

Surface Treatment of Polymers for Adhesive Bonding

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Synopsis

Further studies of a new and highly effective method for the surface treatment of low surface energy polymers for adhesive bonding are reported. Mechanisms are suggested for the increase in the cohesive strength in the surface region of polyethylene when it is exposed to activated species of inert gases. The technique is unique because, in contrast with results obtained with other methods, bulk properties of the polymer such as color or tensile strength and elongation are unaffected and surface properties such as wettability and dielectric properties such as surface conductivity are essentially unchanged.

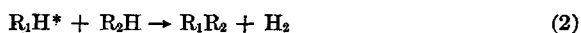
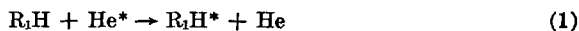
Introduction

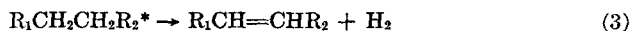
We recently reported a new and highly effective method for the surface treatment of low surface energy polymers for printing and for adhesive bonding.¹ The bonding characteristics produced by this new technique are unsurpassed by those obtained by methods which often result in extensive degradation of the desirable physical and dielectric properties of the polymer.

The new technique is a simple one. The polymer is merely exposed to activated inert gases for a short interval. We have used a low power radio frequency coil^{2,3} to generate the excited species, but any of a number of other methods such as microwave excitation or corona discharge could have been used. The short exposure of polymer to ionic and metastable species of inert gases results in the loss of hydrogen atoms from polyethylene and fluorine atoms from polytetrafluoroethylene. Subsequent reactions lead to the formation of a crosslinked surface layer which has high cohesive strength and is ideal for the production of strong adhesive joints.

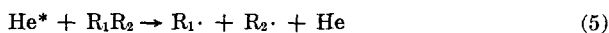
Possible Mechanisms

A variety of approaches could be used to account for what happens to polymer surfaces when they are bombarded with ionic and metastable species of rare gases. For example, the reactions of excited molecules, shown in eqs. (1)-(3), properly account for the increased molecular weight and the vinylene unsaturation observed during bombardment:

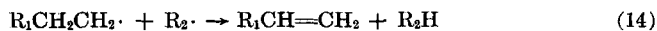




Ion-molecule reactions have been used to explain molecular weight increases which occur in gases in the mass spectrometer and could be invoked to interpret the changes which occur in a polymer when it is exposed to activated inert gases. However, since we have detected the presence of radicals in both polytetrafluoroethylene and polyethylene by spin resonance techniques after the polymers were bombarded with activated helium, we believe that a radical mechanism is most probable. Either of the triplet states, as well as the ionic form of helium, has more than enough energy to rupture a C—H or a C—F bond. The reaction between polyethylene and activated helium and the ensuing reactions are given in eqs. (4)–(9):

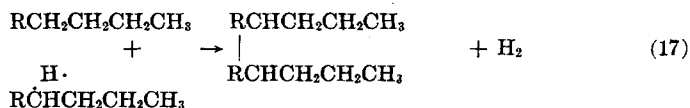


The last three equations show how molecular weight of the polymer might be expected to increase. Since we observed no evidence of production of lower molecular species or carbonaceous products during treatment of polyethylene with activated helium,¹ either carbon-carbon bonds are not ruptured or the radicals formed by scission recombine or react with other radicals to give higher molecular weight species [eqs. (7), (8), and (9)]. This may occur in preference to abstracting hydrogen atoms from adjacent polymer molecules or reacting with available hydrogen atoms [eqs. (10)–(13)] or interacting with other radicals by disproportionation [eq. (14)], for each of these reactions would lead to the production of lower molecular weight species:



Instead, we believe that reactions such as those shown in eqs. (15)–(17) are most probable, for they account for production of transethylenic unsaturation, increased molecular weight, eventual crosslinking, and production of hydrogen as the only gaseous product—all in good agreement with observed results.





Radical formation is shown occurring on the third carbon atom from the methyl group simply because this has been found to be a most reactive site during radiation of low molecular weight hydrocarbons.⁴ In a high polymer, of course, the radical might be produced anywhere along the chain because the energy of the active species is sufficient so that indiscriminate reactions may occur.

