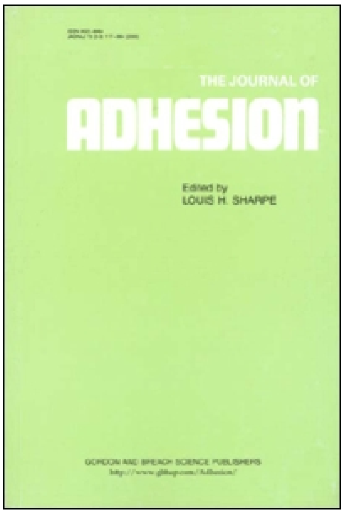

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Surface Treatment of Polypropylene for Adhesive Bonding

by

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ABSTRACT

The CASING (crosslinking by activated species of inert gases) treatment of polypropylene film in both oxygen and nitrous oxide is shown to be an effective surface treatment for conventional adhesive bonding. A crosslinked surface extending to a depth of about 300 Å, apparently independent of exposure time, is produced in both excited oxygen and nitrous oxide.

INTRODUCTION

THE WEAK BOUNDARY layer concept as applied to polymer surfaces has provided direction for the discovery of novel techniques for the adhesive bonding of a wide variety of low surface free energy thermoplastics.[1-3] For example, the critical surface tension of wetting (γ_c) of polyethylene can be made to vary between rather wide limits, while the adhesive joint strength is virtually unaffected,[3,4] provided the weak boundary layer no longer is present. It appears that the critical surface tension of wetting, γ_c, is of relatively minor importance, in the absence of a weak boundary layer, provided the adhesive has formed intimate contact with the polymer substrate prior to solidification. It is important to realize that the adhesive joint strength of a composite structure is largely a function of rheology, design, geometry, etc., while the phenomenon of adhesion is associated with surface chemical (surface tension, melt viscosity, etc.,) principles.[5]

In this paper we shall consider the surface treatment of polypropylene for adhesive bonding. Based on the weak boundary layer concept, we shall explore the various techniques used to prepare the surface of polypropylene prior to joining with conventional adhesives. Since polypropylene is a non-polar polymer, increasing the surface polarity has become the generally

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accepted method for surface treatment prior to adhesive bonding. As pointed out in earlier work, the introduction of polar groups may indeed affect the wetting properties of the polymer, but this may bear no relationship to the adhesive joint strength that is obtained in a composite structure.[6] In general, the effect of a surface treatment on the mechanical properties of the surface region of the polymer have been ignored. While, in general, the wetting characteristics of an oxidized polyolefin surface do improve, there is no assurance that a strong adhesive joint will result when the polymer is joined with conventional adhesives. If the increase in polarity of the surface were the only consideration, then highly polar polymers would indeed be simple to join. This is not the case. Nylon with a rather high critical surface tension of wetting (γ_c = 46 dynes/cm) is difficult to join unless surface treated.[7] Surface treatments which usually are effective for crystallizable polymers, increase the mechanical strength of the surface region by virtue of crosslinking or by a change in the morphological structure of the surface region.[3] The wetting characteristics of the polymer may or may not be altered.[6]

Earlier, the CASING technique was applied successfully to a large variety of thermoplastics which included polyethylene, polytetrafluoroethylene, nylon and poly (vinyl fluoride). Polypropylene was not amenable to the CASING technique when the rare gases were employed. However, Hansen, et al.,[8] did find that exposure of polypropylene to a glow discharge in pure oxygen improved the wetting characteristics as well as the joint strength when the film was bonded with conventional adhesives. Gases are considered to be inert unless there is some excitation process which activates them. Oxygen, in this context, is considered to be inert.

EXPERIMENTAL

The CASING treatment is described elsewhere.[8] The methods used for the formation of adhesive joints and the testing of adhesive joint strengths have been reported in previous publications.[3,10] In brief, the test specimens used in these experiments comprise a composite of aluminum-epoxy adhesive-treated polypropylene film-epoxy adhesive-aluminum, tested by shear in tension.

