

Adhesive Bonding of Polyethylene

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Synopsis

The treatment of polyethylene film with aqueous ammonium peroxydisulfate solutions prior to adhesive bonding to aluminum has been studied. Such pretreatments resulted in the formation of adhesive joints of high strengths when bonded with a conventional epoxy adhesive. The effect on the tensile shear strength of adhesive joints of variations in the treatment time and temperature and the peroxydisulfate concentration has been examined. The use of certain catalysts for the reaction has also been studied. Tensile shear strengths at least as high as with other pretreatment methods have been obtained.

INTRODUCTION

In recent years interest in the principles underlying adhesion and the strength of adhesive joints of low surface energy solids has increased rapidly. Several theories have been proposed, as summarized by Huntsberger¹ and Schonhorn,² and although considerable advance has been made, the matter has not yet been completely resolved.

The importance of wetting of the substrate by the adhesive as a prerequisite for obtaining a strong adhesive bond has received much attention.³⁻⁵ It has been stressed that if, due to poor wetting, the real area of contact between adhesive and substrate were small, strong adhesive bonds would be unlikely to result. Hence considerable attention has been paid to the relative values of the surface tension of the adhesive and of the substrate.^{4,6} In many cases the approach has been either to formulate an adhesive of low surface tension⁴ or, more commonly, to raise the critical surface tension of wetting of the polyolefin. It has been known for some time that certain oxidative pretreatments of polyethylene lead to improved adhesive strengths.^{7,8} At the same time, as pointed out by Schonhorn⁹ attempts to demonstrate conclusively a correlation between the degree of wetting of the substrate by the adhesive and the strength of the adhesive bond formed have failed. Voyutskii and Deryaguin¹⁰ have criticized this so-called adsorption theory on thermodynamic grounds.

More recently, Hansen and Schonhorn¹¹ described a technique for obtaining adhesionable polyolefins which does not change the wettability of the

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polymer to any significant extent. They proposed that the low adhesive strength shown by polyolefins is not simply ascribable to their low surface energy but results at least in part from the presence on the surface of the polymer of a region of low molecular weight material which has poor mechanical strength properties. It is suggested that if this "weak boundary layer" were removed prior to bonding, greatly improved bond strengths would be obtained. The "casing" technique which they introduced is said to crosslink this low molecular weight material, thus producing a region of greatly improved mechanical strength.^{11,12} It has been shown that even if the surface free energy of polyethylene is reduced by this treatment, strong adhesive bonds still result.¹³

An alternative solution to the weak boundary layer problem has been proposed in which the polyolefin is allowed to solidify from the melt against a high energy surface, such as gold foil. This promotes the formation of a transcrystalline, rather than an amorphous, surface layer.^{14,15} The mechanical properties of such a transcrystalline surface region have been shown to be superior to those of the bulk polymer.¹⁶ Even polytetrafluoroethylene is said to form strong adhesive bonds when treated in this way.⁹

In the present work, the strength of polyethylene-aluminum adhesive joints was examined after pretreatment of the polymer surface with an aqueous solution of ammonium peroxydisulfate. This substance was chosen because it is a strong oxidizing agent and a polymerization initiator by a free radical mechanism.

EXPERIMENTAL

Materials

Additive-free, high density polyethylene was obtained from Rumianca ($\bar{M}_n \sim 1.3 \times 10^4$), commercial-grade Rigidex 50 ($\bar{M}_n \sim 1.3 \times 10^4$) from BP Plastics, and additive-free low density polyethylene, WNC-18 ($\bar{M}_n \sim 2.7 \times 10^4$), from Imperial Chemical Industries Ltd.

Araldite AV100 and HV100 were supplied by Ciba ARL Ltd. Aluminum (BS 1476) test pieces ($4\frac{1}{2} \times 1 \times \frac{1}{8}$ in.) were obtained from Northern Metals Ltd.

Ammonium peroxydisulfate (BDH Analar grade) was used without further purification. Deionized water was used in all experiments.

All other chemicals were of AR quality.

All polymer samples were supplied in powdered or granular form. They were compression molded into sheets 5 mil thick between sheets of poly-(ethylene terephthalate) film (Melinex) and using 5 mil Melinex film as a shim.

