

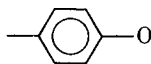
NOTES

Adhesion of Elastomers to Rigid Substrates—Three Substrates with Unexpectedly High Adhesion

We wish to report some initial observations on three substrates (adherends) that show unexpectedly high adhesion to simple elastomers (adhesives) under conditions where weak bonds would be anticipated, namely, low testing rates, moderate temperatures, and with the elastomer layer lightly crosslinked or physically entangled to prevent liquidlike flow.¹ The data are presented in Table I along with typical results for other substrates taken from the literature and some new results with a polystyrene substrate. Clearly, the adhesion of the elastomers used here to poly(2,6-dimethyl-1,4-phenylene oxide) (PPO), polysulfone, and polycarbonate is anomalously high. With these substrates cohesive failure of the elastomer occurred at high peel forces, whereas with other substrates interfacial failure was observed at low peel forces. Even in the two cases where cohesive failure was not observed with PPO, the work of adhesion was more than six times the work of adhesion for a similar polystyrene specimen.

It is interesting to speculate about why such strong bonds are formed with these three plastic substrates. One could suggest that chemical bonds are formed between the adherend and the adhesive during the free radical crosslinking reaction of the elastomer layer. The effect is still present, however, with uncrosslinked EPR, and this polymer does not contain double bonds. Furthermore, swelling in pentane for a few hours was sufficient to destroy the adhesion between crosslinked polybutadiene and both PPO and polysulfone. The corresponding adhesion to polycarbonate remained intact even after soaking in pentane for several days. It seems unlikely that the force generated on swelling a crosslinked elastomer layer would be sufficient to break chemical bonds, and we conclude that they are not formed in the cases of PPO and polysulfone, at any rate.

The structures of the three polymers have one thing in common, which, as shown in Table II, is a



group in the repeating unit of the backbone. Polystyrene, as is well known, has an aliphatic hydrocarbon backbone and the phenyl groups are in side chains. Possibly a specific interaction between the elastomer layer and the electron-rich backbones occurs.

Alternately, the improved adhesion may be due to greater compatibility between the resins and polybutadiene, as already suggested by Iyengar and Erickson.⁴ Some solubility parameters, one indicator of compatibility, for the various adhesives and substrates used in this study are given in Table III. Clearly, many of the bond strengths in Table I can be reconciled with the statement that stronger bonds are formed if the solubility parameters are nearly the same. However, if indeed the solubility parameters of polystyrene and PPO are nearly identical as suggested by the authors whose data are referred to in Table III,^{5,6} then solubility parameter considerations cannot solely account for the observed differences in the work of adhesion between these two substrates and simple elastomers.

Finally, it should be noted that PPO and polystyrene have been shown to be compatible in all proportions.⁷⁻¹¹ This compatibility has been attributed to "intrinsic attraction" between PPO and polystyrene. Possibly such attractive forces also exist between the three plastics showing the unexpectedly high adhesion and the rubbers bonded to them. Work on these systems is continuing.

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TABLE I
Effect of Substrate on Adhesion^a

Substrate	Elastomer ^b	Work of adhesion (J/m ²) ^c		Reference
		50 cpm	25 cpm	
Polyethylene terephthalate ^d	SBR ^e	—	32(I)	2
	Dicup (1)			
Aluminum	EPR ^f	—	5(I)	2
	SBR ^e	—	176(I)	
Pyrex glass ^g	Dicup (1)			3
	Polybutadiene ^h	—	609(I)	
Quartz	Dicup (0.05)	—	38(I)	3
	Dicup (0.2)	—		
Polystyrene ⁱ	Polybutadiene ^h	—	590(I)	3
	Dicup (0.05)	—		
PPO ⁿ	Polybutadiene ^h			j
	Lauroyl peroxide (6.39)	129(I)	—	
	Sulfur ^k	11(I)	—	
	EPR ^l	120–300(I)	—	
	SBR ^m			
	Lauroyl peroxide (6)	150(I)	—	
Polycarbonate ^o	Polybutadiene ^h			j
	Lauroyl Peroxide (10)	~500(c)	—	
	Dicup (0.1–1)	~460(c)	—	
	Sulfur ^k	76(I)	—	
Polysulfone ^p	EPR ^l	1200–1660(I)	—	j
	SBR ^m			
Polycarbonate ^o	Lauroyl peroxide (6)	>1000(c)	—	j
	Polybutadiene ^h			
Polysulfone ^p	Lauroyl peroxide (6)	~500(c)	—	j
	Polybutadiene ^h			
Polysulfone ^p	Lauroyl peroxide (6)	~480(c)	—	j
	Dicup (0.1)	~460(c)	—	

