

## Surface Crosslinking of Polyethylene and Adhesive Joint Strength

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### Synopsis

Exposure of polyethylene film to UV radiation at wavelengths of  $\leq 2537 \text{ \AA}$  is sufficient to induce surface crosslinking and to facilitate the formation of strong adhesive joints to these surfaces with conventional adhesives. Reduction of the vapor pressure in the reaction vessel to about 1 torr apparently maximizes the efficiency of the crosslinking process. Examination of the treated films which have been exposed for times necessary to form strong adhesive joints has revealed an absence of surface oxidation. It appears that crosslinking to improve the mechanical strength of the surface region of the polyethylene is sufficient to allow the formation of strong adhesive joints.

### INTRODUCTION

Recently, in a critical examination of the effect of a hydrogen glow discharge on the surface properties of polyethylene, Hudis and Prescott<sup>1</sup> and Hudis<sup>2</sup> have corroborated the earlier findings of Schonhorn and Hansen<sup>3</sup> that extensive crosslinking occurs in the surface region of the polyethylene. Hudis,<sup>2</sup> in his investigation of the coupling mechanism which exists between the plasma and the polymer, has demonstrated that the ultraviolet radiation produced by the glow discharge is partially responsible for the surface crosslinking of polyethylene.

Hudis<sup>2</sup> distinguishes between two possible theories to account for the phenomenon of surface crosslinking. The gel formation as a function of exposure time to the radiation is compared to a diffusion theory<sup>3,4</sup> and an exponentially attenuated light theory.<sup>5</sup> Hudis<sup>2</sup> finds excellent agreement between the measured gel-versus-dose curve and the theoretical curve based on a light theory for a monochromatic light beam at  $1849 \text{ \AA}$ . The gelation curve for the glow discharge case can be explained by using the identical theory but applied to a spectrum of light covering the range from  $1200 \text{ \AA}$  to  $1900 \text{ \AA}$ .

Crosslinking of polymers or monomers by UV irradiation has been well documented in the literature.<sup>6</sup> Recently, Kujirai et al.<sup>7</sup> have examined the crosslinking of polypropylene by ultraviolet irradiation in vacuo. Under these conditions, they report that polypropylene can be crosslinked directly by ultraviolet irradiation. Infrared examination of the polypropylene before and after exposure to the UV in vacuo revealed no absorptions that suggest oxidation.<sup>7</sup>

## EXPERIMENTAL

We have subjected polyethylene to UV irradiation in both helium and air at a variety of pressures, exposure times, and wavelengths. We have varied the light source (a variety of lamps having wavelengths of 1849 Å, 2537 Å, 3000 Å, and 3500 Å) as well as the envelope (Supersil quartz, quartz, and Pyrex) used to contain the samples.

Approximately 9 g polyethylene (Marlex 5003) powder was molded at 150°C for 2 min between two 20 cm × 20 cm × 0.025 cm FEP Teflon films separated by a 0.025 cm FEP shim around the edges. The pressure was slowly increased to 20 kg/cm<sup>2</sup> and maintained at this level during the molding operation. The temperature was lowered to 80°C while maintaining the 20 kg/cm<sup>2</sup> pressure. The pressed sheet had a final thickness of 0.03 cm.

The polymer sheet was cut into six 2.5 cm × 15 cm strips. A strip was placed into either a quartz, Pyrex, or Supersil tube and was located in the center of a Rayonet photochemical reactor RPR208 (Southern New England Ultraviolet Co., Middletown, Conn.). The tube was then flushed with gas several times before adjusting to a definite pressure. The sample was exposed to the desired UV radiation for a specified interval of time. Pressure was recorded with an absolute pressure gauge (Wallace and Tiernan, Belleville, N.J., Model FAR 160, range 0–800 torr and Serial No. FA160, range 0–100 torr).

Following the UV exposure, the strips were cut into four 3.75 cm × 2.0 cm pieces to be used in the preparation of adhesive joints.

The epoxy resin DER332LC (Dow Chemical Co., Midland, Mich.) was a diglycidyl ether of bisphenol A, having an epoxy equivalent weight of 179 maximum (the pure material would have an epoxy equivalent weight of 170), a total chloride content less than 0.1% by weight, and a viscosity of 6400 cP maximum at 25°C.