Procedure

Treatment of the polymer film was accomplished in the following way: the film was cut into pieces approx 6×3 in. and a hole was punched in each end. Sixteen such pieces were threaded on a glass framework using short

sections of glass tubing as spacers between the sheets. A rectangular tank (capacity approximately $4\frac{1}{4}$ litres) was filled with water and equilibrated in a thermostat at the required temperature. The ammonium peroxydisulfate was added (to form a 0.26 *M* solution unless otherwise stated), and then the polymer film on the framework was inserted in the tank in such a way that the film pieces were vertical. After the desired time had elapsed, the framework was removed from the tank and each piece of polymer film was washed in water and hung overnight, with a small weight on one end, over silica gel to dry. The polymer was then stored in sealed plastic bags until required. In all operations, the polymer film was handled with tweezers.

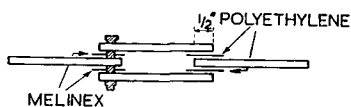


Fig. 1. Diagrammatic representation of a double lap joint.

Double lap joints were used in all adhesive strength tests. The polymer film was cut into pieces approx $1\frac{1}{4} \times 1\frac{1}{2}$ in. and made into double lap joints 1 in. wide with $\frac{1}{2}$ in. overlap (shown diagrammatically in Figure 1) using Araldite AV100/HV100 as the adhesive. Melinex film was inserted at the bolted end to compensate for the polyolefin and glue thicknesses so as to minimize possible peel effects. The glued end of the joints was held together during cure with a small clip and the whole arrangement was cured in an oven at 60°C for 3 hr.

After cooling, the tensile shear strength of the joints was measured on a Hounsfield horizontal tensometer using a draw rate of 0.25 in./min. Joints were made in sets of 20 and the values were averaged, a scatter of $\pm 20\%$ being the maximum range in most cases. All joints were tested on the day of preparation.

The critical surface tension of wetting of the polymer film⁶ before and after treatment was determined by measurement of contact angles using a traveling microscope with a goniometer eyepiece. The mounting for the polymer film could be tilted to any angle.

Electron micrographs of shadowed treated and untreated polymer film were taken on a Phillips EM300 electron microscope. Stereoscan micrographs were also taken.

ATR infrared spectra of treated and untreated polymer film were obtained on a Perkin-Elmer 257 spectrophotometer using a KRS-5 crystal.

RESULTS

Effect of Temperature and Time of Treatment

Experiments were performed with additive-free, high density polyethylene (Rumianca) and commercial-grade, stabilized high density poly-

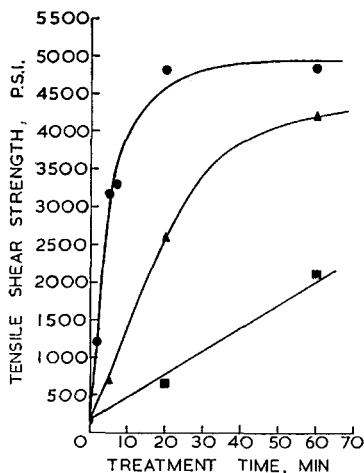


Fig. 2. Effect of treatment time and temperature on the tensile shear strength of polyethylene-aluminum double lap joints. Polymer, Rumanca treated with $(\text{NH}_4)_2\text{S}_2\text{O}_8$, 0.26M: (●) 70°C; (▲) 50°C; (■) 30°C.

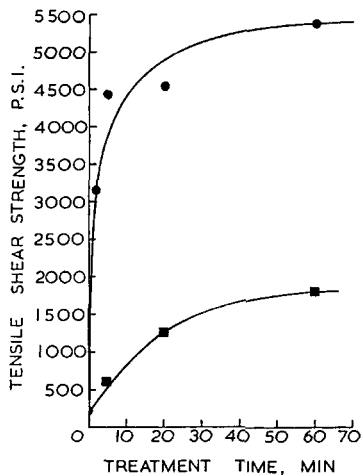


Fig. 3. Effect of treatment time and temperature on the tensile shear strength of polyethylene-aluminum double lap joints. Rigidex 50 treated with $(\text{NH}_4)_2\text{S}_2\text{O}_8$, 0.26M: (●) 70°C; (■) 30°C.

ethylene (Rigidex 50) in which the polymer was treated for various times at different temperatures. No discoloration or other damage was apparent in the treated film. In all cases, the treated polymer film was made into double lap joints and subjected to tensile shear tests on the day following treatment.

Sets of joints using untreated polymer film were also made for comparison. The values of the ultimate tensile shear strength were calculated taking the bonded area which failed under the applied load to be approxi-

mately 0.5 square in. The actual length of overlap was measured in each case. The results are shown in Figures 2 and 3. It is seen that at a given treatment temperature the shear strength of the joints increased with increasing treatment time up to a certain value, after which further increases in treatment time had little additional effect.

