Polyester Adhesion to Chromium-Coated Steel for Poly(ethylene terephthalate) and an Isophthalate Copolymer

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SYNOPSIS

The performance of PET [poly(ethylene terephthalate)] and a copolymer of PET has been tested as an adhesive for chromium-coated steel. Crystallinity in the polyesters is found to limit adhesion, probably by restricting chain mobility. Lamination temperatures above the melting point of each polyester give the best adhesion. Degradation of the polyesters at yet higher temperature resulted in both reduced polymer cohesion and adhesion.

Optimum bonding to steel was obtained at lamination temperatures between 230 and 275°C for the copolyester and between 280 and 300°C for PET. The standard laminate compression time was 15 min at 50 kg/cm^2. Adhesion was evaluated by the ASTM T-peel test. Assessments were made by both the peel energy and the peak load for peel.

INTRODUCTION

Many kinds of surface-treated steels are in wide commercial use. In the container application of steel sheet, thermoset coatings are usually applied after forming. This is because thermoset coatings do not meet all requirements for high formability, resulting in low productivity or cracked coating. Precoated steel with thermoplastic coatings can be one of the best solutions for such applications, due to their potential formability and high efficiency in production.

In this study, the adhesion of two crystallizable polyesters on chromium-coated steel has been investigated. They are PET and a copolymer of PET. Poly(ethylene terephthalate), PET, is the most commercially important polyester, due not only to its excellent chemical stability and outstanding physical properties, but also to its low cost. Its properties are also readily changed by copolymerization.

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EXPERIMENTAL

Materials

The PET film for lamination was obtained from DuPont with a thickness of 50 μm. The number-average molecular weight was 50,000. A copolymer of ethylene terephthalate and ethylene isophthalate was also chosen for the lamination on coated steel. This copolymer film was 40-μm thick and has a weight-average molecular weight of 73,100. This specific copolymer film was obtained from Toyobo, Japan. The surface-treated steel chosen for this study was chromium-coated steel, known as tin free steel (TFS). This steel is 0.22-mm thick and has an average metallic chromium coating weight of 100 mg/cm^2 and an average oxide chromium coating weight of 15 mg/cm^2, as provided by Nippon Steel Corporation, Tokyo, Japan.

Procedure

The procedure developed for making a homogeneous lamination in a steel/polyester/steel system is as follows:

The steel sheets were degreased by dipping in trichloroethylene for 1 min, then wiped with a lint-free cloth. Relaxed film was prepared just before the lamination by a sandwiching process. The polyester films were relaxed between steel sheets without pressure for 2–3 min, at 185°C for the copolyester and at 250°C for PET. The relaxed films were then laminated by pressing between two steel sheets at 250°C for PET (185°C for copolyester) for 2 min under a pressure of 50 kg/cm^2. This was followed by quenching to ambient temperature in water.

Secondly, pressed laminates were transferred to an oven held at a constant temperature between 250 and 300°C for PET and 190 and 350°C each for 1–30 min, and then quenched to ambient temperature in water.

To investigate the adhesion durability, some of the pressed laminates were also placed in boiling water for 2–12 h before measurement of the T-peel force.

Peel Experiments

Test specimens were peeled at an angle of 180°, according to ASTM-D-1876-72, the standard test method for peel resistance of adhesives (T-peel test). For all experiments, the Instron cross-head separation rate was 350 mm/min. The test laminates were 15-mm wide and 150-mm long. All peel experiments reported here were carried out only at room temperature. Results of T-peel tests were expressed as peel energy and as the peak load of the peel force. Peel energy was evaluated by the area below the load-extension curves, and was calculated as energy necessary to peel the specimen for the length of 30 mm. Load and energy can be influenced by stiffness of the steel sheet which was held constant in these tests.

RESULTS AND DISCUSSION

Figure 1 illustrates the effect of the laminate annealing temperature upon the T-peel energy for PET bonded to TFS. Each symbol represents a separate datum. Comparative tests show a lower peel force exhibited by unrelaxed PET film, regardless of the annealing temperature. To provide a reliable evaluation of lamination conditions upon adhesion, all reported experiments were carried out with relaxed polyester films.

For bonding annealed at 265°C and below, limited wetting occurred (below the T_m of PET), resulting in poor adhesion. The failures observed during these T-peel tests were a mixture of adhesive and cohesive. As shown in Figure 2(a), the cohesive portion of the failures showed numerous deep cracks. Observation of the edges of these cracks at higher magnification reveals that they are not smooth, probably due to elongation during peeling [Fig. 2(b)].

