

Generalized Approach to Adhesion via the Interfacial Deposition of Amphipathic Molecules. III. Adhesion of Polyethylene to Stainless Steel

HAROLD SCHONHORN, *Bell Telephone Laboratories, Incorporated, Murray Hill, New Jersey,*

Synopsis

Oriented monolayer adhesives of stearic acid have been employed to bond polyethylene to stainless steel. Bonding time, bonding temperature, and rate of peel are several of the parameters that here varied to determine their effect on the final peel strength. Peel strengths of about 90 lb./in. width were obtained for monolayer coated specimens. When the specimens were fabricated properly, only cohesive failure of the polyethylene resulted. Irradiation of the bonded specimens resulted in considerable lowering of the peel resistance of the nonmonolayer coated specimens, relatively small differences being noted for those prepared with the oriented monolayer adhesive.

Introduction

It has been demonstrated^{1,2} that the interfacial deposition of oriented condensed monolayers of amphipathic molecules (e.g., stearic acid, octadecylamine) onto a sulfochromated, pure aluminum surface resulted in a bonding medium possessing a high degree of uniformity and specificity. The purpose of this communication will be to illustrate further, the use of the oriented monolayer adhesive bonding technique in the adhesion of polyethylene to stainless steel.

Kraus and Manson³ and Lasoski and Kraus⁴ have investigated the adhesion of polyethylene to stainless steel by measuring the tensile strengths of the bonded structures. They demonstrated that in the limit of small film thicknesses, polyethylene adheres to the steel surfaces with a bonding strength equal to or exceeding the tensile strength of the polymer. The fractured specimens in their work showed that bond failure had occurred partially at the interface and partially through the polymer film. Lasoski and Kraus⁴ were successful in disrupting the bonds to the extent of producing 100% failure in adhesion by preadsorbing onto stainless steel a "monolayer equivalent" of decanoic acid. This monolayer equivalent was sufficient to reduce the adhesion to a small fraction of the original value.

The amphipathic molecule chosen by Lasoski and Kraus⁴ and the manner in which it was adsorbed onto the stainless steel accounts for the observed lack of adhesion. They added dropwise to the stainless steel surface a

n-heptane solution containing enough decanoic acid to cover the surface with a monolayer, assuming an area per molecule of 20Å.² This technique of monolayer deposition undoubtedly resulted in considerable multilayer formation as well as a random distribution and orientation of the surface active material.

A condensed oriented monolayer properly deposited onto a metal surface can increase the adhesion between adherends, thereby, resulting not in the adhesional failure observed by Lasoski and Kraus, but in cohesive failure of the polyethylene.^{1,2} Stearic acid has been employed in the present investigation to demonstrate how the general approach proposed previously^{1,2} can be adapted to the system stainless steel-polyethylene.

Experimental

Details of the materials used and the manner in which the monolayers are transferred to the metal surfaces are described in previous communications.^{1,2} The stainless steel was 18/8 type 302. Three bonded specimens were peeled for each reported value. The results are reproducible within $\pm 5\%$ of the recorded value. All experiments reported here were carried out at room temperature (21–23°C.) unless otherwise noted.

Results and Discussion

In Figure 1 are shown the forces required to peel polyethylene from a metasilicated stainless steel surface with and without an adsorbed monolayer of stearic acid. The stearic acid was deposited at a surface pressure of 30 dynes/cm. from a trough containing a 0.0004*M* solution of chromium-(III) chloride. Test specimens were bonded for 10 and 20 min. at a temperature of 177°C. The bond strengths are enhanced considerably when the oriented condensed monolayer is interposed between the polymer and metal substrate. Approximately, a one-to-one correspondence in transfer of a condensed monolayer of stearic acid at the air-water interface to the metasilicated metal surface was established by using radiolabeled stearic acid.

For a peel rate of 5 in./min. there is a 1.5-fold increase in the resistance to 180° peel when a monolayer of stearic acid is adsorbed prior to bonding. Although there is an apparent convergence of the peel force to some common value, there is still a threefold increase in bond strength at a peel rate of 2 in./min. Longer bonding times at 177°C. lower the contact angle of molten polyethylene on stainless steel. In a previous investigation² it was established that the maximum bond strength was obtained when the contact angle $\theta = 0$. This phenomenon is reflected in the increase to peel resistance for specimens bonded for 20 min. as shown in Figure 1. When the contact angle reaches equilibrium, no further increase in bond strength is apparent, indeed, the degradation of the polymer exposed to these high temperatures for prolonged periods of time reduces the resistance to peel.

