethylene, Al foil was etched with a sulfuric acid-dichromate solution ($H_2SO_4/K_2Cr_2O_7/H_2O = 10/1/30$) for 10 min at 70°C, washed with water thoroughly, and dried for 5 hrs in vacuo at room temperature. Al plate was polished by No. 400 emery paper before the above chemical etching. The sandwich of Al foil/PE powder/Al plate was pressed for 20 min at various temperatures. Immediately after pressing, the laminate was slowly cooled with air at room temperature, or quenched with water, ice water, or liquid nitrogen. In some cases, the laminate was cooled very slowly in the press for 4–6 hrs to obtain larger spherulites. The 180° peel strength of the laminate was measured at a crosshead speed of 30 cm/min. The thicknesses of Al foil, Al plate, and PE adhesive are 50 μ, 500 μ, and about 150–200 μ respectively. The locus of failure was always near the interface of Al foil and PE.

Figure 1 shows the increase of the peel strength by quenching. The increase of the peel strength with higher bonding temperature is due to the increase of adhesion. The better wetting of Al surface with melt PE and the generation of polar groups resulting from oxidation of PE are the main reasons of the increase of adhesion. The decrease of the peel strength with higher bonding temperature over 190°–210°C is based on the failure of degraded surface layer of PE. Figures 2 and 3 show the effect of very slow cooling in the press