A remarkable enhancement of the T-peel force, showing improved bonding for PET, was attained by annealing above 270°C. Here the failure becomes mostly cohesive. This suggests that the adhesive force between PET and TFS has approached the cohesive force of PET itself. As shown in Figure 2(b), the fracture surface for this case looks slightly rough.

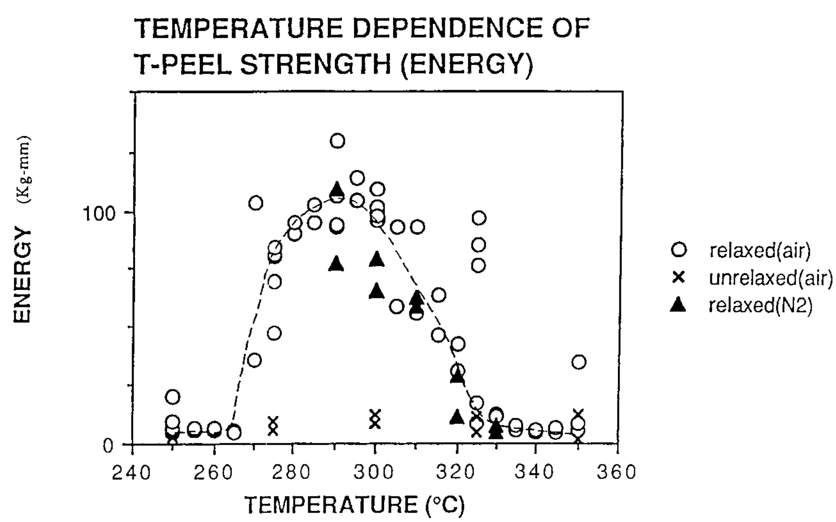

Figure 1 Temperature dependence of T-peel strength (energy) for PET.

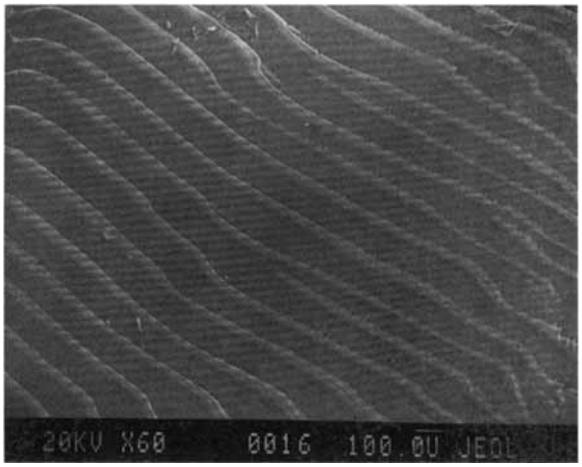

Figure 2(a) SEM of the fracture surface of relaxed PET which was laminated at 250°C. Cohesive portions have big deep cracks.

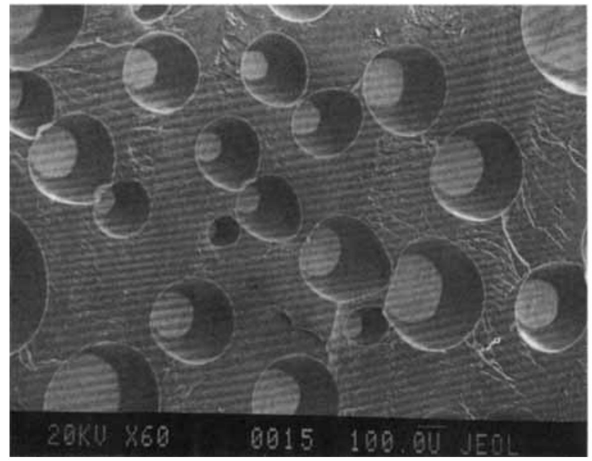

Figure 3 SEM of the fracture surface of relaxed PET which was laminated at 315°C. Numerous small bubbles are observed in the PET layer. At the bottom of the bubbles, the surface of the steel sheet can be seen.

The melting characteristics of the PET film, obtained by DSC, was T_m (onset) = 245°C, T_m (peak) = 256°C, T_m (termination) = 265°C. Crystals thus appear to behave as crosslinks below T_m, limiting the molecular chain mobility at the interface and reduce adhesion. On the other hand, above its melting point, the molecules are mobile, giving rise to wetting and better adhesion.