Diethylaminopropylamine (Miller-Stephenson Chemical Co., Inc., Philadelphia), the curing agent, was distilled under nitrogen through a 6-in. Vigreux column, and the first fraction was discarded. The product distilling at 68°C/26 mm pressure was stored in the dark in tightly stoppered glass containers prior to use.

The epoxy adhesive consisted of 100 parts by weight of the above resin and 7 parts by weight of the diethylaminopropylamine, thoroughly mixed and used immediately. The lap shear adhesive joints were cured in a 70°C forced-air oven for 16 hr under a 5-kg load.

## RESULTS AND DISCUSSION

Although a large number of excited species are present in a glow discharge, crosslinking by the CASING technique<sup>9</sup> may have been accomplished, in part, by the UV radiation which is also an integral component of the glow discharge. Hudis<sup>2</sup> has shown that the short wavelengths (<1800 Å) which are absorbed by polyethylene are particularly effective for inducing crosslinking. If the surface crosslinking that is generated by UV

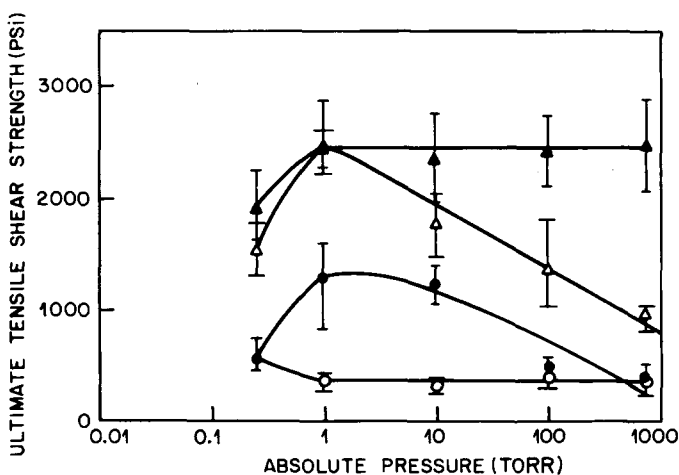


Fig. 1. Strengths of lap shear composites containing polyethylene films which had been exposed for varying lengths of time, in a quartz tube, to UV radiation at 2536 Å. Helium pressure in the tube had been varied from 0.25 torr to 760 torr: (○) 1-min exposure; (●) 10-min exposure; (△) 30-min exposure; (▲) 60-min exposure.

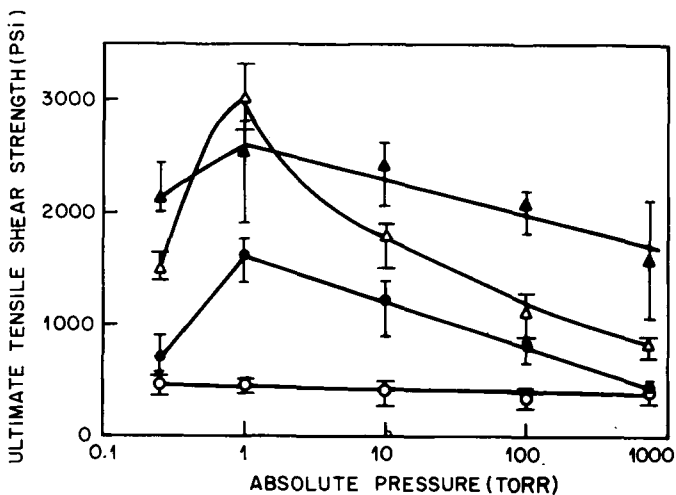


Fig. 2. Strengths of lap shear composites containing polyethylene films which had been exposed for varying lengths of time, in a quartz tube, to UV radiation at 2537 Å. Air pressure in the tube had been varied from 0.25 torr to 760 torr: (○) 1-min exposure; (●) 10-min exposure; (△) 30-min exposure; (▲) 60-min exposure.

irradiation strengthens the mechanically weak surface layer that is suspected to be present on polyethylene film,<sup>10</sup> then the UV treatment should constitute a surface treatment suitable for the formation of strong adhesive joints.