Results

The appearance of polyethylene, like its wettability, is unaffected by exposure to activated helium for far longer intervals than are required to produce greatly increased cohesive strength in the surface region which permits the formation of strong adhesive joints. However, after long exposure (16 hr.) to activated helium, the surface region of polyethylene becomes yellow to amber in color, indicating the development of conjugated unsaturation. This suggests that many unsaturated groups are introduced into each polymer molecule. Since a uniform insoluble gel is produced after very short exposure (one second) to activated species of helium generated at about 100 w. of rf power without an observable color change, we believe that many crosslinks are formed between adjacent molecules. The crosslink density is probably considerably greater than that normally observed during chemical crosslinking or during high energy irradiation, but it is limited to polymer molecules in the surface region.

When simple hydrocarbons such as *n*-octadecane are bombarded by ionic and metastable species of helium or other inert gases, similar results are obtained. Some of the sample is unaffected (presumably that beneath the surface, for the exposed material acquires a skin resembling that observed on paint during drying). However, some is converted to slightly higher molecular weight hydrocarbons, and some is polymerized. The data in Figure 1 illustrate the formation of higher molecular weight products from *n*-octadecane. Treated and untreated specimens are compared by thermogravimetric analysis using a shallow pan in air at a rise in temperature of 2°C./min. Transethylenic unsaturation was observed by infrared analysis of the skin but was not detected in the bulk of the material beneath the surface skin.

We also believe that bombardment with activated species of inert gases results in crosslinking of the surface of polytetrafluoroethylene, although this is difficult to demonstrate because of the insolubility and general intractability of the untreated polymer. However, since perfluorokerosene can be converted from a volatile liquid to a hard polymeric solid of much higher molecular weight, as shown by the thermogravimetric analysis data

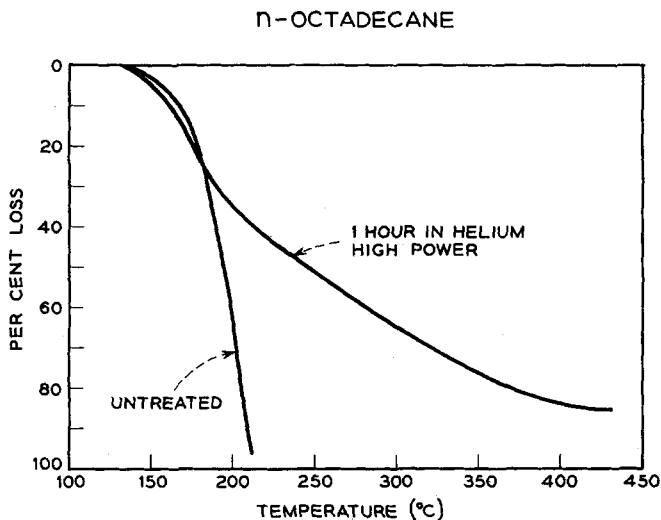


Fig. 1. Thermograms of *n*-octadecane before and after exposure to activated helium. Samples were heated from room temperature on a shallow pan in air at a rise in temperature of 2°C./min. The treated sample was a sticky semisolid. High power is about 100 w.

in Figure 2, we infer that the surface region of polytetrafluoroethylene, like that of polyethylene, is crosslinked by exposure to activated inert gases. Transethylenic unsaturation is also observed by infrared techniques, as