One phenomenon clearly takes over another at yet higher temperature, see Figure 3. For bonding above 300°C, the peel force tends to decrease, likely due to degradation of PET. Fractures are totally cohesive and many small bubbles are observed in the PET layer. The fracture surface is rough with small cracks. The initial step of thermal degradation of PET is a random scission of the chain at an ester linkage. It is reported to proceed above 280°C.[1,2] Oxidation may also be involved as PET annealed above 300°C becomes brownish and brittle. However, the data in Figure 1 also show that annealing in a nitrogen atmosphere, which should retard oxidative degradation, resulted in almost no improvement in T-peel strength.

Figure 4 illustrates the effect of annealing temperature upon the T-peel energy for each polyester. A drastic shift of the low temperature end of the bond stability envelope is observed for the copolyes-

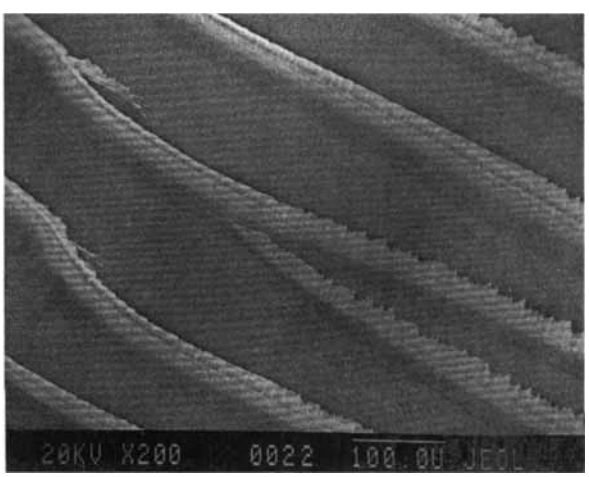

Figure 2(b) SEM of the fracture surface of relaxed PET which was laminated at 250°C. The edges of these cracks are not smooth.

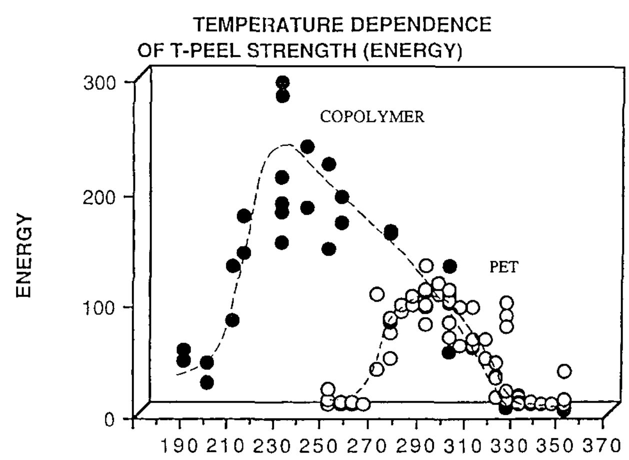

Figure 4 Temperature dependence of T-peel strength (energy).

ter. Up to 215°C, yet below the copolyester T_m, insufficient wetting occurred for good adhesion: the peel values were low and the failure observed during these T-peel tests was mostly adhesive. The surface was basically flat and smooth with a slight replica on the film of the surface finish of the steel plate. This indicates that copolymer was mobile enough to flow to some extent into the surface roughness of the steel plate, but it did not sufficiently wet to form a strong bond.

Above 230°C, a remarkable enhancement of the T-peel force was observed for the copolyester. The failure observed here was a mixture of adhesive and cohesive failure. This indicates that the flow and wetting between copolymer and steel have proceeded, resulting in better bonding.

The melting of the relaxed copolymer film shows T_m (onset) = 175°C, T_m (peak) = 225°C, and T_m (termination) = 230°C. Crystals thus again appear to behave as a crosslinker below T_m, limiting the molecular motion at the interface and reducing adhesive bonds. Above its melting point, the molecules are more mobile, leading to wetting and better adhesion.

Figure 5 illustrates the effects of the laminate annealing temperature upon the peak load for failure. As often the case with failure tests, a wide scattering is observed. The trend of phenomena, however, is the same as reported in Figure 1. The measured tensile strength of the same PET film, at the same cross-head separation rate of 350 mm/min, was 13.4 kg/15-mm width.