The type of failure of the joints was markedly different in the high and low strength cases. The untreated polymer film showed apparent adhesive failure, i.e., after fracture of the joint the polymer surface seemed unaffected, and separation appeared (on the macroscopic level) to have occurred at the polymer-adhesive interface. In joints which failed at about 1000 psi, the polymer film was frequently torn, especially across the ends of the joint. Where fracture occurred at high loads, a considerable amount of cohesive failure of the polymer was evident. Extensive areas were torn out of the polymer film and the whole surface was roughened. In the highest load cases, the failure was a mixture of cohesive failure of the polyolefin film, failure of the adhesive, and failure at the adhesive-aluminum interface, or, in some instances, failure of the aluminum around the bolt hole.

Double lap joints were also made with unstabilized low density polyethylene, WNC-18. The polymer was treated as above for 60 min with 0.26*M* ammonium peroxydisulfate at 70°C and made into joints of 1 in. overlap. Fracture occurred at 1970 psi, while joints made with the untreated polymer showed strengths of 270 psi. The failure in the treated cases was again at least partly cohesive failure of the polymer film.

Change in Peroxydisulfate Concentration

Several experiments were performed in which Rumianca was treated with ammonium peroxydisulfate solutions in the concentration range 0.04 to 0.52*M* at 70°C for 5 min. The polymer was made into double lap joints and tested as before. The results are shown in Figure 4. Evidently, the

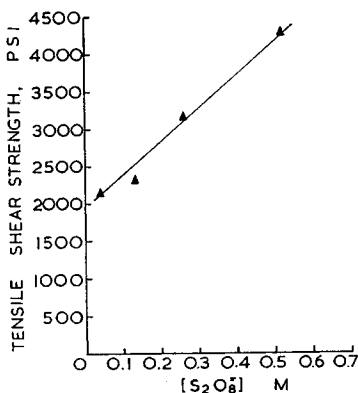


Fig. 4. Effect of peroxydisulfate concentration on the tensile shear strength of polyethylene-aluminum double lap joints. Rumianca, treatment time 5 min, 70°C.

dependence of the magnitude of the effect produced by this treatment on the peroxydisulfate concentration is small, at least in this concentration range.

Aging of Treated Polyolefin Film

The effect on the tensile shear strength of aging of the treated polyethylene film was examined. Sufficient polymer for four sets of joints was usually treated in each batch. One set of joints was made on the day following treatment, as described above, and the rest of the polymer was stored at room temperature in sealed plastic bags. Sets of joints were then made after various times. The results are shown in Table I.

The tensile shear strength of samples subjected to long treatment times remained constant or fell somewhat (up to 20%) over a period of about three months. For samples treated for a short time, the joint strength appeared to show an increase with time.

TABLE I
Effect of Aging of the Polymer after Treatment^a on Ultimate
Tensile Shear Strength of Polyethylene-Aluminum Double Lap Joints

Treatment time, min	Rumianca		Rigidex 50	
	Days after treatment	Tensile shear strength, psi	Days after treatment	Tensile shear strength, psi
Treatment temperature 70°C				
60	1	4850	1	5400
	11	4900	16	4550
	43	4220	40	4770
	—	—	82	4220
5	1	3170	1	4440
	29	4130	29	4320
	56	3600	60	4250
	89	4150	—	—
2	1	1200	1	3150
	34	3260	54	3280
	—	—	92	3410
Treatment temperature 30°C				
60	1	2120	1	1800
	19	1530	35	1620
	50	1900	—	—
	99	1680	—	—
5	—	—	1	610
	—	—	35	770
	—	—	72	890

^a With 0.26M (NH₄)₂S₂O₈.

Catalyzed Reactions

The possibility of accelerating the treatment of the polyolefin film was investigated. For this purpose small amounts of silver and copper sulfates

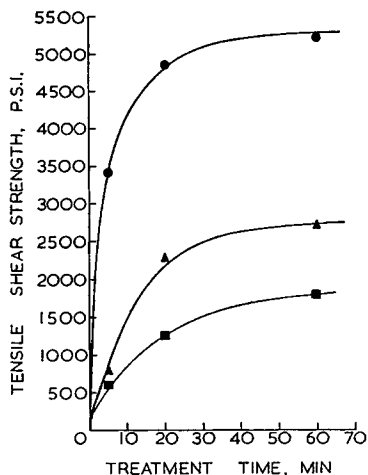


Fig. 5. Influence of catalysts on the tensile shear strength of polyethylene-aluminum double lap joints. Rigidex 50, treated with $(NH_4)_2S_2O_8$, $0.26M$, $30^\circ C$: (●) $2 \times 10^{-3}M$ Ag_2SO_4 ; (▲) $1 \times 10^{-2}M$ $CuSO_4$; (■) uncatalyzed.