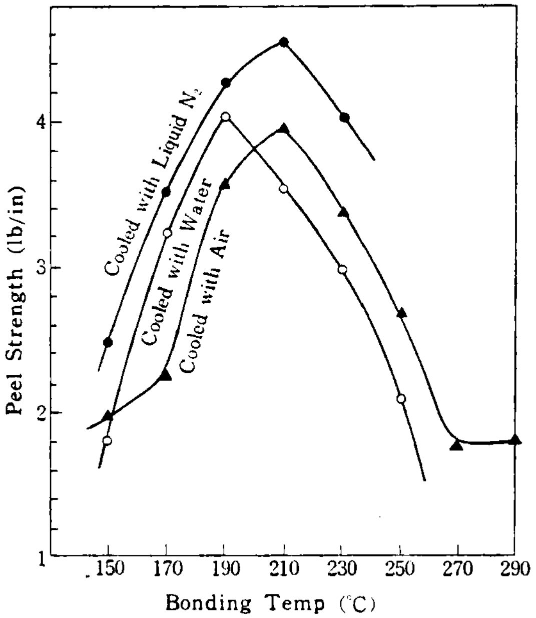

FIGURE 1 Effect of rapid cooling of Al/PE/Al laminate on peel strength

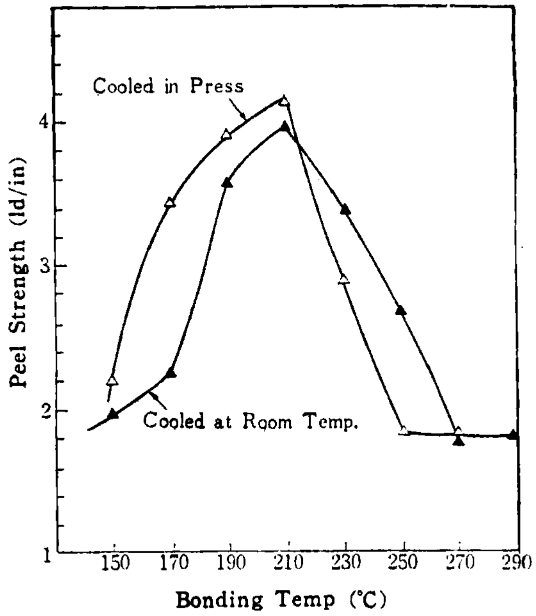

FIGURE 2 Effect of slow cooling of Al/PE/Al laminate on peel strength

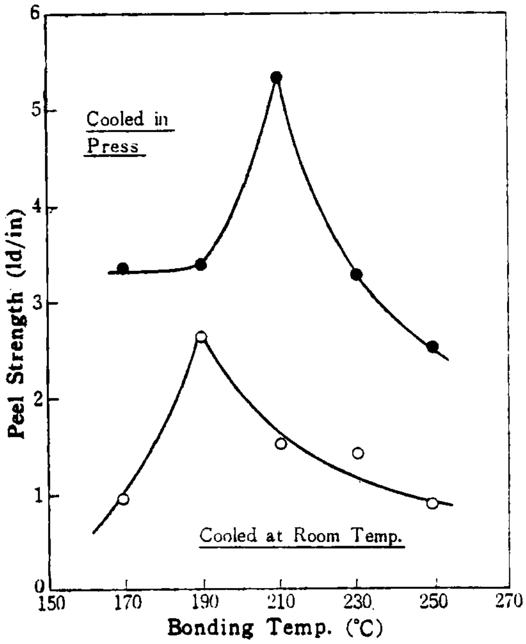

FIGURE 3 Effect of slow cooling of Al/PE/Al laminate on peel strength

on the peel strength. Figure 3 is the result obtained with a different Al foil/PE/Al plate combination. The increase of the peel strength by very slow cooling is the opposite result of our expectation.

In order to examine the crystalline morphology of PE, Al foil/PE/Al foil laminates were cooled from melt by the same methods as the Al foil/PE/Al plate laminates for peel test. In this case, the thickness of PE was about 1,500 . Figures 4, 5, and 6 show the polarizing microscopic photographs of the cross section of PE peeled from the Al foil/PE/Al foil laminate, which were cooled slowly with air, rapidly with liquid nitrogen, and very slowly in the press, respectively. Figure 4 shows that the region of deformed spherulites of various sizes extends to near the interface with Al. Figure 5 shows that the small spherulite region extends from the Al interface to the depth of about 400 μ. In Figure 6, the spherulites have considerably larger size, and show the extinction ring. The thickness of PE adhesive of Al foil/PE/Al plate laminate for peel test was about 150–200 μ. In Figure 4, the transcrystalline structure of about 20–40 μ depth is observed at the surface of PE peeled off mechanically by hand from Al foil. Schonhorn[5] reported that the transcrystalline structure was removed by mechanical peeling.

The decreases of modulus, density, and crystallinity of PE by quenching were confirmed by the measurements of dynamic shear modulus, density, and infrared spectra, respectively.

The locus of failure in peel test of the laminate was investigated. Figures 7 and 8 show the electron micrographs of replicas of Al foil surfaces peeled off from PE. In Figure 8, the lamella structure of PE is observed. The locus of failure was always at the surface layer of PE, regardless of cooling methods. Even in case of lower bonding temperature of 150°C, a very thin layer of PE or WBL was observed on the Al surface. From these facts, the failure of WBL of PE surface was confirmed. The thickness of PE deposited on the surface of Al foil increased with higher bonding temperature. This is due to the propagation of the degradation of PE by oxidation, which results in the generation of a new WBL composed of degradation products of PE.

Polyethyleneterephthalate

Polyethyleneterephthalate (PET) has been unable to be used as a hot-melt adhesive. The reason is that on cooling from melt, PET turns into a brittle, white powder-like product. This is owing to the rapid growth of crystals in random directions. Various amorphous polyesters are obtained by the copolycondensation of different acids and alcohols, which are available commercially as polyester adhesives. We found that a high bond strength was obtained by quenching PET from melt, which turned PET into an amorphous state.