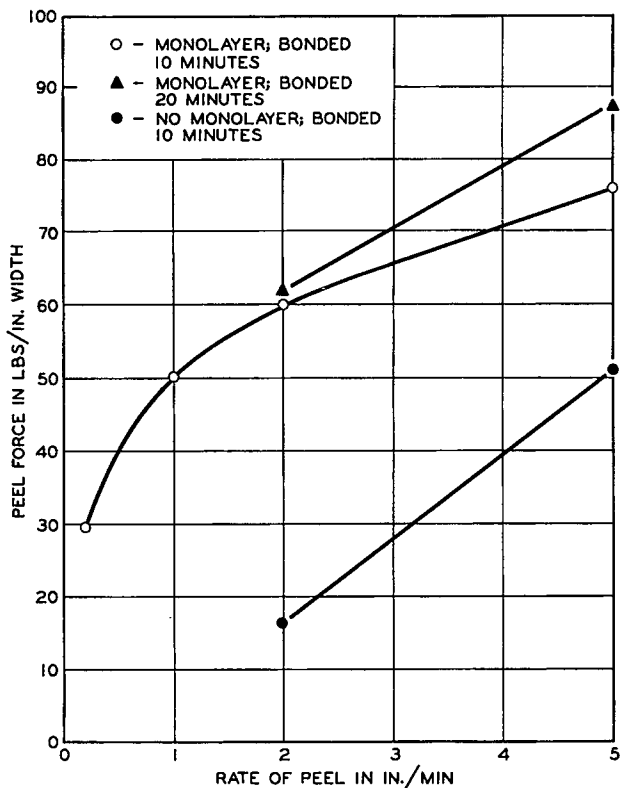


Fig. 1. 180° peel test (ASTM D903) for polyethylene bonded at 177°C. to stainless steel having an adsorbed monolayer of stearic acid deposited at 30 dynes/cm. from a trough containing a 0.004M chromium(III) chloride solution.

Figure 2 illustrates the effect of longer bonding times and rate of peel on monolayer and nonmonolayer coated specimens. In all cases, the units were bonded for 20 min. at 177°C. The trough substrate from which the monolayer was transferred was, as before, 0.0004M chromium(III) chloride. At peel strengths of over 90 lb./in. width, the polymer adherend is on the verge of tearing. Therefore, the values obtained at a peel rate of 10 in./min. and greater reflect primarily the rheological properties of the polyethylene. In all cases, where a monolayer is employed, 100% cohesive failure of the polyethylene is achieved, no stainless steel surface is visibly exposed after bond rupture. When no monolayer is adsorbed, some steel surface is exposed. The monolayer equivalent of decanoic acid used by Lasoski and Kraus⁴ to decrease adhesion, further points out the necessity to produce an ordered array of condensed amphiphathic molecules. The effect of an oriented condensed monolayer interposed between polar and nonpolar adherends is contrary to the work of investigators in the adhesives field because of their neglect to orient properly the monolayer forming material. Bikerman⁵ has employed oleic acid and ethyl

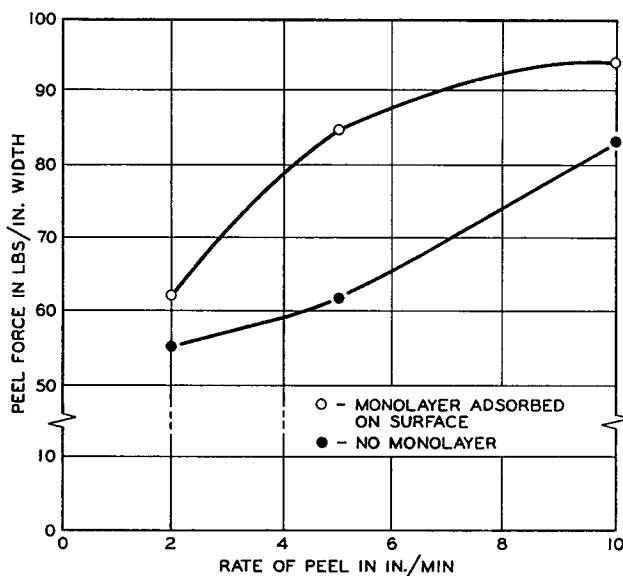


Fig. 2. 180° peel test (ASTM D903) for polyethylene bonded at 177°C. for 20 min. to stainless steel having an adsorbed monolayer of stearic acid deposited at 30 dynes/cm. from a trough containing a 0.0004M chromium(III) chloride solution.