were used. The results are shown in Figure 5. It is seen that at $30^\circ C$ the addition of $2 \times 10^{-3}M$ silver sulfate had an effect on the adhesive joint strength approximately equivalent to a $40^\circ C$ rise in the reaction temperature. The effect of $1 \times 10^{-2}M$ copper sulfate was somewhat less pronounced.

Other Investigations

Various experiments were performed in an effort to determine the nature of the effect the peroxydisulfate solution had on the polyolefin film.

ATR infrared spectra were run on treated (60 min at $70^\circ C$, $(NH_4)_2S_2O_8$, $0.26M$) and untreated samples of Rumianca and Rigidex 50, but no significant differences were apparent. In all cases small carbonyl peaks were visible. Hence, if the polymer was oxidized by the peroxydisulfate to any extent, the effect must have been confined to the very surface region of the polymer film such that the thickness of this region was small compared with the depth examined by this technique (of the order of 1000 \AA).

The critical surface tension of wetting, γ_c , of treated and untreated samples of Rumianca and Rigidex 50 was determined by measurement of the contact angle of a variety of liquids on the polymer. The results were assessed according to several methods: that of Bartusch¹⁷ using diethyl phthalate and those of Zisman⁶ and Foulkes¹⁸ using methylene iodide, glycerol, and water as the liquids. In all cases, γ_c for the treated samples was no more than 5 dynes/cm greater than for the untreated samples.

The possibility that the peroxydisulfate solution etched the polyolefin surface, as is the case with some strong oxidizing agents on polyolefins,^{19,20} was examined by means of electron micrographs. The only difference

appeared to be a slight sharpening of the features in the treated case. Similarly, effectively no difference between treated and untreated samples was observable in Stereoscan micrographs.

As an indication of whether the peroxydisulfate initiated crosslinking of the polyethylene, a sample of Rigidex 50 in the granular form (surface area approx $24 \text{ cm}^2/\text{g}$) was treated for 60 min at 70°C with $0.26M$ $(\text{NH}_4)_2\text{S}_2\text{O}_8$, washed, dried and extracted with *p*-xylene. An untreated sample was also extracted. After two days the untreated sample had dissolved completely, while after four days the treated sample retained an apparently insoluble residue which amounted to approx 1% by weight of the original material.

The rate of disappearance of peroxydisulfate from solution in the presence of polymer was found, by titration of aliquots removed at intervals, to be at the most 2% greater than the rate in the absence of polymer.

In all cases considerable gas evolution occurred, at least part of this being ozone.

DISCUSSION

It is clear from the results presented above that, despite the hydrophobic nature of polyethylene, contacting the surface of polyethylene film with an aqueous peroxydisulfate solution has a profound effect on the shear strength of adhesive joints formed subsequently.

Organic peroxides are known to initiate radical reactions in polyolefins. Rado et al. investigated the effect of benzoyl peroxide on polyolefins and reported that, for polyethylene, crosslinking is the predominant result,²¹ while for polypropylene a mixture of degradation and branching occurs.²² The "casing" technique of Schonhorn, which consists of bombarding the polymer with activated inert gases, causes rapid crosslinking of the surface by a free radical mechanism. There is evidence for believing that some of the oxidative methods cause crosslinking of the surface regions of the polymer being treated,²³ and it has been claimed that such methods are effective in raising the shear strength of adhesive joints because the weak boundary layer has been removed in this way.¹²

In aqueous solution, peroxydisulfate ion undergoes thermal decomposition to generate two sulfate radical ions.²⁴ Oxidation reactions of peroxydisulfate in aqueous solution with a wide range of organic substances, such as alcohols, amines, and esters, have been reported.²⁵ Reactions with substances as chemically inert as polyethylene do not appear to have been mentioned. The mechanism of these oxidations is not entirely clear, as a complex set of free-radical chain reactions is involved.^{24,25} Furthermore, small amounts of certain ions, notably silver, have been shown to catalyze such reactions considerably.^{24,25}

In the present work, the lack of any significant difference between the ATR spectra of the treated and untreated samples indicates that little oxidation of the polyethylene surface occurred. This conclusion is supported by the small change in the value of the critical surface tension of wetting of the treated polymer compared with the untreated sample.