Polyethylene specimens which were UV irradiated at 2537 Å in reduced pressures of helium and air in a quartz container and were then incorporated in lap shear joints produced the results illustrated in Figures 1 and 2. It

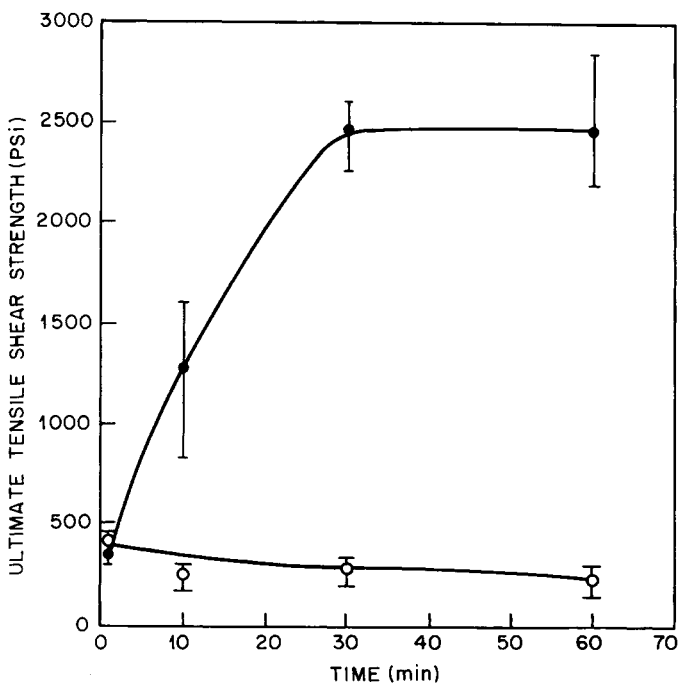


Fig. 3. Strengths of lap shear composites containing polyethylene films which had been exposed for varying lengths of time in either quartz (●) or Pyrex (○) tubes to UV radiation at 2537 Å. Helium pressure in the tubes was kept constant at 1 torr.

is quite apparent that a reasonably short exposure to the UV radiation modified the surface region, permitting the attainment of strong joints.

The longer times required for UV irradiation to produce an effect similar to the CASING technique are consistent with the significantly lower quantum yields when compared with high-energy (Van der Graaff or  $\gamma$ -radiation)<sup>11</sup> crosslinking. These high-energy radiation processes are perhaps 100–500 times more effective than UV irradiation.<sup>12</sup> Although Hudis did not attempt to study the effect of pressure on the extent of crosslinking, the data in Figures 1 and 2 clearly illustrate the importance of working at reduced pressure to maximize the efficiency of the process. At present, there appears to be no plausible explanation for the decreased efficiency of the process at pressure lower than 1 torr.

The data in Figures 3 and 4 illustrate that specific wavelengths are responsible for the surface crosslinking. The difference between quartz and Pyrex containers using the 2537 Å is understandable since Pyrex is quite transparent above 3000 Å but opaque to the UV below about 2800 Å. The quartz used in our investigation transmits about 85% of the radiation at 2537 Å and 93% at 3000 Å. Figure 5 is a composite of the joint strength data plotted as a function of time for varying pressures of helium. For wavelengths of 3000 Å and 3500 Å, low joint strengths were obtained for both Pyrex and quartz containers (Figs. 6a and 6b). Apparently, wave-