^a Peel tests at 180°C were carried out as previously described.¹

^b The curing agents and the percent of each are listed under the elastomer. Procedures for curing varied and are described for specific elastomer-substrate pairs.

^c Two speeds are given because literature data are not available at 50 cpm, where our data are most complete. We tested our samples at a variety of crosshead speeds from 0.05 to 50 cpm. When cohesive failure (c) occurred at 50 cpm, it occurred at all speeds used. The differences between 50 and 20 cpm were slight. I = predominantly interfacial failure; cpm = cm per min.

^d Mylar, Type A (E. I. du Pont de Nemours and Co.).

^e Ameripol 1513 (Goodrich-Gulf Chemicals, Inc.)-A 60/40: butadiene/styrene cold emulsion SBR rubber. Cured samples were prepared by swelling 1 phr Dicup and 1 phr PBNA from diethyl ether into a thin sheet of rubber, drying, and curing after bond formation for 30 min at 150°C. Dicup = dicumyl peroxide. PBNA = phenyl-β-naphthylamine.

^f Vistalon 404 (Enjay Chemical Co.).

^g 7740 Glass (Corning Glass Works).

^h Diene 35 NFA (Firestone Tire and Rubber Co.)—an anionically polymerized polybutadiene rubber. Cured samples were prepared by mixing with variable amounts of peroxide on an open mill and curing after bond formation. With Dicup cures were carried out for 2 hr at 150°C. With lauroyl peroxide 6 hr at 85°C was used.

ⁱ Styron 678 (Dow Chemical Co.).

^j This work.

^k Cured samples were prepared by mixing on an open mill and curing after bonding for 9 hr at 65°C. The recipe contained 100 parts polybutadiene, 12 parts Butyl Eight, 1.5 parts Altax, 1.5 parts sulfur, 3 parts zinc oxide, and 0.5 parts stearic acid. Interfacial failure in these cases may be due to the presence of sulfur at the interface.

¹ EPR 404 (Enjay Chemical Co.).

^m Ameripol 1502 (Goodrich-Gulf Chemicals, Inc.)-A 76.5/23.5: butadiene/styrene cold emulsion SBR rubber; cured after bond formation for 6 hr at 85°C.

ⁿ (General Electric Co.).

^o (Cadillac Plastic and Chemical Co.).

^p (Scientific Polymer Products, Inc.).

TABLE II
Repeat Units in Substrate Backbones

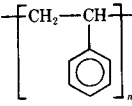
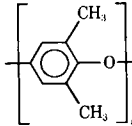
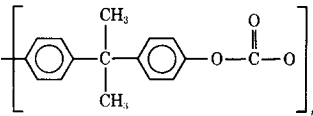
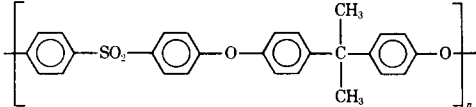
Substrate	Repeat unit
Polystyrene	
PPO	
Polycarbonate	
Polysulfone	

TABLE III
Solubility Parameters of Selected Polymers¹²⁻¹⁴

Polymer	δ
Polyethylene terephthalate	10.7
Polystyrene	9.3
Poly(2,6-dimethylphenylene oxide)	9.3 ^a
Polybutadiene	8.4
EPR	7.9
SBR (60/40)	8.7
SBR (75/25)	8.6

^a Based on χ values determined by Schultz,⁵ a private communication from MacKnight,⁶ and published values of δ for polystyrene.

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