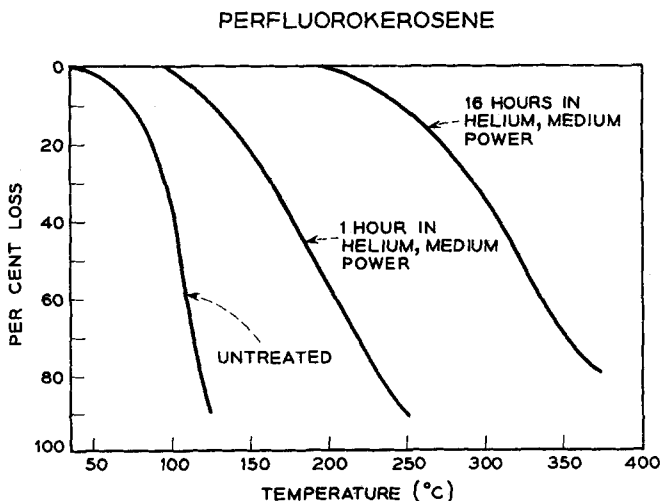


Fig. 2. Thermograms of a perfluorinated hydrocarbon before and after exposure to activated helium. Samples were heated from room temperature on a shallow pan in air at a rise in temperature of 2°C./min. The sample of perfluorokerosene treated with helium for 16 hrs. was a hard, brittle solid, while the sample treated for 1 hr. was a sticky liquid. Medium power is less than 50 w.

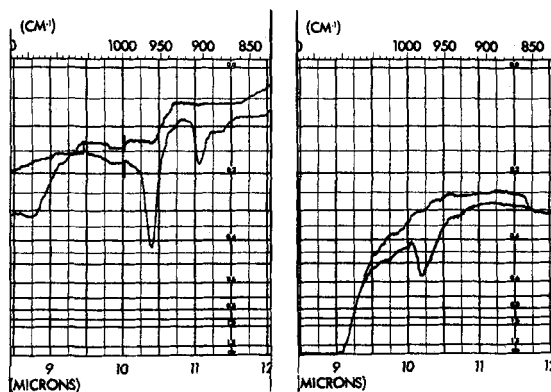


Fig. 3. ATR infrared spectra of Marlex 5003 polyethylene are shown on the left, G-80 polytetrafluoroethylene on the right (KRS-5 50/20/2 mm.). The lower curve in each case is that obtained after 10 min. exposure to activated helium at high power. The upper curves were obtained on the same samples after they were immersed in a solution of bromine in CCl_4 in the dark at room temperature and then dried in a vacuum oven at 40°C . overnight. The peaks at 964 cm^{-1} for polyethylene and at about 982 cm^{-1} for polytetrafluoroethylene indicate the formation of transunsaturation during CASING.

shown in Figure 3. The unsaturation in the surface region of both polyethylene and polytetrafluoroethylene can be eliminated by addition of bromine, as shown in Figure 3. No significant difference between the strength of adhesive joints prepared from samples of polymer exposed to activated helium or exposed to activated helium followed by addition of bromine was observed, indicating that the transethylenic unsaturation produced by exposure to activated inert gases has an insignificant role in the formation of strong adhesive joints between treated polymer and conventional adhesives. We conclude that the great improvement in adhesive joint strength which is observed is due to the formation of a cross-linked surface layer which has high cohesive strength. We call this new surface treatment technique CASING (Crosslinking by Activated Species of Inert Gases).

The effects of bombardment with activated inert gases—and all inert gases produce essentially the same effects—are restricted to the surface regions of the polymer. Interestingly, the reactions which occur take place very much more rapidly (if not exclusively) in amorphous materials than in crystalline materials. For example, *n*-hexatricontane, $\text{C}_{36}\text{H}_{74}$, which melts at about 70°C ., is essentially unchanged after exposure to activated helium at 30°C . because it is highly crystalline at this temperature. However, when it is melted and exposed to activated helium while molten, its molecular weight, as determined by gel permeation chromatography, increases in about the same manner as does that of *n*-octadecane, which melts when exposed to activated helium. In both cases where the hydrocarbon was molten, insoluble gel (crosslinked polymer) was also produced. We believe, therefore, that when semicrystalline polymers such as polyethylene

and polytetrafluoroethylene are treated with activated species of inert gases, reactions which occur are mainly confined to noncrystalline regions of the polymer.

We have used a simple technique to estimate the thickness of the cross-linked layer produced by CASING. Polyethylene specimens in film form were exposed to activated inert gases for varying lengths of time and then placed in refluxing xylene in a Soxhlet extractor for 16 hr. Gel fractions were obtained after drying the residue in a vacuum oven at 70°C. for 24 hr. The residues were not visible after short exposure to activated helium but after longer treatment the residues were in the form of uniform films whose geometry was remarkably similar to the original specimen. On the basis of a projected density of 1.0 g./cm.³ for the crosslinked film, calculated film thicknesses are readily obtained from the weight of the film. Figure 4 shows a plot of the film thickness as a function of bombardment time. A remarkable effect is observed. All of the excited gases appear to yield similar gel fractions even though their ionization potentials and diffusion coefficients in polyethylene are considerably different.⁵ This implies that the same mechanism—possibly the diffusion of hydrogen atoms—is responsible for the uniform increase in thickness of the crosslinked skin which is observed when polyethylene is exposed to a variety of activated inert gases.