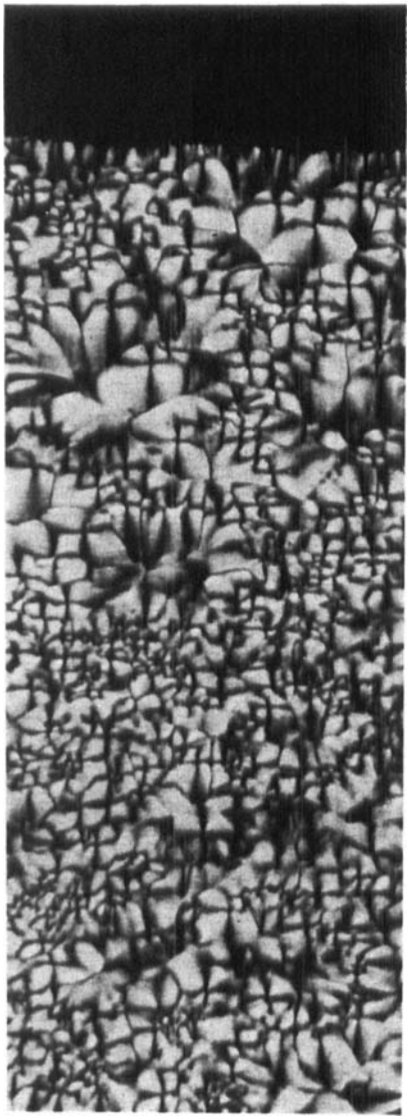

FIGURE 4 Polarizing microscopic photograph of polyethylene cooled with air at room temperature from melting at 210°C

FIGURE 5 Polarizing microscopic photograph of polyethylene cooled rapidly with liquid N_2 from melting at 210°C

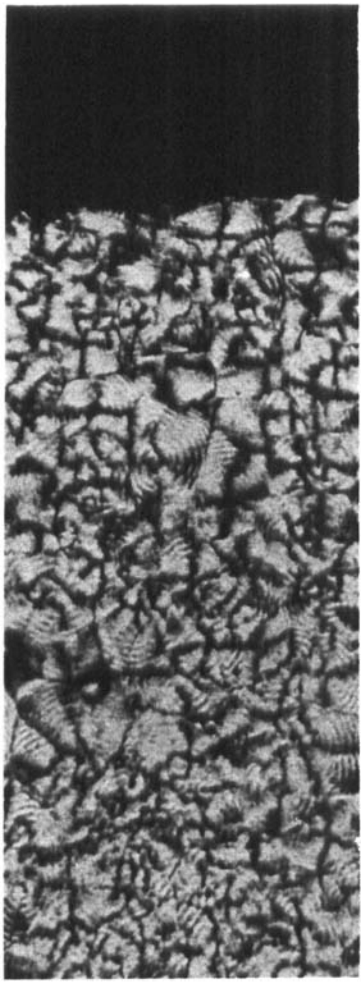

FIGURE 6 Polarizing microscopic photograph of polyethylene cooled slowly in hot press from melting at 210°C

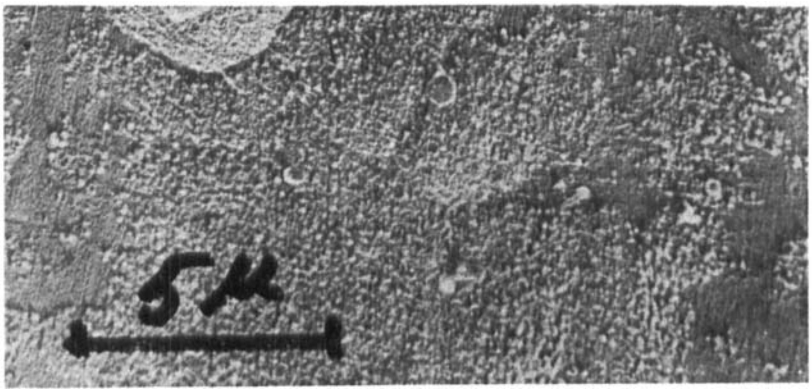

FIGURE 7 Electron micrograph of a replica of aluminum foil surface after peel test. The specimen was bonded with polyethylene powder at 170°C, and then cooled rapidly with liquid nitrogen