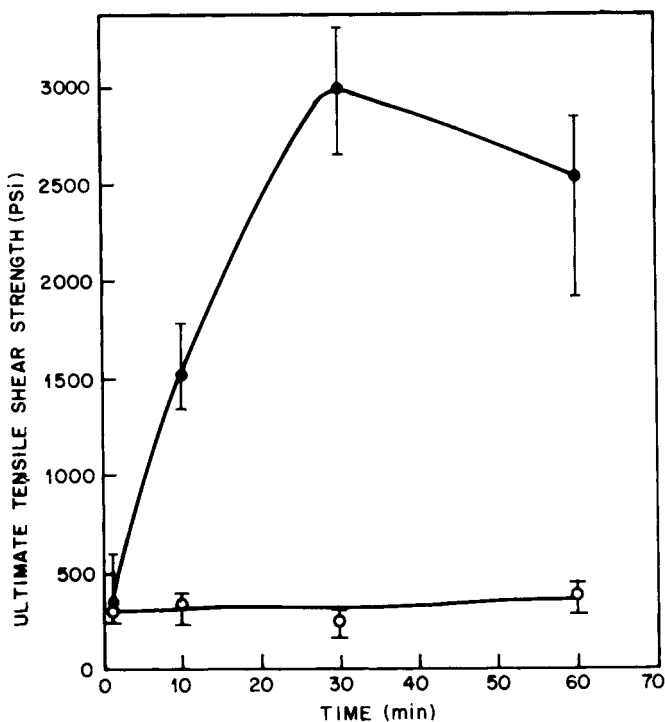


Fig. 4. Strengths of lap shear composites containing polyethylene films which had been exposed for varying lengths of time in either quartz (●) or Pyrex (○) tubes to UV radiation at 2537 Å. Air pressure in the tubes was kept constant at 1 torr.

lengths in excess of 3000 Å are not able to couple with polyethylene and induce crosslinking.

The work of Hudis and Prescott<sup>1</sup> points out that exposure of polyethylene to UV irradiation to yield a sizable gel fraction is only effective for low wavelengths ( $\leq 1849$  Å).

To examine the effect of wavelength on the extent of surface modification of the polyethylene, the polymer was placed in a Supersil quartz envelope and exposed to 1849 Å. These data are shown in Figure 7. Times as short as 1000 sec in either air or helium are sufficient to produce crosslinked surface layers capable of forming strong joints. When an examination of the joint strength versus wavelength is examined in Figure 8, it becomes evident that the lower wavelengths are more effective in crosslinking for a given time interval. However, if a definite depth of crosslinking is accomplished, then the joint strengths should level out to a constant high value. This is apparent from Figure 9 where the joint strength is plotted as a function of the  $\sqrt{t}$ . Apparently, up to the time of about 30 min, the joint strength increases in a linear fashion. Beyond the 30-min period, the joint strength reaches a plateau, but there is a continual increase in gel fraction.

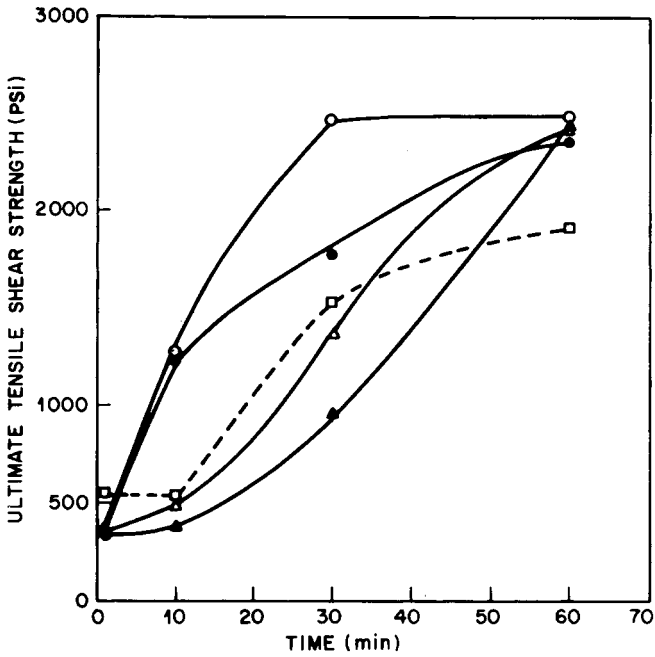


Fig. 5. Strengths of lap shear composites containing polyethylene films which had been exposed for varying lengths of time in quartz tubes to UV radiation at  $2537 \text{ \AA}$ : (□) 0.25 torr; (○) 1.0 torr; (●) 10 torr; (△) 100 torr; (▲) 760 torr.