Figure 5 shows joint strength data for the bombardment of polyethylene with activated helium as a function of time. The low values at 60°C. reflect the cohesive strength of the epoxy adhesive when cured at this temperature. Failure in this instance occurs in the adhesive phase. At higher cure temperatures, polyethylene is the weaker material and failure

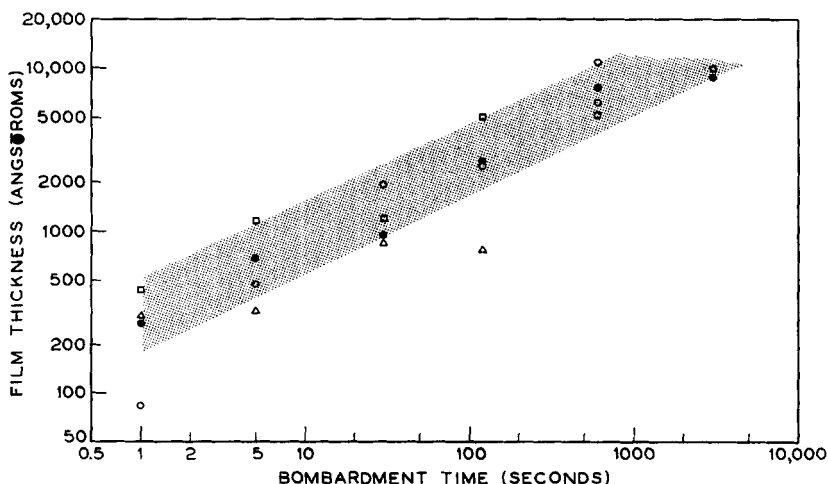


Fig. 4. The estimated film thickness as determined from the gel fraction after Soxhlet extraction is plotted as a function of bombardment time for a variety of activated gases: (□) hydrogen (1 mm. pressure); (●) helium (1 mm. pressure); (Δ) helium (0.4 mm. pressure); (○) neon (1 mm. pressure).

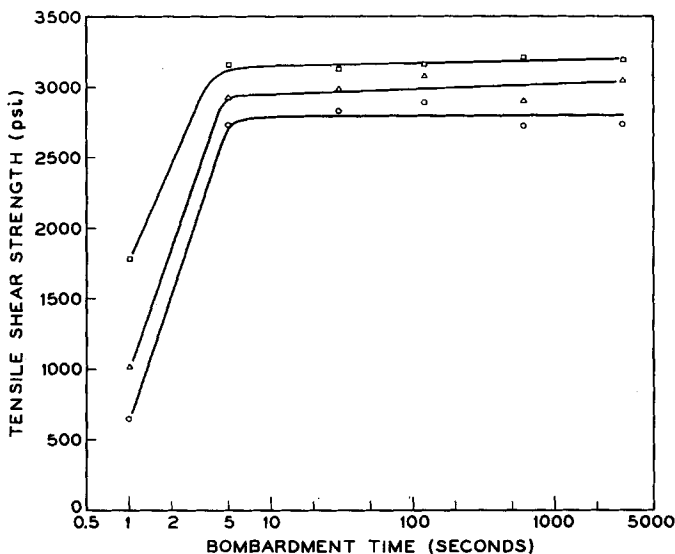


Fig. 5. The tensile shear strength of the composite aluminum-epoxy adhesive-helium CASED polyethylene-epoxy adhesive-aluminum is plotted as a function of the bombardment time with activated helium at 1 mm. pressure. (O) 60°C.; (Δ) 82°C.; (\square) 104°C.