The polypropylene was a Profax #6512 supplied in 10 mil sheets by Hercules Corp. The polymer sheet was used without any attempt to remove stabilizers or other additives.

RESULTS AND DISCUSSION

Unlike polyethylene, exposure to activated inert gases, (i.e., helium, argon, etc.), is not an effective surface treatment for polypropylene prior to adhesive bonding. When polypropylene is bombarded with helium in the glow discharge, the joint strengths obtained with lap shear specimens are quite low. A possible explanation is that in the presence of the activated rare gases the polypropylene undergoes as much scission as it does crosslinking.[11,12] Both Okada[11] and Lyons and Dole[12] have demonstrated this quite clearly. Therefore, with no change in the crosslink density, the surface region of the polymer has essentially the same mechanical strength before and after treatment in the activated inert gas.

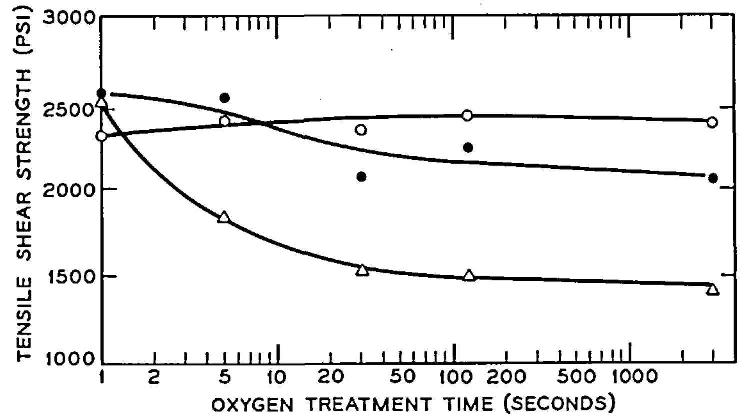

Figure 1. The tensile shear strengths of the composite, aluminum-epoxy adhesive-treated polypropylene film-epoxy adhesive-aluminum. For untreated polypropylene, the joint strengths are about 100 psi.

○ — 60°C cure temperature of the epoxy adhesive. All joints were kept at 60° for a period of 16 hours, then cooled slowly.

● — 82°C cure temperature of the epoxy adhesive. All joints were kept at 82°C for a period of 16 hours, then cooled slowly.

△ — 104°C cure temperature of the epoxy adhesive. All joints were kept at 104°C for a period of 16 hours, then cooled slowly.

Earlier, Hansen, *et al.*,[8] have shown that when polypropylene is exposed to oxygen in the glow discharge a surface region is generated which, when bonded with conventional adhesives, results in strong joints. In Fig. 1 is a plot of the tensile shear strength with polypropylene film treated in an oxygen glow discharge for varying lengths of time. It appears from Fig. 1 that a short exposure of the polypropylene film to the excited oxygen is sufficient to render the polypropylene bondable with conventional epoxy adhesives. In addition to increasing the mechanical strength of the surface layer, the polymer is made more wettable, that is, the contact angle of water is essentially zero when placed on the polypropylene surface. Also evident from Fig. 1 is that the surface region decreases in mechanical strength with excessive oxygen bombardment. Since the joint strengths for the composite aluminum-epoxy adhesive-aluminum are in excess of those reported in Fig. 1, at all temperatures, we feel the variation of joint strength with temperature is related to the polypropylene surface treatment.[10] At higher bonding temperatures, the excessive crosslinking by prolonged exposure to the oxygen glow discharge may have the effect of degrading (mechanically) the surface region of the polypropylene or a possible syneresis of some agent which results in the formation of a weak boundary layer. Considerably more work is needed in this area. This results in a lowering of the joint strength of the final