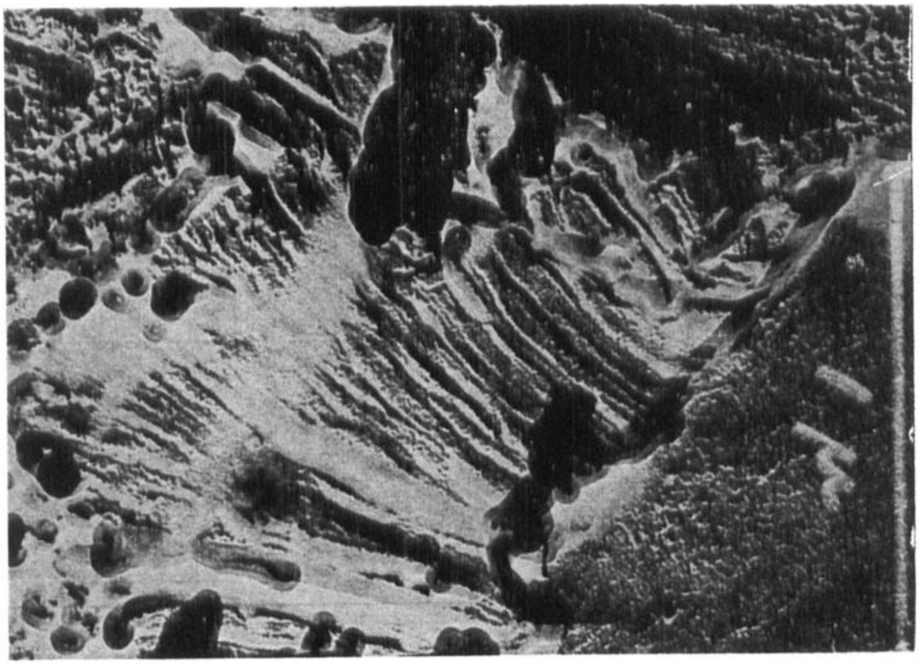

FIGURE 8 Electron micrograph of a replica of aluminum surface after peel test. The specimen was bonded with polyethylene powder at 290°C, and then cooled at room temperature

The cross lap joint specimen (bond area: 1 in^2) was made by pressing the sandwich of steel plate/PET film/steel plate (2 × 1 × 0.2 in) for 10 min at 295°C. After quenching, the tensile bond strength was measured.

Figure 9 shows that the tensile bond strength increases by quenching with water by about 10 times compared with slow cooling with air at room temperature. Figure 10 shows the polarizing microphotograph of PET cooled slowly with air from melt at 295°C. The PET is composed of large, closely packed spherulites. Figure 11 shows the PET which was melted at 295°C, annealed at 240°C for 10 minutes, and quenched with water. In this photograph, a number of the islands of small spherulites are observed in the sea of amorphous phase. In case of quenching immediately from melt at 295°C, a perfectly amorphous PET was obtained. These results show that a high tensile bond strength is obtained by turning PET into an amorphous state. Then, the quenched specimens were annealed at various temperatures of 23°–110°C for various time intervals from 10 min to 10,000 hrs. The bond strength decreased rapidly with longer annealing time over 100°C, but the decrease was a little below 90°C. The density of PET increased rapidly with longer annealing time over 90°C, but did not change below 80°C. Figure 12 shows the relationship between the bond strength and the density of PET after annealing. From these results, it was found that the tensile bond strength decreased suddenly over the PET density of about 1.37 (crystallinity: about 30%), and that the sudden decrease of the bond strength was due to the

