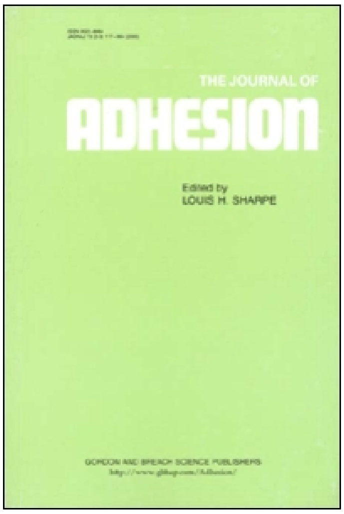

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Study on a Vinyl Ester/Methyl Methacrylate Based Reactive Acrylic Adhesive Toughened by Hydroxyl Terminated Polybutadiene

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The effect of addition of a hydroxyl-terminated liquid polybutadiene (HTPB) rubber on the morphology, adhesive, thermal and mechanical properties of a vinyl ester (VE)/methyl methacrylate (MMA) based reactive acrylic adhesive has been investigated. Phase separation was observed in the cured HTPB-modified acrylic adhesive. Low levels of HTPB enhanced the adhesive properties and the optimum adhesive strength was observed at about 10 wt% HTPB. HTPB modification had no significant effect on the thermal properties, but decreased the mechanical strength, which was attributed to the inadequate bonding of the rubber particles. Introduction of a chemical link between HTPB and VE by toluene diisocyanate coupling showed significant improvement in adhesive and mechanical strength.

KEY WORDS Reactive acrylic adhesive; vinyl ester; rubber-modified adhesive; joint strength; glass transition temperature; morphology.

1 INTRODUCTION

Reactive acrylic adhesives, also referred to as "second generation" or "modified acrylics," are an alternative to epoxy adhesives. They have the added advantages of rapid rate of strength build up at room temperature and better joint strength with a variety of substrates even with unprepared surfaces.[1] Reactive acrylic adhesive formulations[2] normally consist of two parts which are individually storage stable. The first comprises a solution of unsaturated oligomers and elastomers in acrylic monomers along with suitable stabilizers and the second contains appropriate activators to generate free radicals. When the two parts are brought into contact, polymerisation occurs by a free radical mechanism and no heat is required for the curing process.

The acrylate monomers most commonly used in reactive acrylic adhesives are methyl or short-chain alkyl methacrylates.[2] Methacrylated epoxy resin (vinyl ester resin) dissolved in methyl methacrylate monomer and cured with an organic peroxide catalyst can provide a reactive acrylic adhesive system. Vinyl ester resin (VE) provides unsaturation sites for cross-linking with methyl methacrylate (MMA) and the cured matrix gives excellent thermal and mechanical properties. But the VE/MMA based reactive acrylic adhesive is prone to fail catastrophically due to the brittleness of the cured matrix. The well-practised chemical technique discovered by McGarry and co-workers[3] for imparting toughness to brittle cross-linked polymers involves introduction of a rubber phase into the polymer matrix. When the low modulus rubber particles are dispersed and linked to the brittle polymer matrix, the force which induces and propagates cracks is dissipated by the rubbery phase and prevents the catastrophic failure of the adhesive joint. The most popular elastomers used to toughen acrylic adhesive formulations are chlorosulphonated polyethylene,[4] carboxyl- or vinyl-terminated butadiene/acrylonitrile copolymers[5] and polyurethane rubbers.[6] This paper describes the modification of a VE/MMA based reactive acrylic adhesive composition with a hydroxyl-terminated liquid polybutadiene (HTPB), an "inhouse" product developed for use as a solid propellant binder. The adhesive joint strength, mechanical properties, thermal stability and morphology of the reactive acrylic adhesive compositions containing varying levels of HTPB have been investigated. We also report the effect of modification of a vinyl ester resin with an isocyanate-terminated prepolymer, obtained from HTPB and toluene diisocyanate (TDI), on the properties of the adhesive formulation. Chemical toughening of epoxies with hydroxyl-terminated poly(butadiene-co-acrylonitrile) using TDI as coupling agent has been reported recently by Sankaran *et al.*[7]

2 EXPERIMENTAL

2.1 Materials

Araldite Gy 250	a liquid DGEBA resin, epoxy value -5.3 eq. kg^{-1}. (Hindustan Ciba Geigy Ltd., Bombay, India)
Methacrylic acid:	(Spectrochem Pvt. Ltd., Bombay, India)
Imidazole:	(Sisco-Chem Industries, Bombay, India)
Methyl methacrylate:	(BDH Chemicals, Poole, England)
Benzoyl Peroxide:	(Amrut Industrial Products, Bombay, India)
N,N dimethyl *p*-toluidine:	(Koch Light-Laboratories Ltd., England)
Hydroquinone;	(SD-Fine Chem Pvt. Ltd., Bombay, India)
Toluene diisocyanate:	(Bayers, FRG)
HTPB:	(Vikram Sarabhai space Centre, India). Table I gives the characteristics of HTPB.