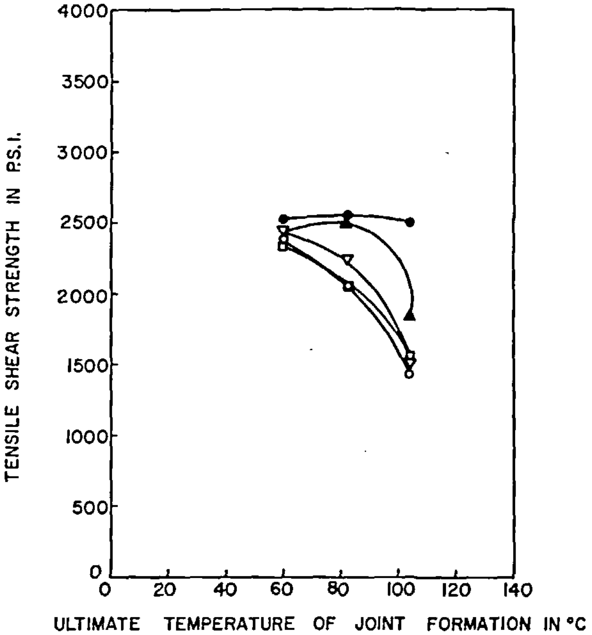

Figure 2. The tensile shear strengths of the composite, aluminum-epoxy adhesive-treated polypropylene epoxy adhesive-aluminum plotted as a function of the ultimate temperature of joint formation. Polypropylene was CASING treated in oxygen for various times at 1 mm pressure and 100 watts.

● — 1 second exposure
▲ — 5 seconds exposure
□ — 30 seconds exposure
▽ — 120 seconds exposure
○ — 3000 seconds exposure

composite. This is observed more easily in Fig. 2 where the joint strength data are plotted as a function of bonding temperature. At low bonding temperatures (60°C), the joint strength is virtually unaffected by an increase in exposure to the glow discharge. However, at higher bonding temperatures there is a marked decrease in the joint strength with increasing bombardment time.

Hansen, *et al.*,[8] found a sizable weight loss due to ablation of the polypropylene when exposed to excited oxygen. A gel fraction examination [6,9] of the polypropylene subsequent to treatment in the glow discharge with oxygen revealed a crosslinked surface layer of about 300 Å. Since there is great difficulty in retrieving this amount of polymer, no attempt was made to analyze the residue. However, attenuated total internal reflection infrared analysis of the treated polymer before extraction revealed a complex spectrum containing a wide variety of oxygenated species. The crosslinked surface layer did not get thicker with longer exposure to the glow discharge, indicating the ablative nature of the excited oxygen. Under the conditions of our experiments, fragmentation of the crosslinked layer and additional crosslinking offset one another.

Although the treatment of polypropylene in excited oxygen in an adequate surface treatment for adhesive bonding, it suffers in that the treatment surface has a mottled appearance. To circumvent this defect, other gaseous environments were investigated. Okada[11] and Lyons and Dole[12] have shown that polypropylene irradiated with Cobalt-60 in the presence of nitrous oxide exhibits a greatly increased crosslink density. Since the CASING technique results in both crosslinking and scission, with scission being favored in polypropylene, it was felt that the CASING treatment in the presence of N_2O would promote crosslinking and minimize scission. Similar behavior is expected in both treatments, however, the CASING treatment is confined to the surface layer with no appreciable degradation of mechanical properties as takes place in the Cobalt-60 treatment. In view of these results, polypropylene film was exposed to a glow discharge in the presence of nitrous oxide.