occurs in the polyethylene phase. In all cases we did not observe failure between the epoxy adhesive and the aluminum substrate. It is seen that exposure to excited helium for as little as one second at high power (about 100 w.) is sufficient to result in improved tensile shear strength, for the strength of joints prepared from untreated polyethylene film is less than 500 psi. From Figure 4 we see that the thickness of the crosslinked skin developed after exposure to excited helium for one second is about 200-500 Å. Apparently, this is the upper limit of the thickness of the weak boundary layer normally present on the surface of untreated polyethylene. The data in Figure 5 show that a dramatic increase in joint strength occurs between one second and five seconds of exposure to activated helium at about 100 w. Presumably this increase could be obtained by shorter exposure at higher power, if desired, for all that is required for the formation of strong joints with an adhesive having the proper contact with the polymer is a strong crosslinked surface region about 500-1000 Å. thick.

Discussion

Repeated failure to prepare strong adhesive joints for the epoxy adhesive-polyethylene system, even though the wettability requirements were satisfied ($\theta \approx 0$), led to the conclusion that in melt-crystallized films of polyethylene, a weak boundary layer was generated at the liquid-air interface.⁶ Further evidence which strengthened this conclusion was the ability to form strong adhesive joints in the polychlorotrifluoroethylene-epoxy adhesive system using a conventional epoxy adhesive ($\gamma_{LV} \approx 33$ dyne/cm.).⁷ This

indicates that the polychlorotrifluoroethylene does not have an inherent weak boundary layer while polyethylene, with essentially the same critical surface tension of wetting,⁸ does have an inherent weak boundary layer.

Strong joints can be made to polyethylene surfaces which have been oxidized by a variety of techniques.⁹⁻¹¹ The general belief has been that the presence of polar groups on the polymer creates an affinity for the polar epoxy adhesive which improves wettability and results in a strong adhesive joint. CASING results in strong adhesive joints without changing wettability of the polymer. We believe that other surface treatments (oxidation) are effective because they, like CASING, remove the weak boundary layer normally present on the surface of polyethylene. During CASING, the polymer molecules at and near the surface are knitted together to form a crosslinked matrix having high cohesive strength. We and others¹² have observed a crosslinked skin on polyethylene after surface treatment by corona discharge and chemical etching. This probably accounts for the strong joints formed by the use of these techniques. The mere presence of polar groups would not be sufficient if they were organized in a layer having low mechanical strength. The notion of polarity is associated with the compatibility rule of deBruyne¹³ which has been shown to be wrong in part.¹⁴

To demonstrate the presence of the weak boundary layer in polyethylene, we attempted to eliminate it by several techniques and observe the resultant joint strengths obtained with a conventional epoxy adhesive in the composite: aluminum-epoxy adhesive-polyethylene-epoxy adhesive-aluminum. The bottom curve in Figure 6 is based on joint strength data obtained from untreated polyethylene film. All experiments were performed below the melting point of polyethylene since above the melting point it will spread on the cured epoxy adhesive surface and in this process will preclude the weak boundary layer and result in strong joints.¹⁴ The weak boundary layer in polyethylene is also precluded when it is melted on other high energy surfaces that do not have weak boundary layers.¹⁵ In this process, a transcrystalline layer is formed at the solid-liquid interface on cooling. Apparently, this results in generation of a surface at the interface whose characteristic strength is similar to if not greater than that of the bulk polymer.¹⁶

During ordinary processing of polyethylene, cooling of the melt takes place against a low energy surface. Transcrystalline growth probably does not occur to any great extent and weak boundary layers are formed at the surface.

It was felt that the weak boundary layer was comprised of low molecular weight polymer molecules which were forced to the surface during recrystallization of the melt,¹⁷ so we hoped to minimize their presence by reforming single crystals of well-characterized fractionated high molecular weight polyethylene. However, on remolding, relatively weak boundary layers were generated and only slight increases in joint strength were observed (Fig. 6). Wettability of the molded fractionated single crystal mat was essentially the same as the untreated film.

To avoid recrystallization from the melt, which apparently creates a weak boundary layer in polyethylene, we resorted to other techniques such as solvent extraction.¹⁸ Specimens suitable for joint strength measurement were prepared and extracted in a boiling 1:1 hexane-heptane solution for several minutes. The specimens were not swelled appreciably, and resultant joint strengths were considerably greater than those obtained with untreated film. Again γ_c was about 35 dyne/cm. When boiling octane was used to extract the low molecular weight polymer from polyethylene film, considerable swelling occurred. Upon removal of the solvent, additional lower molecular weight material was transported to the solid-air interface and only weak joints could be obtained.