These observations, together with the formation of a gel fraction in the treated samples, favor crosslinking of the surface region of the polyethylene as the main effect of the treatment on the polymer. Similarly, the results of the aging experiments support this view. After short treatment times at 70°C, the adhesive bond strength was found to increase considerably with time during storage at room temperature, indicating that once the radical activity was transferred to the polymer, the reaction could proceed even after removal of the original reagent, i.e., the peroxydisulfate. It is therefore suggested that pretreatment of the polyolefin surface with an aqueous peroxydisulfate solution leads to greatly increased bond strength in polyethylene-aluminum double lap joints because of the greatly improved mechanical properties of the surface region of the polymer brought about by this treatment.

The extent of the improvement in adhesive bond strength achieved by this method appears to be at least as high as that obtained by other techniques. Exact comparisons between results obtained by different workers is difficult because of the variation in joint geometry, test procedure, and polyethylene samples used. It seems preferable to consider the value of the adhesive bond strength after treatment relative to the value obtained by the same workers on untreated samples of the same polymer, rather than the absolute values of the joint strength, as a measure of the improvement in adhesive bond strength brought about by that treatment. The limit of usefulness of this approach is reached where the failure of the joint is due to cohesive failure of the bulk polymer or of the adhesive, since in these cases the bulk properties of the particular polymer or adhesive determine the strength of the joint.

Brewis²⁶ has measured the adhesive bond strength of polyethylene after various pretreatments, such as immersion in chromic acid and in organic peroxides and γ -irradiation, and found up to a tenfold increase in bond strength for Rigidex 50. Similarly, Schonhorn et al.^{11,12} reported increases of this order for Marlex 5003 treated by the "casing" method, while polyethylene solidified against aluminum foil gave approximately a sixfold increase in adhesive bond strength.¹⁴ The greatest improvement in bond strength reported in this work is about a 30-fold increase compared with the untreated samples. However, joint failure in the previous work was stated to be cohesive failure in the bulk of the polymer or the adhesive.¹¹ Hence it can be said that the peroxydisulfate pretreatment is at least as effective as other techniques in promoting the formation of strong adhesive bonds.

The difference between the joint strength of the stabilized and unstabilized polyethylene samples is interesting. The effect of the shorter treatment times (2 and 5 min) at 70°C on the Rigidex 50 was much greater than on the Ruminanca (Figures 2 and 3). From infrared spectra it was found that the vinyl group content of the Rigidex 50 sample was 1.7 vinyl groups/1000 carbon atoms compared with 0.05 vinyl groups/1000 carbon atoms for the Ruminanca. Hence, if the radical attack on the polymer proceeded via the double bonds, this large difference in double bond content

would be important. At lower temperatures, this effect was not observed. It may be that the stabilizers in the Rigidex 50 had some effect in that case.

The aging experiments indicate that two effects can occur with time, an increase or a decrease in the adhesive strength of the joints. It is suggested that the decrease arose from diffusion of lower molecular weight material from the substrate into the surface region²⁷ and slow degradation of the crosslinked surface layer. In samples which were treated for only a short time, it is proposed that some radical activity remained in the polymer and that the crosslinking reaction therefore proceeded slowly until all the radicals were terminated. The diffusion and degradation referred to above would also proceed at the same time, offsetting to some extent the effect of crosslinking.

The catalysis by Ag^+ of peroxydisulfate oxidations and of various chain reactions has been the subject of many investigations.^{24,25} It appears that reactions involving Ag^{+2} and possibly Ag^{+3} occur. In certain circumstances, small amounts of Cu^{+2} have been found to catalyze the chain reactions of peroxydisulfate ion.²⁴ Again it has been proposed that it is the availability of different oxidation states of the copper which is responsible for its catalytic activity.²⁴ In both cases, an induced decomposition of peroxydisulfate occurs giving an increased rate of radical production.

The results of this work demonstrate that strong adhesive bonds can be formed with polyethylene without markedly changing its critical surface tension of wetting, which is in agreement with previous findings.¹³ This is not to say that good wetting between adhesive and substrate is not desirable but merely that it may not be sufficient for the formation of a joint of high adhesive strength. According to Bickerman,²⁸ the probability of true adhesion failure in an adhesive joint is very small. Hence, it is concluded that substantial improvements to the strength of adhesive joints can best be achieved by ensuring that the mechanical properties of the surface region of the substances to be jointed are as high as possible.

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