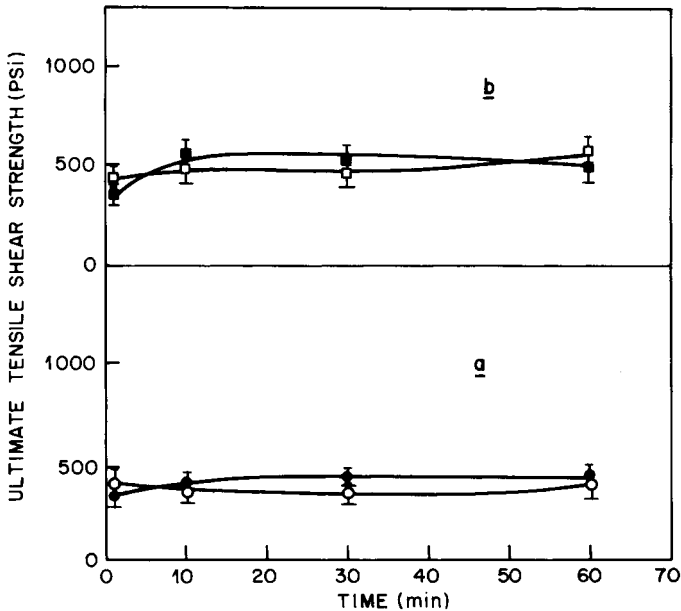


Fig. 6. (a) Strengths of lap shear composites containing polyethylene films which had been exposed for varying lengths of time in either quartz (●) or Pyrex (○) tubes to UV radiation at  $3000 \text{ \AA}$ . Helium pressure in the tubes was kept constant at 1.0 torr.

(b) Strengths of lap shear composites containing polyethylene films which had been exposed for varying lengths of time in either quartz (■) or Pyrex (□) tubes to UV radiation at  $3000 \text{ \AA}$ . Air pressure in the tubes was kept constant at 1.0 torr.

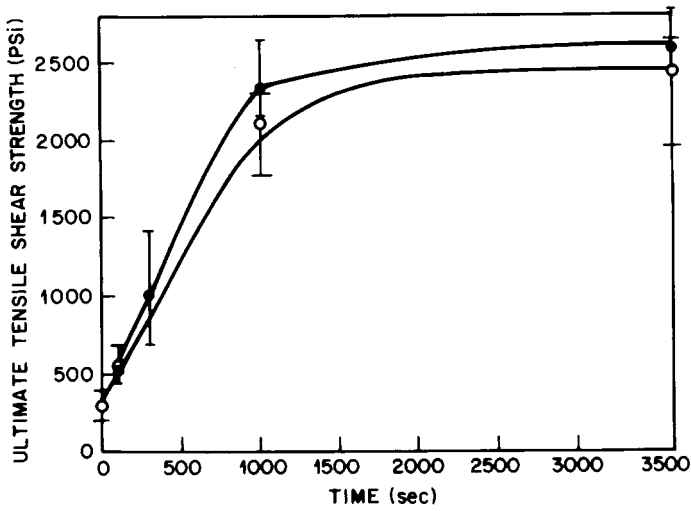


Fig. 7. Strengths of lap shear composites containing polyethylene films which had been exposed for varying lengths of time in a Supersil quartz tube to UV radiation at  $1849 \text{ \AA}$ . Air (O) or helium (●) pressure was kept constant at 1.0 torr.

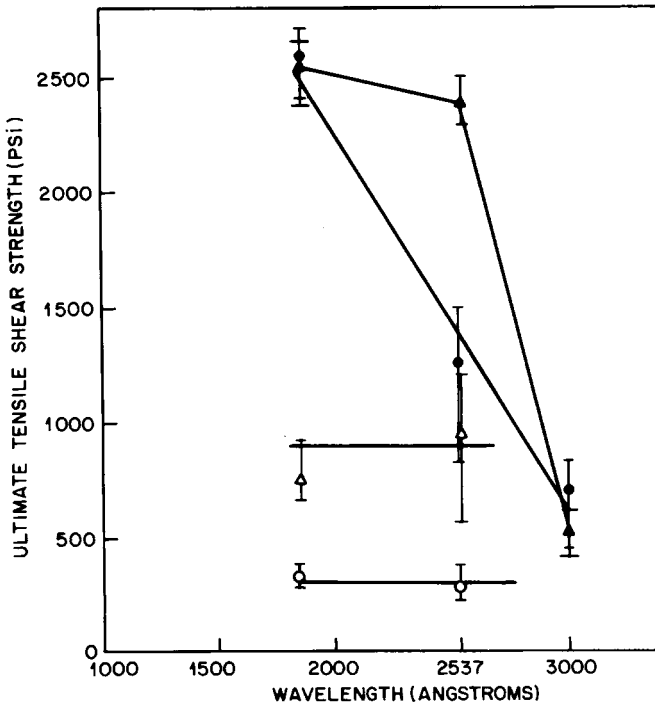


Fig. 8. Strengths of lap shear composites containing polyethylene films which had been exposed to a variety of wavelengths for varying lengths of time. Helium ( $\Delta$ ) or air (O) pressure was kept constant at 1 torr: ( $\blacktriangle$ ) helium in quartz for 1000 sec; ( $\triangle$ ) helium in quartz for 100 sec; (O) air in quartz for 100 sec; ( $\bullet$ ) air in quartz for 1000 sec.