At 275°C, longer annealing times for PET result in a higher peel force. At 300°C, the maximum force on annealing is found at shorter times, 10–15 min,

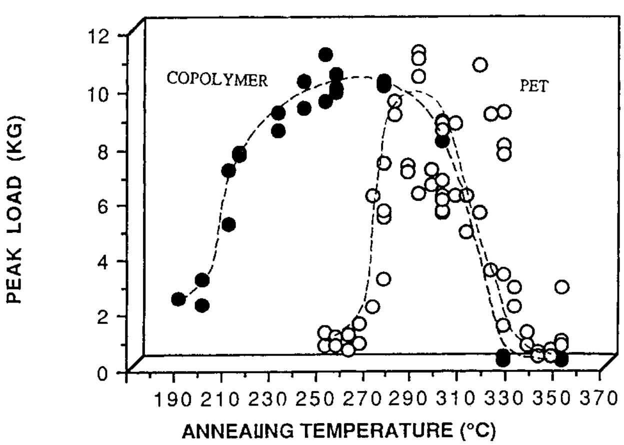

Figure 5 Temperature dependence of T-peel peak load.

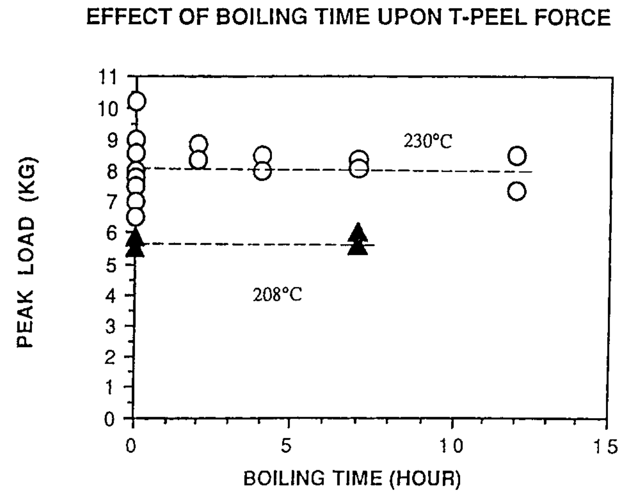

Figure 6 Effect of boiling time upon T-peel force.

with peel force decreasing at longer annealing times. At lower temperature, degradation is reduced, so that longer annealing time gives better wetting, resulting in a higher peel force. On the other hand, at the highest temperatures, degradation proceeds rapidly, giving rise to poor mechanical properties. As a result, longer annealing time can cause better wetting, but may also lead in a lower peel force, due to a lower cohesive energy for degraded polyester. Annealing in nitrogen atmosphere did not retard the degradation. Trace oxygen and moisture may have been present.

Figure 6 illustrates the effects of the boiling water treatment upon the peak load of the T-peel force for the copolyester laminates. The samples annealed at 230°C for 15 min showed a slight decrease in the energy, but almost no decrease in the peak load. The failures of the boiled specimens were slightly more cohesive than the failures of the unboiled specimens. The same trend was observed with the samples annealed at 208°C for 15 min. Moisture intrusion at the interface thus seems to be insufficient to disrupt the interface, since bonding was not significantly reduced.

CONCLUSION

The copolyester provides a wider and lower temperature window for adhesive bonding to steel than did PET. The bonding energy to the chromium-coated steel achieved for the copolymer was twice that of PET, as indicated in Figure 4.

Adhesion of the polyesters to chromium-coated steel is restricted by crystallinity. Higher molecular mobility, resulting from a higher laminate annealing temperature, and aided by crystal melting, gives birth to good wetting. The resultant highest peel force is about 230°C for the copolyester, and 290°C for PET. Longer annealing time at around the crystal melting point gives rise to better wetting, but it may also allow imperfect crystals to become perfect, resulting in brittleness.

Annealing at yet higher temperature brings about reduced mechanical performance, probably due to chain scission.

The well-bonded copolyester samples, annealed at 230°C for 15 min, appear resistant to moisture intrusion and hydrolysis, as shown by boiling water treatment. However, the crystallinity which increases during the boiling treatment can possibly deteriorate the copolymer performance as an adhesive. It has become clear that wetting, degradation, and crystallinity are all important in determining bonding strength in these steel/polyester/steel laminate systems.[1,2]

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