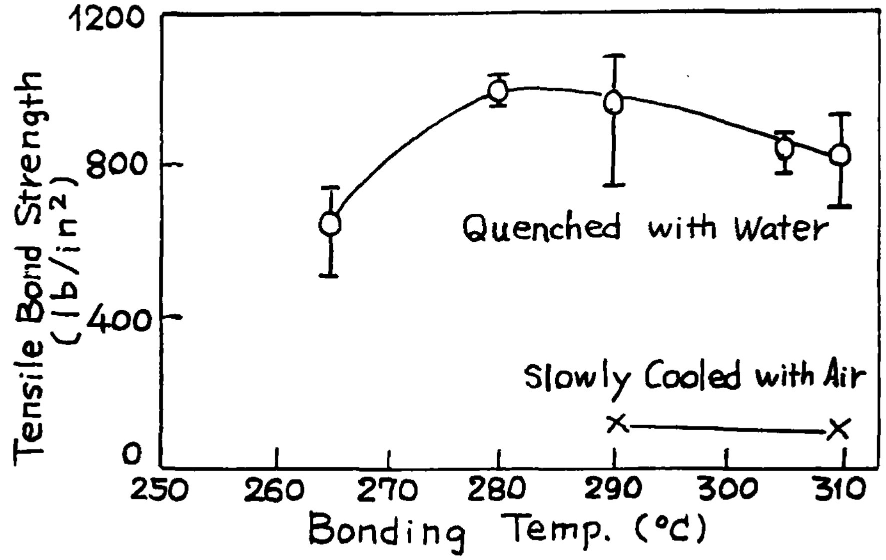

FIGURE 9 Tensile bond strength of steel/PET/steel composite

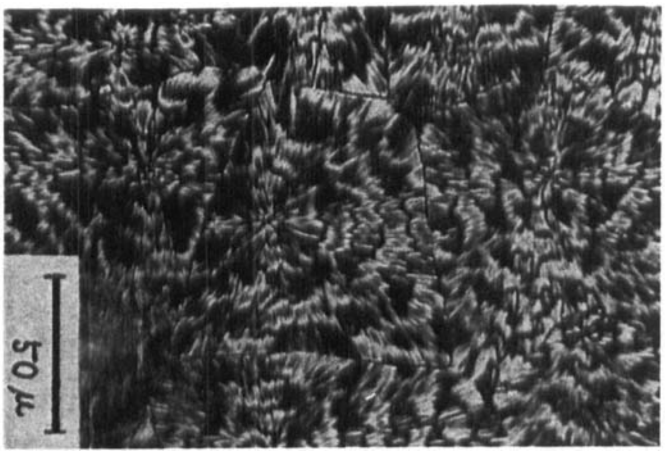

FIGURE 10 Crystal of PET cooled with air at room temperature from melt at 295°C

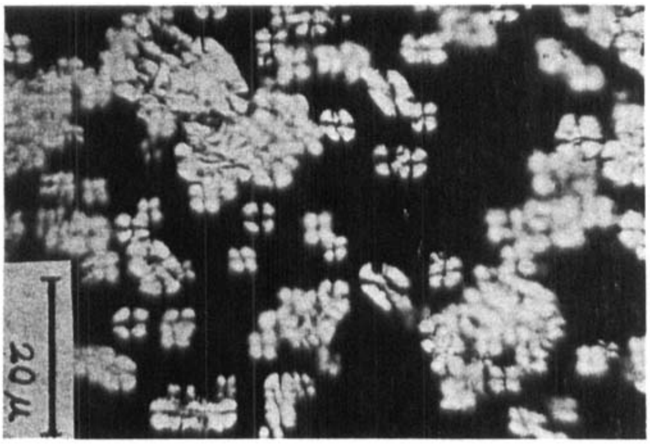

FIGURE 11 Crystalline nuclei of PET quenched with water from 240°C

overall generation of numerous small spherulites. According to the observation with the naked eye, the mode of failure was the interface for higher bond strength, but was the mixture of the interface and the cohesive failure of PET for lower bond strength.

Nylon 12

The specimens for the tensile bond test were made by pressing the sandwiches of steel plate/Nylon 12 powder (thickness: about 100 μ)/steel plate for 10 min

