

NOTES

Adhesive Bonding of Polypropylene

INTRODUCTION

In a previous study it was found that immersion of polyethylene film in an aqueous solution of ammonium peroxydisulfate enabled strong adhesive joints to be formed when the polymer was bonded to aluminum. This method has now been applied to polypropylene.

Additive-free polypropylene powder HF20C from Imperial Chemical Industries Ltd. was used in this study. All experimental procedures were as previously described.¹

RESULTS AND DISCUSSION

Figure 1 shows the results of tensile-shear tests on double lap joints, made after treatment of the polymer film with 0.26*M* ammonium peroxydisulfate at 70°C for various lengths of time.

Where joints failed at high loads, the polymer film was frequently torn. In joints which failed at low loads, the polypropylene appeared unaffected. Roughening of the polymer film, due to small pieces being torn out of the surface, as occurred with polyethylene in joints which failed at high loads,¹ was not observed with polypropylene. The aging effects noted with polyethylene were not apparent in this case. No trend was observed in the adhesive joint strengths over a period of about three months.

Table I shows the effect of variation in the treatment temperature.

TABLE I
Effect of Treatment Temperature on Tensile Shear
Strength of Polypropylene-Aluminum Double Lap Joints^a

Treatment temp, °C	Treatment time, min	Tensile shear strength, ^b psi
2 ^c	60	220
20	60	290
30	60	350
40	60	970
70	60	3220
80	25	2610
90	10	3510

^a Treatment, 0.26*M* (NH₄)₂S₂O₈.

^b All bonding done at normal room temperature using Araldite AV100/HV100 and cured for 3 hr at 60°C. Values averaged over 20 joints.

^c Treatment procedures performed in a cold room, temperature 0–3°C.

Attempts were made to catalyze the treatment using small amounts of Ag⁺ and Cu²⁺. However, it was found that the concentration of these additives which substantially increased the effectiveness of the peroxydisulfate treatment of polyethylene¹ was ineffective in the case of polypropylene under the same conditions, but that at low tempera-

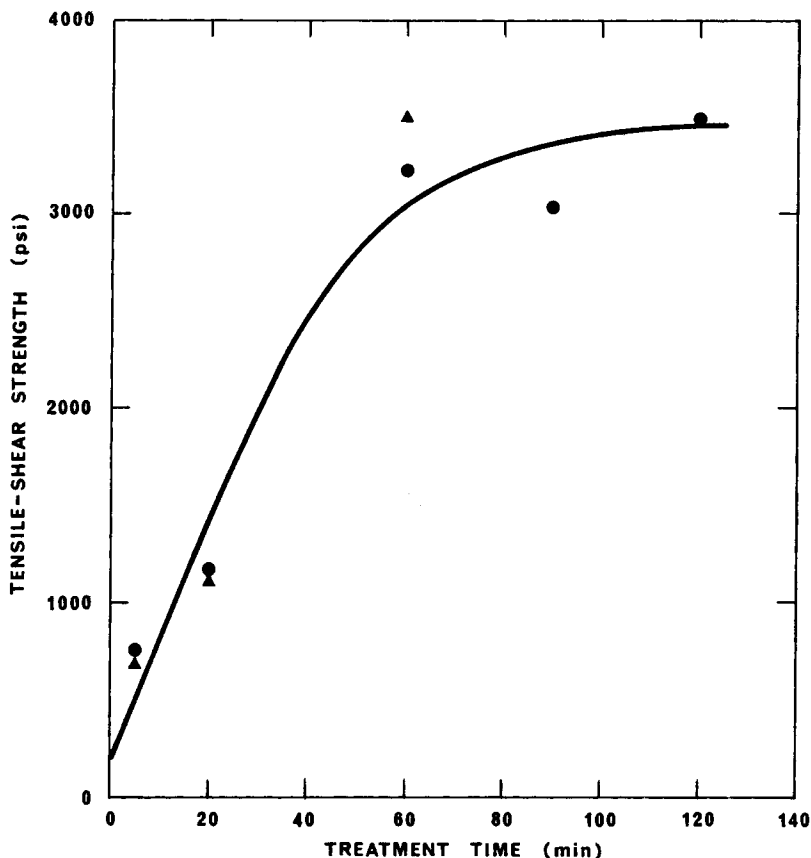


Fig. 1. Effect of treatment time on tensile shear strength of polypropylene-aluminum double lap joints. Treatment, $0.26M$ $(NH_4)_2S_2O_8$; $70^\circ C$: (●) no catalyst; (▲) $2 \times 10^{-3}M$ Ag_2SO_4 .

tures Ag^+ did increase the effectiveness of the treatment. The presence of Cu^{2+} appeared to have a deleterious effect on the adhesive joint strength. These effects are shown in Table II and Figures 1 and 2.