The weak boundary layer was partially eliminated by bombardment of the polymer with high energy electrons. The results in Figure 6 show that stronger joints were obtained—but not shown is the fact that bulk properties of the polymer were seriously affected. Although the γ_c was raised since irradiation was done in air, joint strengths were about the same as those obtained by the solvent extraction technique.

The uppermost curves in Figure 6 are results obtained with surface treatment techniques which both result in crosslinking and strengthening of the weak boundary layer without affecting bulk properties of the polymer. High joint strengths were obtained after both CASING (5 sec. in excited helium) and after etching with glass cleaning solution (4 min. at 80°C.), which, like all oxidative surface treatments also causes ablation of some of the polymer at the surface and changes wettability of the polymer. For untreated polyethylene and for polyethylene after CASING, $\theta_{H_2O} > 90^\circ$; after etching with glass cleaning solution (sodium dichromate-sulfuric acid), $\theta_{H_2O} \div 30^\circ$.

Other Polymers

Although maximum adhesive joint strength is achieved after 5 sec. of exposure to activated helium with polyethylene (Fig. 5), a longer CASING time is required to eliminate the weak boundary layer in polytetrafluoroethylene and attain high adhesive joint strength, as shown in Figure 7. This is probably partially a result of the slightly greater difficulty in rupturing carbon-fluorine bonds than carbon-hydrogen bonds, but mainly due to the relatively unreactive nature of radicals in polytetrafluoroethylene as compared with those in polyethylene. It is anticipated that the use of higher power would decrease the exposure time required to attain maximum joint strength with polytetrafluoroethylene. It should be noted that since the wettability of the polymer is unchanged and the surface tension of the adhesive is quite high with respect to achieving a reasonable degree of wetting, that the results shown in Figure 7 are remarkable. Joint strengths comparable to those resulting after chemical etching of polytetrafluoroethylene^{19,20} can be obtained by CASING without discoloration of the polymer. We also believe that if an adhesive having the proper γ_{LV} and cohesive strength were used, joint strength probably would be further increased.

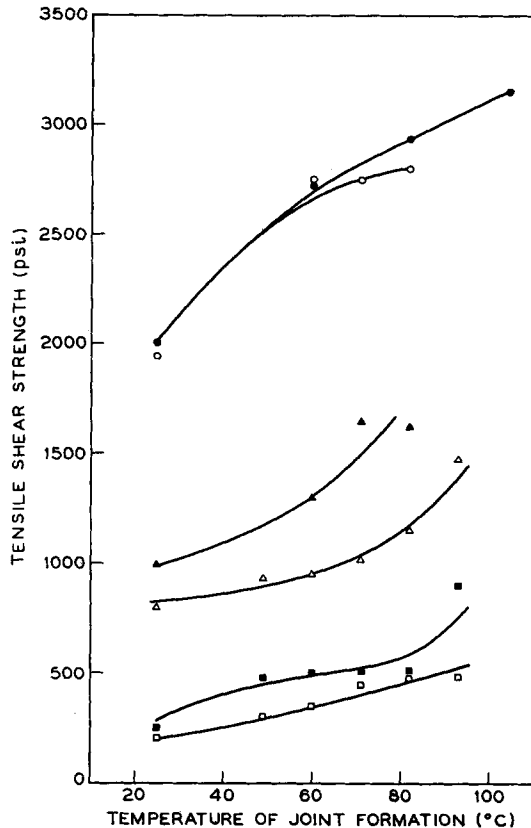


Fig. 6. The tensile shear strength of the composite aluminum-epoxy adhesive-polyethylene-epoxy adhesive-aluminum plotted as a function of the temperature of the joint formation for a variety of surface treatments on the polyethylene: (□) untreated polyethylene (no surface treatment); (■) Marlex 5003 polyethylene crystallized from 0.04% solution in xylene at 85°C. then molded into 10-mil sheets at 160°C. No surface treatment; (Δ) polyethylene film exposed to vapors of a boiling 1:1 hexane-heptane mixture for 5 min.; (▲) polyethylene film irradiated with a Van der Graaff generator to a dose of 10 Mrad.; (○) polyethylene film exposed to glass cleaning solution at 80°C. for 4 min.; (●) CASSED polyethylene, exposed to activated helium at 1 mm. pressure and high power for 5 sec.

