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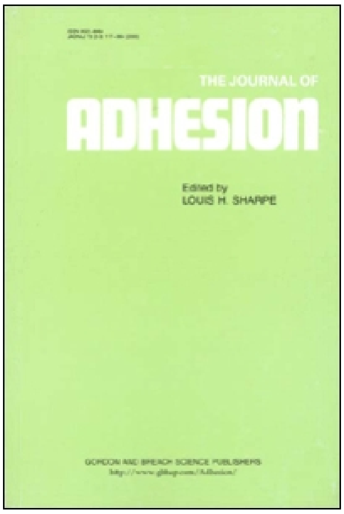

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NOTE

The Use of Triallyl Cyanurate in Bonding PVC Plastisols to Steel

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INTRODUCTION

The use of diallyl phthalate as the basis for a non-extractable plasticizer for poly(vinylchloride) (PVC) is well-known. Used in conjunction with a primary plasticizer and a polymerization initiator, a plastisol coating for steel can be formulated which is oil or grease tolerant and can also be used for bonding some structural steel parts if the area is relatively large compared with the load to be applied. Defrayne and Twiss[1] describe the bonding of automobile hood assemblies by vinyl plastisol adhesives and Schneberger[2] emphasizes their use in the automobile industry though neither article gives the formulations employed. Commercial formulations giving pull-off strengths of the order of 1 to 4 MN . m^{-2} always incorporate a proportion of a phenol-formaldehyde resin or even an epoxy, but sound-deadening and other coatings of steel do not necessarily need this reinforcement. Phillips and Longworth[3] particularly studied the use of diallylphthalate (DAP) as a polymerizable plasticizer and the consequent improvement in adhesion to mild steel. Sherlock[4] used a simple formulation without additives when investigating the effect of surface cleaning and conversion coatings (oxides and phosphates). It was suggested that, as outlined below, improved adhesion would be expected if a small proportion of triallyl cyanurate (TAC) were added to the polymerizable plasticizer. This paper shows this expectation to be achieved although the proportion of the more expensive TAC needed for substantial increase in bond strength is greater than was hoped.

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FORMULATIONS USED AND EXPERIMENTAL DETAILS

As with all polymeric plasticizers, some monomeric plasticizer must also be used if a desirable degree of flexibility is to be retained. This follows simply from consideration of the glass transition temperatures of the components. Dinonyl phthalate (DNP) was chosen as the monomeric material and in most of the work to be described was used at 40 pphr (parts per hundred parts of resin) with Breon 130/1 as the PVC resin. To this was added 3 pphr of a standard lead stabilizer. With this basic formulation the polymerizable additives given in Table I were used.

TABLE I

Formulation of polymerizable PVC plastisols

		Compound								
Series		1	2	3	4	5	6	7	8	9
A	Diallyl phthalate	40	30	20	10	0				
	Tri-allyl cyanurate	0	10	20	30	40				
	Benzoyl peroxide	←		0.8		→				
B	Diallyl phthalate	20	20	20	20	20	20	20	20	
	Tri-allyl cyanurate	0	5	10	15	20	25	30	40	
	Benzoyl peroxide	0.4	0.5	0.6	0.7	0.8	0.9	1.0	1.2	
C	Diallyl phthalate	40	35	30	25	20	15	10	5	
	Tri-allyl cyanurate	0	5	10	15	20	25	30	35	
	Benzoyl peroxide	←			1.0				→	
D	Diallyl phthalate	5	10	15	20	25	30	35	40	
	Benzoyl peroxide	←			1.0				→	

It will be appreciated that the initiator was held constant at 2% of the polymerizable monomers in series A and B, was 2½% for series C but for series D started at the very high figure of 20% and decreased to 2½% as the DAP increased to its maximum of 40 pphr.

In series A and B the compounds were mixed by ball milling the DNP with pigment, stabilizer and diluent for some two hours; adding the PVC and more diluent and milling for another hour and finally adding the DAP, benzoyl peroxide and the TAC and milling for a further quarter of an hour. For series C and D a high speed Torrance stirrer was used instead of a ball mill. The DNP and pigment with diluent were stirred while the PVC and stabilizer were added slowly. After two hours stirring, the DAP, benzoyl peroxide and TAC were added during a further quarter of an hour stirring.

Steel shim 0.003 inch thick and made of EN2 type steel was used in preparation of the test pieces. This was cut into suitable panels and was coated by a doctor blade technique with the organosol to give a dry coat thickness of 0.003 inch. Two coated panels were put together to give composite test pieces of total thickness 0.012 inch which were cured before testing.