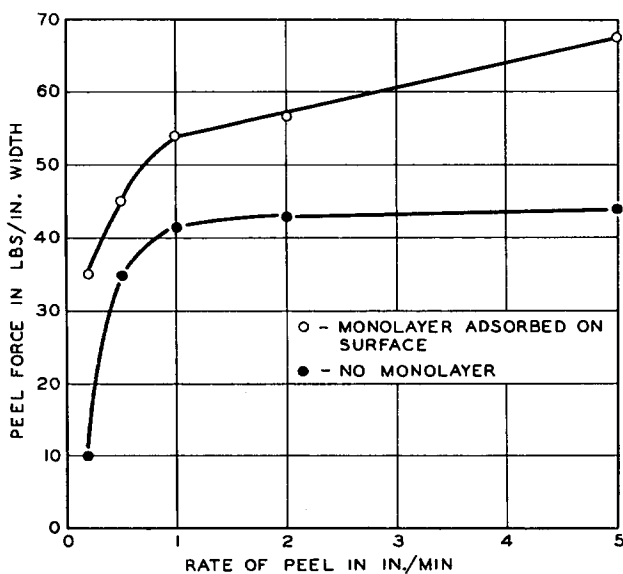


Fig. 3. 180° peel test (ASTM D903) for polyethylene bonded at 205°C. for 10 min. to stainless steel having an adsorbed monolayer of stearic acid deposited at 30 dynes/cm. from a trough containing a 0.0004M chromium(III) chloride solution.

palmitate to demonstrate a decrease in adhesion of polyethylene to aluminum. No attempt was made in his investigation to eliminate multilayer formation which is evidently contributing to the decrease in bond strength. Lack of orientation is detrimental to the final bond strength.

As illustrated in Figure 3, bonding for 10 min. at 205°C. is sufficient to

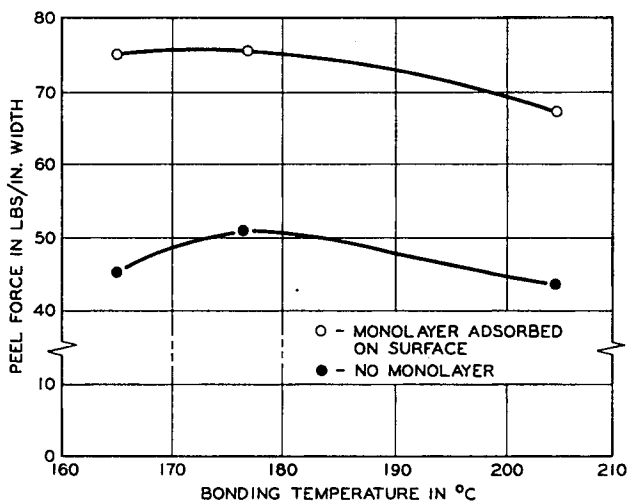


Fig. 4. 180° peel test (ASTM D903) for polyethylene bonded at various temperatures for 10 min. to stainless steel having an adsorbed monolayer of stearic acid deposited at 30 dynes/cm. from a trough containing a 0.0004*M* chromium(III) chloride solution.

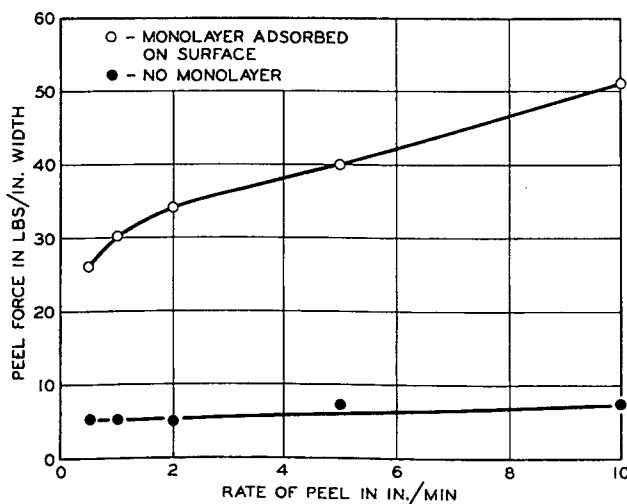


Fig. 5. 180° peel test (ASTM D903) for polyethylene bonded at 177°C. to stainless steel having an adsorbed monolayer of stearic acid deposited at 30 dynes/cm. from a trough containing a 0.0004*M* chromium(III) chloride solution. Irradiated specimens received a dose of 20 Mrad prior to testing.

allow for complete wetting of the stainless steel surface. The difference in the peel strength of the specimens bonded for 20 min. at 177°C. and those bonded for 10 min. at 205°C. is probably due to some polymer degradative mechanism proceeding at the higher temperature. This would induce a weakening of the polyethylene, thereby decreasing the resistance to peel of the bonded samples. At lower peel strengths, failures are somewhat adhesional.