The results of CASING on poly(vinyl fluoride) films are shown in Figure 8. Since joints prepared from treated poly(vinyl fluoride) (Tedlar) are considerably stronger, we conjecture that Tedlar, as normally prepared, has a weak boundary layer which is strengthened by CASING. On the other hand, exposure of poly(vinylidene fluoride) film (Kynar) to activated helium does not result in improved adhesive joint strength (Fig. 9). This indicates that Kynar, as normally prepared, does not have associated with it a weak boundary layer.

The usefulness of the CASING technique with a variety of thermoplastic and thermosetting polymers is being studied and will soon be reported.

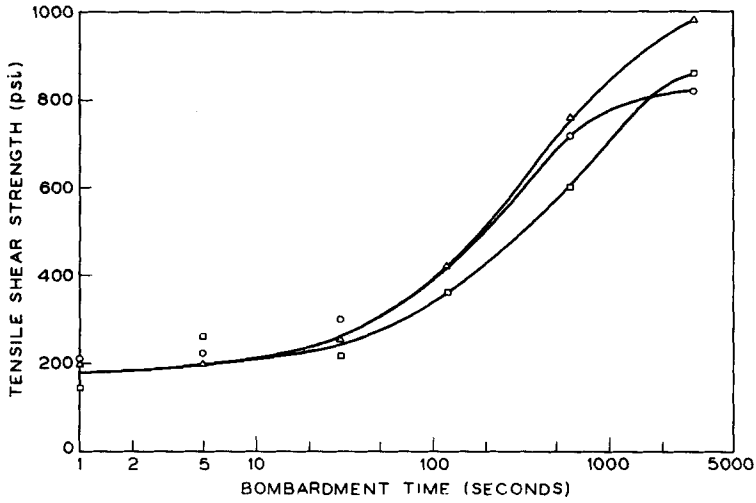


Fig. 7. Tensile shear strength of composite, aluminum-epoxy adhesive-polytetrafluoroethylene-epoxy adhesive-aluminum plotted as a function of bombardment time in activated neon at 1 mm. pressure and high power: (O) 60°C.; (Δ) 82°C.; (\square) 104°C.

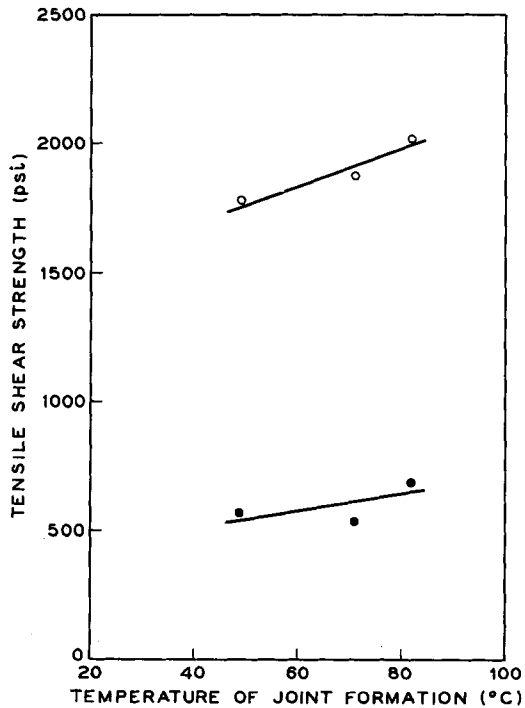


Fig. 8. Tensile shear strength of composite aluminum-epoxy adhesive-poly(vinyl fluoride)-epoxy adhesive-aluminum plotted as a function of the temperature of the joint formation: (\bullet) untreated poly(vinyl fluoride); (O) poly(vinyl fluoride) treated in an activated 1:1 mixture of H_2 :He for 1 hr. at medium power and 1 mm. pressure.