Series A and B were press-cured for 30 minutes at 165°C with a pressure of 200 psi on the press gauge, Series C and D employed the same conditions but at 160°C. The change of temperature was unintended but is not thought to be significant.

The adhesion of the plastisol to steel was measured as a resistance to peeling, the intention being to use 180°C T-peel but the stiffness of the flexible steel imposed a relatively large curvature in the area of separation.

DISCUSSION OF RESULTS

Diallyl phthalate, although quadrifunctional, gives a linear polymer with allylic side chains[5] unless conditions or reagents are adjusted to bring the lower reactivity of the second allyl group into operation. However, to retain flexibility it is desirable that only a small proportion of allylic side chains should form the loci of cross-links. Hence the use of a small proportion of cross-linking material. Triallyl cyanurate possesses three allyl groups of approximately equal reactivity and it is assumed to co-polymerize with diallyl phthalate leading to branched chains and hence to cross-linking. Additionally, the triazine ring is known to have strong affinities for metal substrates and its thermal decomposition gives rise to isocyanate. Indeed it was at one time thought that the efficiency of isocyanates in rubber-to-metal bonding was due to trimerization and adsorption to the surface of the resultant cyanuric compound. Although this has never been established as the mode of operation of isocyanates in metal bonding, there is no doubt about the high level of bond strength obtained. The peel strengths recorded are summarized in Table II. The figures given are the means of 3 for series A and B and of 6 for series C and D.

TABLE II

Mean peel strengths of 2-ply steel composites N . m^{-1}

	Compound							
Series	1	2	3	4	5	6	7	8
A	589	971	589	490	347			
B	589	677	710	657	589	530	490	294
C	981	1059	1334	1432	1776	1138	432	275
D	216	432	628	667	785	785	863	981

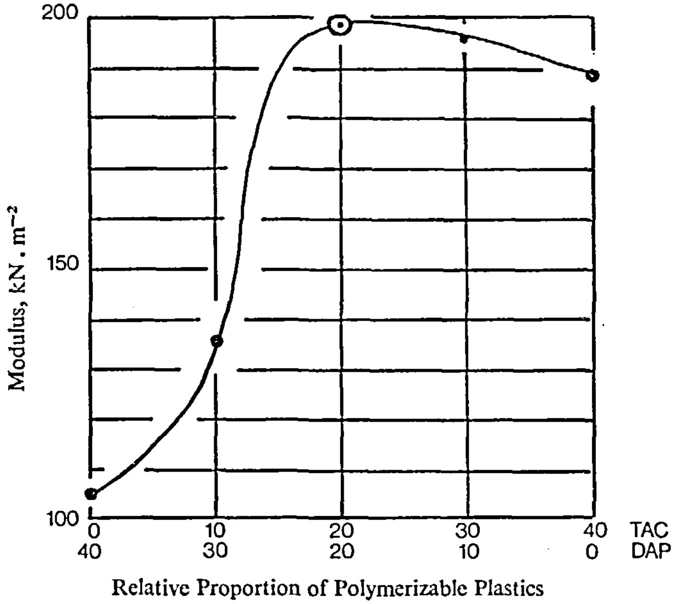

FIGURE 1 Effect on modulus of replacement of DAP by TAC.

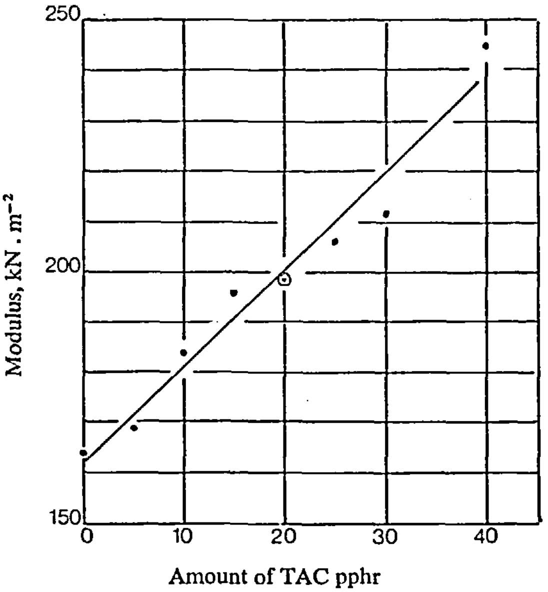

FIGURE 2 Effect on modulus of 20 pphr DAP and increasing amounts of TAC.