No differences were apparent between the infrared spectra of treated and untreated polymer samples using the ATR method. Hence, if the polymer was oxidized by the peroxydisulfate, 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 (about 1000 \AA).¹ After ten days, reaction with *p*-xylene in a Soxhlet extraction apparatus, treated samples yielded an intractible residue. No such residue was obtained from untreated samples.

The tensile-shear strength of adhesive joints after treatment of the polymer at different temperatures shows a correlation with the temperature dependence of the rate of thermal decomposition of peroxydisulfate. Table III shows the tensile-shear strength of adhesive joints calculated for a treatment time of 10 min using the first (approximately linear) part of the adhesive joint strength-versus-treatment time curve for that temperature. Also shown is the data of Kolthoff and Miller² for the rate constant of the thermal decomposition of peroxydisulfate at different temperatures. Both these quantities are shown in Figure 3 as a function of temperature. It is evident that the temperature

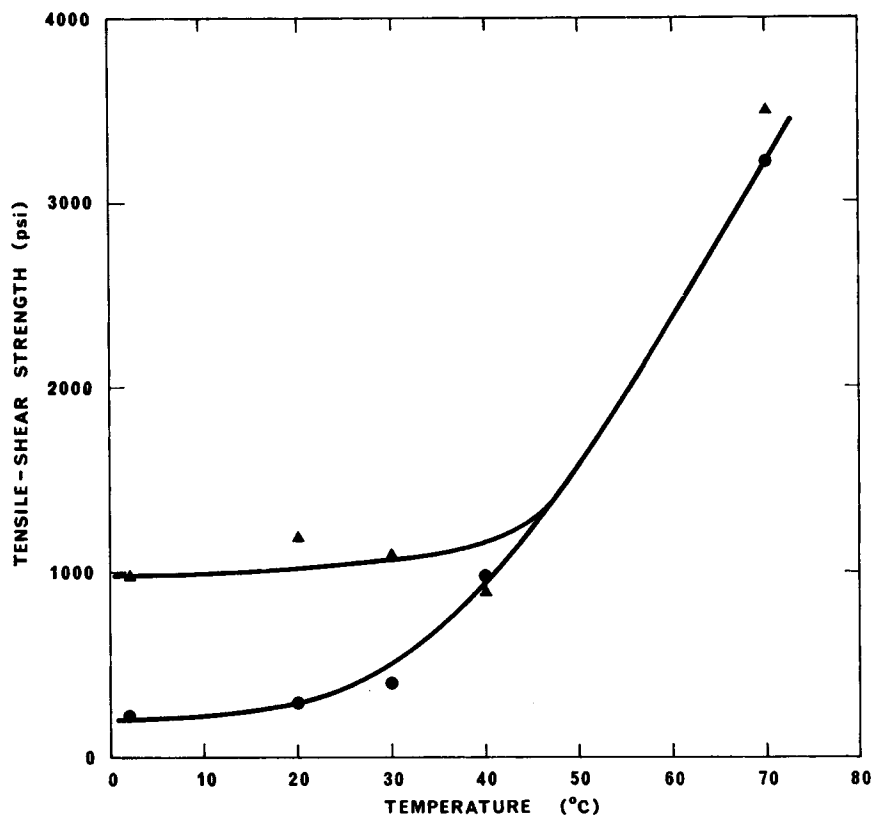


Fig. 2. Effect of treatment temperature on tensile shear strength of polypropylene-aluminum double lap joints. Treatment, $0.26M$ $(NH_4)_2S_2O_8$; 60 min: (●) no catalyst; (▲) $4 \times 10^{-3}M$ $AgNO_3$.

TABLE II
Effect of Silver and Copper Ions on Tensile Shear
Strength of Polypropylene-Aluminum Double Lap Joints^a

Additive	Treatment temp, °C	Treatment time, min	Tensile shear strength, ^b psi	
			with additive	no additive
$2 \times 10^{-3}M$ Ag_2SO_4	70	5	690	760
$2 \times 10^{-3}M$ Ag_2SO_4	70	20	1120	1160
$2 \times 10^{-3}M$ Ag_2SO_4	70	60	3500	3220
$4 \times 10^{-3}M$ $AgNO_3$	40	60	890	970
$4 \times 10^{-3}M$ $AgNO_3$	30	60	1080	350
$4 \times 10^{-3}M$ $AgNO_3$	20	60	1190	290
$4 \times 10^{-3}M$ $AgNO_3$	2°	60	990	220
$1 \times 10^{-3}M$ $CuSO_4$	70	60	2750	3220
$1 \times 10^{-3}M$ $CuSO_4$	70	60	1890	3220

^a Treatment, $0.26M$ $(NH_4)_2S_2O_8$.