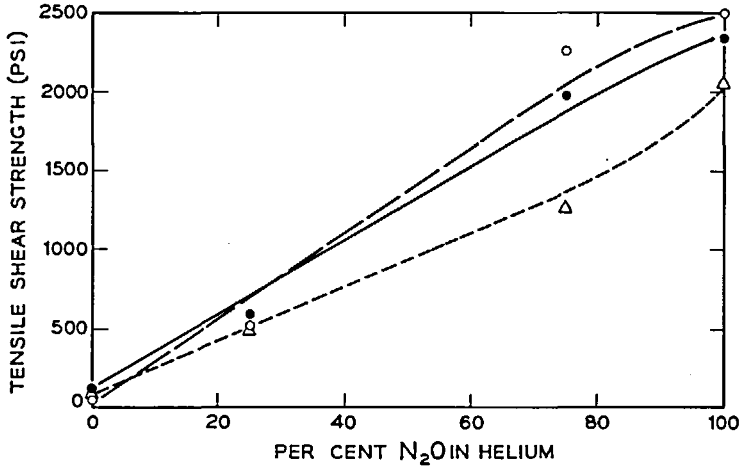

Figure 3. The tensile shear strengths of the composite, aluminum-epoxy adhesive treated polypropylene-epoxy adhesive-aluminum, as a function of the percent nitrous oxide (N_2O) in helium. Exposure was for 10 min. at 1 mm pressure and 100 watts. The joints are for three different cure temperatures of the epoxy.
○ — 60°C cure temperature
● — 82°C cure temperature
△ — 104°C cure temperature

Figure 3 shows the improvement in the joint strength as a function of the percent nitrous oxide in helium. In pure nitrous oxide, tensile shear strengths of about 2500 psi are obtained for a relatively short exposure. Unlike the frosted surface obtained in excited oxygen, no visible changes were observed on the surface of polypropylene treated in excited nitrous oxide. CASING treatment of the polypropylene in nitrous oxide increased the wettability of the surface. Since the exact nature of the surface layer is unknown, no attempt was made to further investigate the wettability effects. Short exposure of the polypropylene to the activated nitrous oxide results in a surface region of high mechanical strength. In Fig. 4 the tensile shear strength is plotted as a function of the nitrous oxide treatment time. As noted

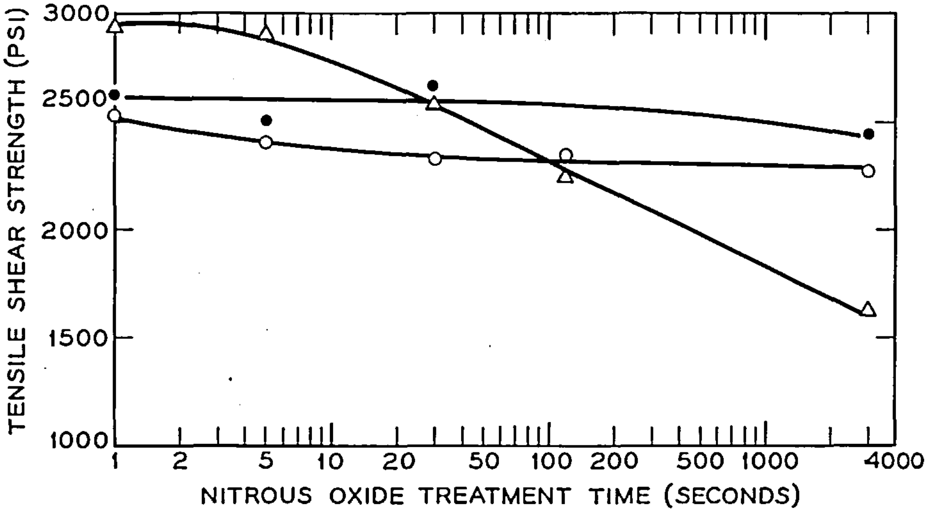

Figure 4. The tensile shear strengths of the composite, aluminum-epoxy adhesive-treated polypropylene-epoxy adhesive-aluminum, plotted as a function of the nitrous oxide treatment time.
○ — 60°C cure temperature
● — 82°C cure temperature
△ — 104°C cure temperature.

earlier with excited oxygen, one second is sufficient to convert the normally weak surface region of polypropylene to one of much higher mechanical strength. When polypropylene is exposed for a longer interval in the presence of activated nitrous oxide then joined at a temperature in excess of 100°C the resultant joint strengths are much lower than those joined at slightly lower temperatures. A similar effect was noted with excited oxygen, but initiating at a lower temperature. In earlier work with polyethylene treated in the glow discharge with rare gases, a thickening of the surface region with increasing exposure time was noted. This effect was not observed when polypropylene was bombarded with pure nitrous oxide for various lengths of time. The effective thickness of the crosslinked surface layer was essentially constant at about 300 A.