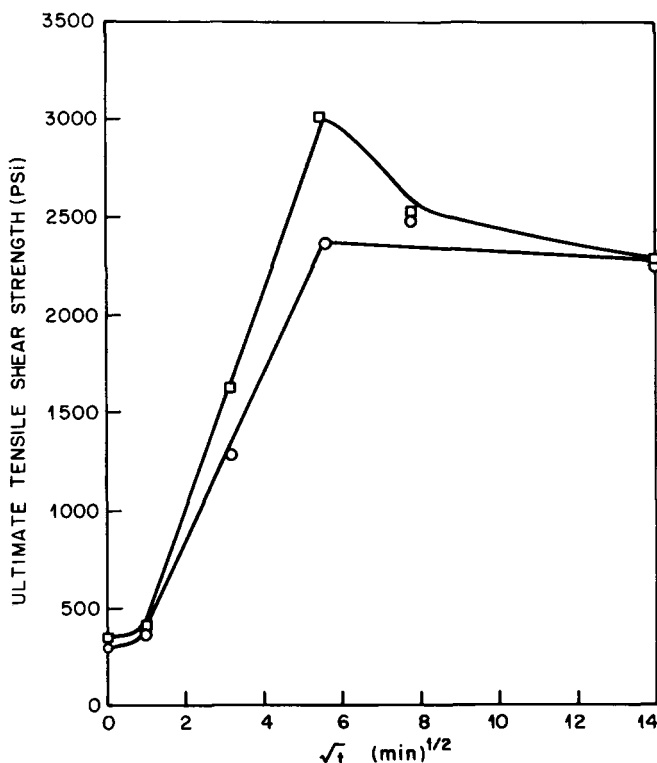


Fig. 9. Strengths of lap shear composites containing polyethylene films which had been exposed to UV radiation at 2537 Å in a quartz tube plotted as a function of  $t^{1/2}$ . Air (□) or helium (○) pressure was kept constant at 1 torr.

Examination of treated films by ATR revealed no detectable oxidation after 60-min exposure to helium or air at a 1 mm of pressure using 2537 Å. After 22 hr of exposure to UV at 2537 Å in helium, no oxidation is recorded; however, there is development of an absorption at  $960\text{ cm}^{-1}$  which may be assigned to transethylenic unsaturation.

The absence of detectable oxidation as determined by ATR is in itself not clear evidence that oxidized species do not exist on the surface of the polymer. Since the depth of penetration of the infrared radiation is the order of microns, it may be impractical to observe oxidation unless a considerable degree has been achieved. Admittedly, x-ray photoelectron spectroscopy would have been a more desirable method to examine the polymer surface for oxidized species, but this equipment was not available during our investigation. Using the wettability approach, we find no polar contributions to the critical surface tension of wetting for exposed polyethylene.

The time scale in the UV treatment is extended in contrast to the glow discharge treatment because of the far greater efficiency of the glow discharge. What is important for this investigation is that strong joints were



prepared with treated polyethylene which show no detectable surface oxidation. This appears to reinforce the notion of the weak boundary layer concept, rather than the driving force for surface modification being a surface oxidation of the polymer as a precursor for adhesive bonding. Wettability results for the treated and untreated polymer films in either air or helium for 1-hr exposure indicated no change in  $\gamma_c$ . Four hours of treatment in air produced a slight increase in  $\gamma_c$  while 4-hr exposure to helium resulted in no change in  $\gamma_c$ . Clearly, strong joints are prepared well below the times required to induce surface changes, as evidenced by infrared and wettability.

From this study, it appears that surface crosslinking is the predominant reaction required to permit the joining of irradiated films with conventional adhesives.

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