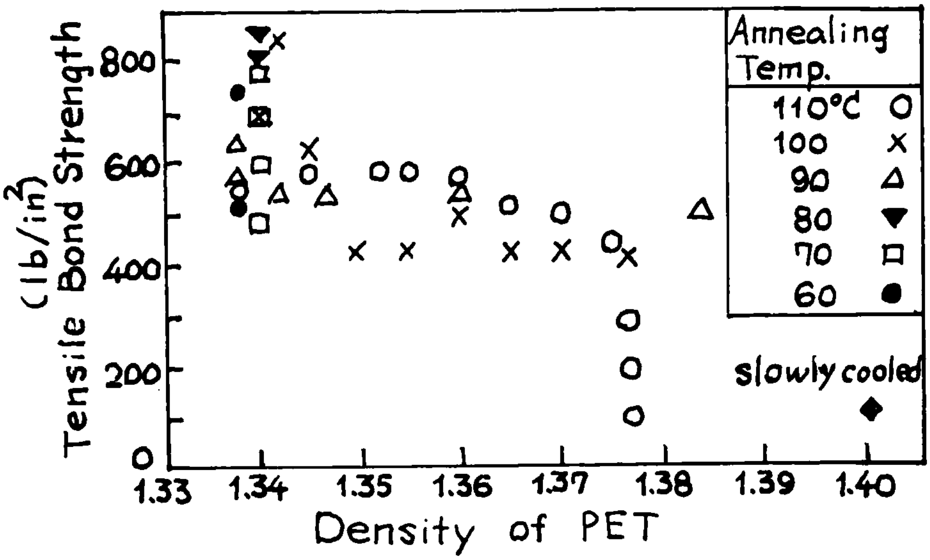

FIGURE 12 Tensile bond strength vs. density of PET

at 200°C. These specimens were cooled slowly with air at room temperature or quenched with dry ice-acetone from melt, and then annealed at 150°C in N_2 atmosphere for 200 hrs.

The tensile bond strength increased somewhat by quenching compared with slow cooling with air. In either case of quenching or slow cooling, the bond strength, the density, and the lower two melting peak temperatures of Nylon 12 increased with longer annealing time, but there was no change in the highest melting peak temperature of Nylon 12. Figure 13 shows the relationship between the bond strength and the density of Nylon 12 after annealing. From these results, it is found that the tensile bond strength increases with higher density of Nylon 12. According to the naked eye observation, the locus of failure was always at the interface.

The specimens for the tensile bond test having various surface morphologies of Nylon 12 were obtained by changing the cooling rate. The results are shown in Table 1. From these results, it is found that the bond strength decreases with lower surface and bulk densities of Nylon 12, but increases with lower densities below about 1.02. In case of the cooling rates of 1.3°C–50°C/min, the transcrystalline region of 20–30 μ depth was observed at the surface of Nylon, the density and crystallinity of which were very high. For example, the surface density of 1.0390 corresponds to the crystallinity of 0.89. On the contrary, in case of higher cooling rates, the amorphous region of several tens of microns depth was observed, the density and crystallinity of

TABLE I

Conditions and results

Sample No.	Cooling rate (°C/min)	Thickness (mm)		Tensile bond strength (psi)	Melting temp. (°C)	Density (25°C) (g/cc)	
		Adhesive	Adherend			Surface	Bulk
1	11.7	0.4	5.0	1368	177.5 169.0	—	1.0208
2	40	0.4	5.0	1006	177.0	—	1.0200
3	750	0.4	5.0	1360	177.0	—	1.0183
4	840	0.4	5.0	1008	176.8	—	1.0180
5	1.3	1.1	0.3	> 1200	176.5	1.0390	1.0288
6	12	1.1	0.3	> 1200	177.0	1.0298	1.0258
7	50	1.1	0.3	780	178.0 170.5	1.0262	1.0255
8	500	1.1	0.3	880	176.5	1.0211	1.0195
9	1000	1.1	0.3	1120	177.0	1.0145	1.0106