The variability in peel strength was examined by the standard errors of the mean. They were less than 10% of the mean strength and were taken as showing reasonable reproducibility and are not needed in the present discussion. The amount of cross-linking increases with compound number in Series A and B and this is reflected in modulus measurements made on films of adhesive cured under the same conditions as the 2-ply steel peel test pieces were made. These measurements are shown in Figures 1 and 2. There is one point common to both series in that it applies to an identical composition; this is circled on the two figures and shows the connection between them. When the total plasticizer is kept constant but the ratio of the monomers is varied, the modulus climbs to a maximum and remains there. With a constant amount of DAP but increasing TAC the crosslink density increases overall with a continuous increase in modulus.

Using steel as the flexible adherends the curvature at the line of separation will be substantially independent of the modulus of the adhesive as also will be the cleavage stress since this depends on the ratio of the moduli of adhesive to adherend. That of steel is so enormously in excess of that of the adhesive that changes in the latter can be ignored. Changes in peel strength will therefore reflect either a change in interfacial adhesion or in cohesive strength and be independent of the geometry which can be regarded as constant. It is therefore possible to plot peel strength against modulus and regard this as equivalent to plotting against cross-linking or cohesive strength. This is done in Figure 3 where curves comparable to those obtained by plotting the tensile strength of rubber against cross-linking are found.[6] This suggests that failure on peeling is by cohesive failure of the adhesive. As argued by Greensmith, Mullins and Thomas[6] there is an optimum degree of crosslinking for the strength of high extensible materials. In the probable absence of crosslinking, or when it is minimal, the bond strength would be expected to increase with increasing molecular weight of the polymeric plasticizer and this is shown by series D in which the ratio of polymerizable monomer to initiator increases thus increasing the length of the polymer chains as the number of chains initiated is decreased. The strength rises steadily throughout this series and although there may be some crosslinking at high initiator/monomer ratios, this is unlikely at the upper end of the series.

Series C shows that optimum bonding is obtained with equal amounts of DAP and TAC when 40 pphr of DNP is present. This result is somewhat surprising and may reflect the initiator/monomer ratios as well as the degree of crosslinking. Although in series A and series C, the initiator/total monomer ratio for optimum strength is 0.8/40 or 1/40, virtually the same, the ratios of initiator to the individual monomers are very different being 1/37 . 5/12 . 5 and 1/20/20 respectively. If the copolymerization ratios for DAP and TAC were known, not only would it be possible to explain the observed results but optimum conditions could more easily be sought. In the absence of such information a more statistically efficient design of experiment would be required to determine optimum conditions for bonding. In view of the number of variables involved and the need to allow for a non-linear response such an experiment would require a large number of compounds.

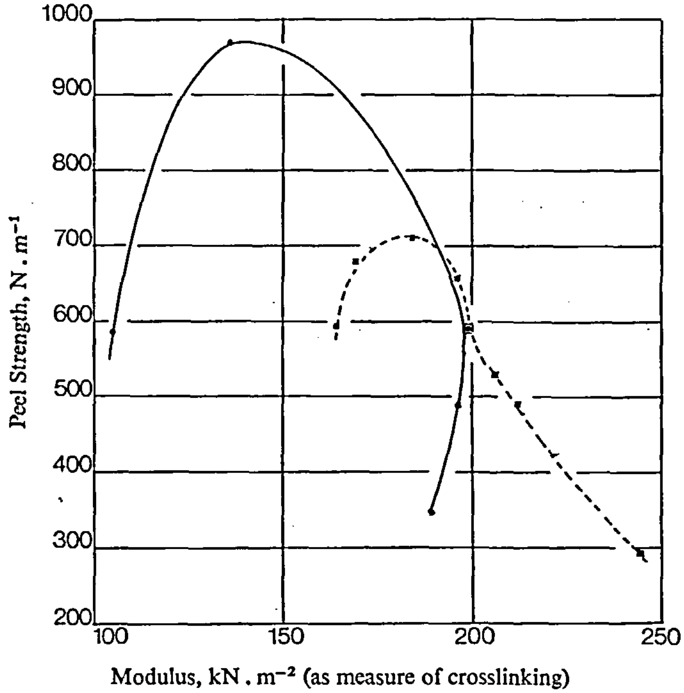

FIGURE 3 Relation between peel strength and amount of crosslinking. Series A, full line; Series B, broken line.

Meanwhile, the present work shows that the incorporation of some TAC does lead to greatly improved bonding and, in the best combination of variables investigated, replacement of half of the DAP by TAC doubles the bond strength. Further replacement leads to declining values.

Acknowledgments

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