Figure 4 summarizes the data of the previous figures for a peel rate of 5 in./min. For a 10-min. bonding period, there is a maximum in the peel strength at about 175°C. It is also obvious, that there is a considerable enhancement of the resistance to peel when a condensed oriented monolayer of stearic acid has been deposited on stainless steel prior to bonding with polyethylene. The parallel nature of the two curves in Figure 4 indicates a uniformly stronger resistance to peel of the monolayer coated specimens throughout the temperature range investigated. The strength increase due to the oriented monolayer adhesive in this adherend system is perhaps greater than in the aluminum-polyethylene system, since in bonding stainless steel mechanical interlocking of the porous substrate with the polymer is precluded. This effect gave the nonmonolayer coated sulfochromated aluminum specimens a reasonably high peel strength. The reason one obtains slightly lower peel strengths in the stainless steel system may be because of the lower real surface area available for bonding than in the porous sulfochromated aluminum surface. The stainless steel surface prior to bonding is quite smooth and nonporous.

The effect of a 20 Mrad Van de Graaff irradiation on the bonded specimens is illustrated in Figure 5. Note the considerable decrease of peel strength in the nonmonolayer coated specimens. The bonding sites of the nonmonolayer coated specimens are apparently destroyed and adhesion reduced to a low value. Although irradiation of the stearic acid coated specimens destroys a portion of the carboxylic acid groups,⁶ the crosslinking of a portion of the hydrocarbon tails to themselves as well as to the polymer matrix results in chemical bonding to the polymer, thereby maintaining a high degree of adhesion. Lower doses would be expected to produce an increase in peel strength as was noted in the aluminum-polyethylene system.^{1,2} Although there is a decrease from 75 to 40 lb./in. width for the monolayer covered specimens at a rate of peel of 5 in./min., the bond strengths of the nonmonolayer coated specimens are reduced from 50 to 7 lb./in. width.

In the future, work will be reported on the tensile strength of stainless steel specimens bonded with polyethylene. Preliminary results indicate that the values obtained employing an oriented monolayer adhesive exceed those in the literature by 100%.

We sincerely thank Mr. J. Struthers, Dr. R. Salovey, Dr. L. H. Sharpe, and the members of the Adhesives Group for their kind assistance in the experimental phase of this work.

References

1. Schonhorn, H., *J. Polymer Sci.*, **A1**, 2343 (1963).
2. Schonhorn, H., *J. Polymer Sci.*, **A1**, 3523 (1963).
3. Kraus, G., and J. E. Manson, *J. Polymer Sci.*, **6**, 625 (1951); *ibid.*, **8**, 448 (1952).
4. Lasoski, S. W., Jr., and G. Kraus, *J. Polymer Sci.*, **18**, 359 (1955).
5. Bikerman, J. J., *J. Appl. Chem. (London)*, **11**, 81 (1961).
6. Swallow, A. J., *Radiation Chemistry of Organic Compounds*, Pergamon Press, New York, 1961.

Résumé

Des adhésifs à couches monomoléculaires orientées formées d'acide stéarique ont été employés pour lier le polyéthylène à l'acier inoxydable. Le temps et la température de liaison, et la vitesse d'écaillage sont les principaux paramètres que l'on peut faire varier pour déterminer leur effet sur la force d'écaillage final. On obtient des forces d'écaillage d'environ 90 livres/pouce de largeur pour des échantillons enduits. Lorsque les échantillons sont préparés proprement, il se produit uniquement rupture par manque de cohésion du polyéthylène. L'irradiation des échantillons liés produit une diminution considérable de la résistance à l'écaillage des échantillons enduits d'une couche monomoléculaire, accompagnée de différences relativement faibles pour les échantillons préparés avec un adhésif à couche monomoléculaire orientée.

Zusammenfassung

Klebstoffe auf Basis orientierter, monomolekularer Stearinsäureschichten wurden zur Verbindung von Polyäthylen mit rostfreiem Stahl verwendet. Zur Bestimmung ihres Einflusses auf die erreichte Abreissfestigkeit wurden mehrere Parameter, darunter Bindungsdauer, Bindungstemperatur und Abreissgeschwindigkeit, variiert. Für monoschichtüberzogene Proben wurden Abreissfestigkeiten von etwa 90 lbs/in. Breite erhalten. Bei geeigneter Herstellung der Proben trat nur Kohäsionsbruch des Polyäthylens auf. Bestrahlung der Verbindungsproben führte zu einer beträchtlichen Herabsetzung der Abreissfestigkeit der monoschichtüberzogenen Proben, wobei verhältnismässig kleine Unterschiede bei den mit Klebstoff auf Basis orientierter monomolekularer Schichten hergestellten Verbindungen auftraten.

Received October 2, 1962