^b All bonding done at normal room temperature using Araldite AV100/HV100 and cured for 3 hr at 60°C. Values averaged over 20 joints.

^c Treatment procedures performed in a cold room, temperature 0–3°C.

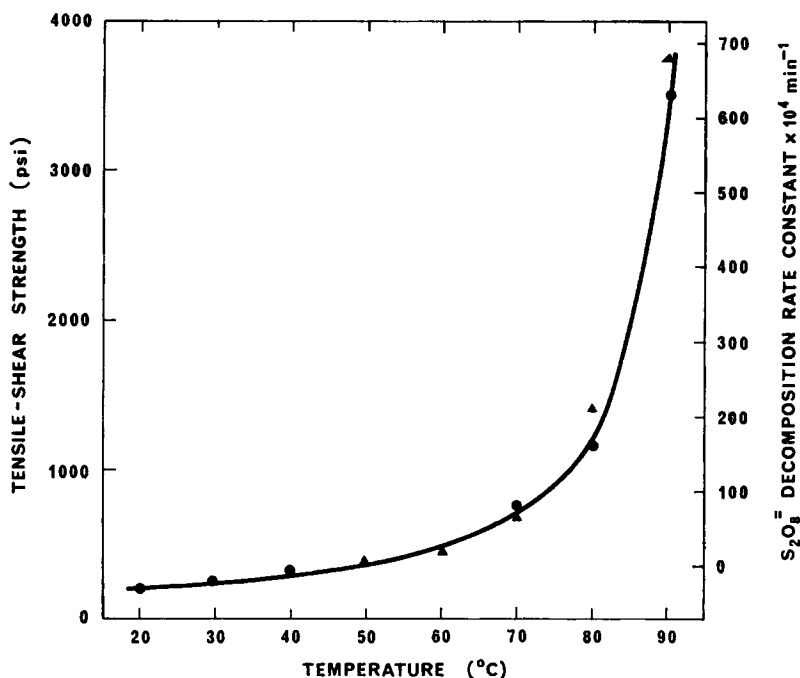


Fig. 3. Dependence of tensile shear strength of polypropylene-aluminum double lap joints and rate constant for the thermal decomposition of peroxydisulfate ion on reaction temperature. Treatment, $0.26M$ $(NH_4)_2S_2O_8$; 10 min (calcd): (●) tensile-shear strength; (▲) thermal decomposition rate constant (data from Kolthoff and Miller²).

dependence of the two quantities is effectively the same over this temperature range. It would appear that, as in the case of polyethylene,¹ it is the products of the thermal decomposition of peroxydisulfate which are responsible for the reactions leading to the improved strength of polypropylene adhesive joints prepared after treatment of the polymer in this manner, rather than, say, surface etching by the peroxydisulfate itself.

TABLE III
Dependence of Adhesive Strength of Polypropylene-Aluminum Double Lap Joints and Rate Constant for Thermal Decomposition of Peroxydisulfate Ion on Reaction Temperature

Temp, °C	Tensile shear strength, ^a psi	Rate constant $\times 10^4$, ^b min^{-1}
20	210	—
30	250	—
40	330	—
50	—	6
60	—	19
70	750	64
80	1160	210
90	3510	680

^a Values calculated for 10 min of reaction time.

^b Data of Kolthoff and Miller.²

Such etching has been claimed for the action of other strong oxidizing agents on polypropylene.³ This is supported by the effect on the adhesive strength of the presence of silver ion, a catalyst for the decomposition of peroxydisulfate.

The rate of the silver ion-induced decomposition of peroxydisulfate has received some attention,⁴ but the temperature range studied was small (18°–25°C) and outside that considered here. The reason for the limitation to the lower temperature range of the effect of silver ion on the adhesive joint strength is unclear. Evidently, at higher temperatures, some other effect becomes the dominant factor.

Both the magnitude of the effect of peroxydisulfate treatment on the adhesive joint strength and its rate of increase with increasing length of immersion time were substantially less for polypropylene than for polyethylene.¹ This was in spite of the fact that the polyethylene was a commercial, stabilized grade, whereas the polypropylene was unstabilized. According to Rado and co-workers,⁵ treatment of polypropylene with benzoyl peroxide causes branching and degradation of the polymer, as opposed to crosslinking, which is the principal effect with polyethylene. It may be that treatment of polypropylene with a peroxydisulfate solution leads to the formation of a surface layer of branched, mechanically interlocked polypropylene molecules, and that it is the presence of this strengthened surface region which is responsible for the higher adhesive joint strengths.

The author wishes to thank Mr. J. N. C. Laycock for his invaluable assistance.

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Received October 12, 1970

Revised November 16, 1970