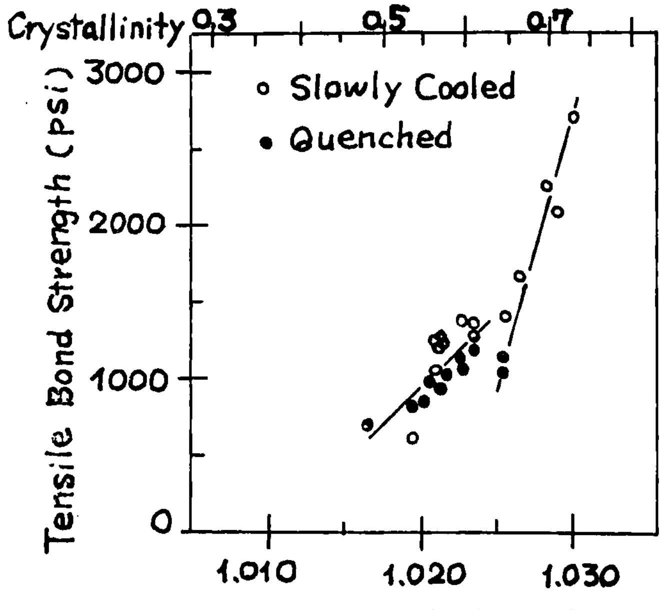

FIGURE 13 Tensile bond strength and density of Nylon 12 of steel/Nylon 12/steel composite annealed at 150°C in N_2

which were very low. For example, the surface density of 1.0106 corresponds to the crystallinity of 0.31.

Nylon 12/Dye Composite

We found that the T-peel strength of Al/Nylon 12/Al laminate increased by about 4 times by adding some dyes to Nylon 12. Figure 14 shows an example of such a phenomenon. In general, it is well known that the size of crystal of polymer decreases by adding fine particles. In our experiment, however, the size of crystal and the modulus of Nylon 12 increased with more adding of dye up to 10 wt%.

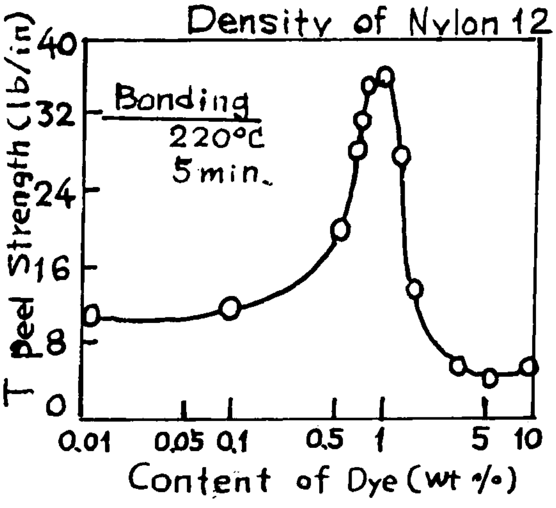

FIGURE 14 T-peel strength of Al/Nylon 12 + dye/Al composite (Dye: Acetoquinone Light Blue BLLZ)

Nylon 12/PET Composite

We found that the T-peel strength of Al/PET/Al laminate increased by adding Nylon 12 in the amount of 50–70 wt% (Fig. 15). The observation by a polarizing microscope showed that Nylon converted from the island phase to the sea phase near the content of 30 wt%. The really globular spherulites of PET were observed near the Nylon content of 70 wt%.

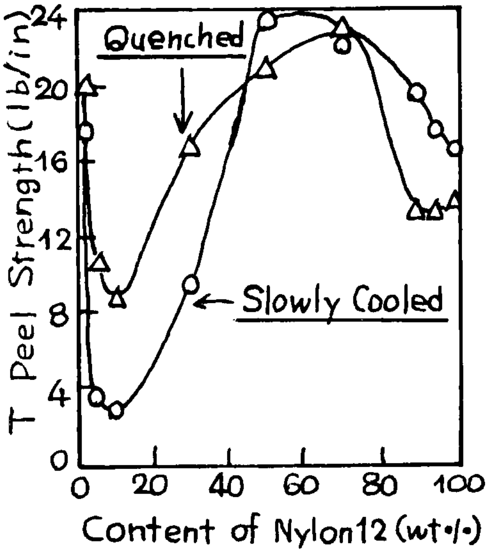

FIGURE 15 T-peel strength of Al/PET + Nylon 12/Al laminate

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