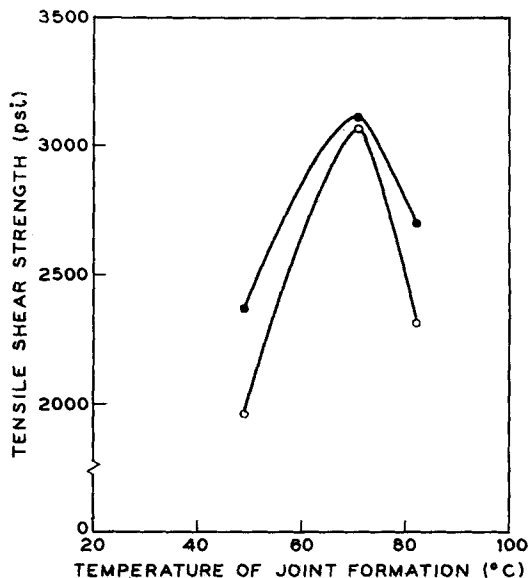


Fig. 9. Tensile shear strength of composite aluminum-epoxy adhesive-poly(vinylidene fluoride)-epoxy adhesive-aluminum plotted as a function of the temperature of joint formation: (●) untreated poly(vinylidene fluoride); (○) poly(vinylidene fluoride) treated in activated helium for 1 hr. at medium power and 1 mm. pressure.

Summary

Adhesive joint strengths and printability resulting from CASING of polymers such as polyethylene and polytetrafluoroethylene are comparable to those resulting from the use of other surface treatment techniques. Further, these high joint strengths are obtained without deterioration of desirable properties of the polymer and without ablation of the polymer. CASING results in the formation of a crosslinked surface layer which has high cohesive strength and is ideal for printing and for the production of strong adhesive joints. Since a crosslinked surface also is produced during oxidative surface treatment of polymers and since lowering the surface tension of an adhesive to satisfy the condition $\gamma_{LV} < \gamma_c$ does not result in strong adhesive joints if a weak boundary layer exists on the surface of the polymer, we feel that it is the elimination of the weak boundary layer that is mainly responsible for the improved results observed after oxidative surface treatments.

The crosslinked layer produced during oxidative surface treatment of polymers such as polyethylene is limited in thickness because of oxidative ablation. The crosslinked layer produced during CASING continues to increase in thickness as exposure to the activated inert gas is continued. For this reason, and because of the nature of the tough skin produced, CASING may also be useful as a method for modifying poly-

mers—as for example by altering abrasion resistance, changing coefficients of friction, and varying diffusion and permeability characteristics.

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Résumé

Des études ultérieures d'une méthode nouvelle et hautement effective pour le traitement de surface de polymères de basse énergie superficielle en vue de problèmes d'adhésion sont rapportées. Des mécanismes sont suggérés pour augmenter la force de cohésion à la surface du polyéthylène lorsqu'il est exposé à des espèces activées de gaz inerte. La technique est unique parce que contrairement aux résultats obtenus par d'autres méthodes, les propriétés en bloc du polymère tel que la couleur et la force à la tension et l'élongation ne sont pas affectées et les propriétés de surface telles que la mouillabilité, et les propriétés électriques, telle que la conductivité superficielle, sont essentiellement inchangées.

Zusammenfassung

Über weitere Untersuchungen einer neuen und sehr wirksamen Methode zur Oberflächenbehandlung von Polymeren mit niedriger Oberflächenenergie zur Herstellung von Klebeverbindungen wird berichtet. Mechanismen für die Zunahme der Kohäsionsfestigkeit im Oberflächenbereich von Polyäthylen bei Einwirkung der aktivierten Spezies eines inerten Gases werden vorgeschlagen. Die Besonderheit des Verfahrens liegt darin,

dass, im Gegensatz zu den mit anderen Methoden erhaltenen Ergebnissen, Polymereigenschaften wie Farbe oder Zugfestigkeit und Dehnung nicht beeinflusst werden und Oberflächeneigenschaften wie Benetzbarkeit sowie dielektrische Eigenschaften, wie Oberflächenleitfähigkeit im wesentlichen ungeändert bleiben.

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