In Fig. 5 a comparison is made of the joint strengths for composites with polypropylene treated in excited nitrous oxide and in conventional glass cleaning solution, and using the more recent approach of Schonhorn and Ryan which involves the nucleation and crystallization of the polymer in contact with a high energy surface.[3] From Fig. 5 it is apparent that the joint strengths for the CASING treated polypropylene are comparable to those obtained for conventional glass cleaning solution. Other excited gases which were tried unsuccessfully to treat the surface of polypropylene were carbon dioxide, hydrogen sulfide and ammonia gas (NH_3). The joint strengths obtained with these gaseous species were similar to the untreated material. Apparently both excited nitrous oxide and oxygen are unique in the treatment of polypropylene films.

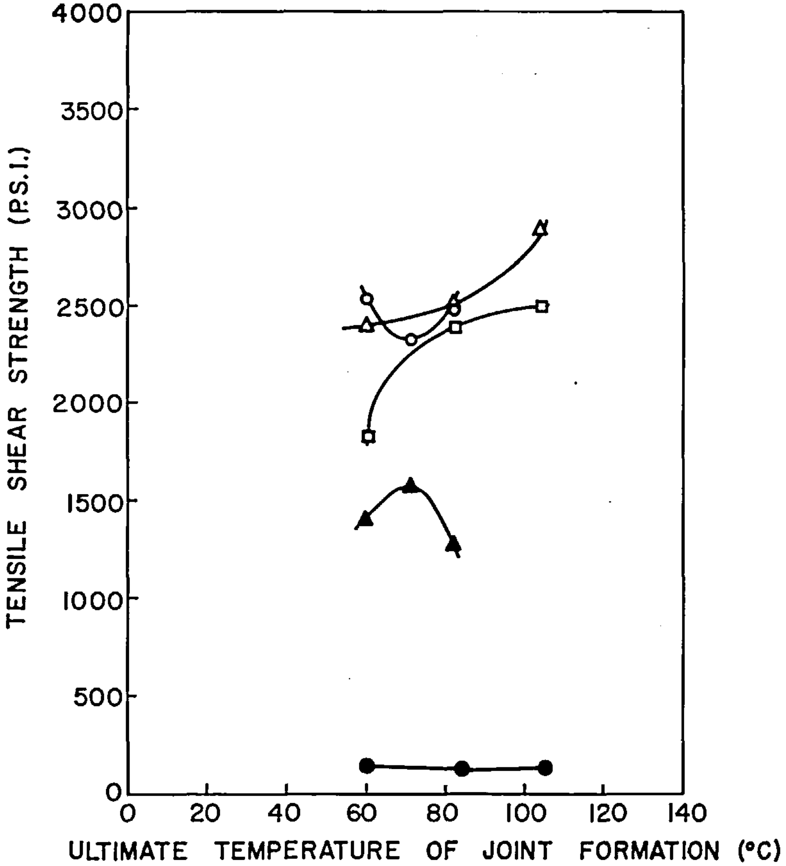

Figure 5. The tensile shear strengths of the composite, aluminum-epoxy adhesive-treated polypropylene-epoxy adhesive-aluminum, plotted as a function of the ultimate temperature of joint formation.

● — untreated
▲ — gold-nucleated polypropylene
□ — CASING treated in oxygen for 5 sec. at 1 mm pressure and 100 watts.
○ — glass cleaning solution treated 4 min. at 80°C.
△ — CASING treated in nitrous oxide for 5 sec. at 1 mm pressure and 100 watts.

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