2.2 Preparation of vinyl ester resin

Vinyl ester resin used for the study was prepared by reacting the epoxy resin with methacrylic acid, using imidazole as the catalyst, by a reported procedure.[8] A 2-L

TABLE I
Typical HTPB properties

Hydroxyl value (mg KOH g^{-1})	42.4
Acid value (mg KOH g^{-1})	0.3
Sp. gravity at 25°C	0.9055
Molecular weight (VPO)	2710
Viscosity at 30°C, Brookfield (cps)	6160

flask equipped with a mechanical stirrer, a condenser, a thermometer and N_2 gas inlet was charged with 1000 g epoxy resin, 480 g methacrylic acid, 1.2 g imidazole and 1 g hydroquinone. The flask was then purged with N_2 and heated slowly to 115 ± 5°C in an oil bath and held at that temperature with stirring until the acid value was reduced to below 10 mg KOH g^{-1}.

2.3 Preparation of —NCO terminated prepolymer

A 250 ml flask, equipped with a stirrer, reflux condenser and N_2 gas blanket was charged with 66.2 g HTPB, 8.7 g TDI and 0.66 g dibutyl tin dilaurate catalyst (—OH/NCO 1:2). The mixture was stirred at room temperature for one hour. Then 75 g methyl methacrylate was added and the flask was gradually heated to 60°C for two hours to produce a 50% solution of —NCO terminated prepolymer in methyl methacrylate monomer. The reaction was monitored by estimation of —NCO content by *n*-butylamine titrimetry. The NCO content of the solution was 1.5 wt%.

2.4 Adhesive formulation

A typical reactive acrylic adhesive formulation used for the study is illustrated in Table II.

Vinyl ester, HTPB, hydroquinone and *N,N* dimethyl *p*-toluidine were dispersed in methyl methacrylate monomer. Benzoyl peroxide (recrystallised from $CHCl_3/CH_3OH$, purity 98%) was added just before use of the adhesive.

The —NCO terminated prepolymer of HTPB and TDI was incorporated into the adhesive formulation by co-reacting into the —OH of the vinyl ester resin. The co-reaction was carried out at 60°C until the IR spectrum showed no band corresponding to the —NCO group (2270 cm^{-1}).

TABLE II
Typical composition of the reactive acrylic adhesive

Vinyl ester/liquid rubber	75 g
Methyl methacrylate monomer	25 g
Hydroquinone (stabilizer)	0.2 g
Benzoyl peroxide (iniator)	3.5 g
N,N dimethyl *p*-toluidine (accelerator)	0.2 ml

2.5 Test methods

2.5.1 *Joint strength* Lap shear strength and T-peel strength were determined on a B51 SWP aluminium alloy as per ASTM-D-1002 and ASTM-D-1876, respectively. The specimens were etched with $Na_2Cr_2O_7/H_2SO_4$, washed with tap water and dried. The adhesive formulation was applied on both sides over the area to be bonded and mated using contact pressure to a bond line thickness of approximately 0.08 mm and cured at room temperature for 24 hours. The joint strength was measured on an Instron model 4202 at a cross-head speed of 10 mm/min.

2.5.2 *Tensile properties* Tensile strength and % elongation at break of the cured adhesive formulations were measured from dumbells cast directly in a silicone mould. Dumbells were cured for 24 hours at room temperature and the stress-strain properties measured on an Instron model 4202 at a cross-head speed of 10 mm/min.

2.5.3 *Thermal properties* Differential scanning calorimetry (DSC) was used to determine the glass transition temperature (Tg) of the cured adhesive formulation. A DuPont Thermal Analyser with 902 DSC cell was used to take the DSC thermogram at a heating rate of 10°C/min. The DSC curve of the room-temperature-cured sample indicated a residual cure exotherm; therefore, the Tg was determined after soaking the sample at 120°C for 10 minutes.

The thermodegradative stability of the cured adhesive formulation was determined by thermogravimetric analysis (TGA) using a DuPont 951 Thermogravimetric Analyser at a programmed heating rate of 10°C/min. in N_2 atmosphere.

2.5.3 *Morphology* To investigate the morphology of the cured adhesives, a scanning electron micrograph (SEM) technique was used. The fractured surface of the tensile test specimen was cut and mounted on an aluminium stub using conductive silver paint. The specimen was vacuum coated with a thin layer of gold. A scanning electron micrograph of the fractured surface was then obtained using a Stereoscan 250 MK-3 Cambridge instrument at 1000× magnification.

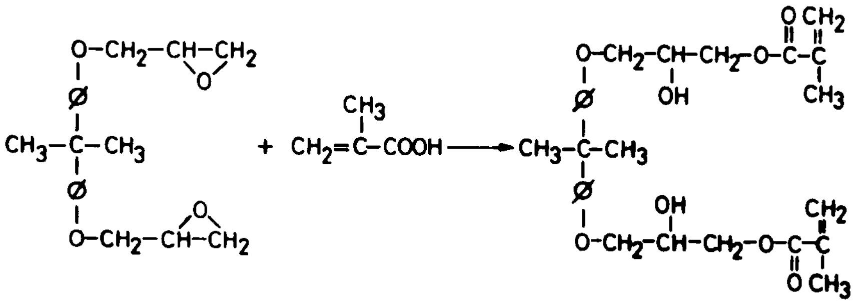


FIGURE 1 Chemical reaction of methacrylic acid with epoxy resin.

RESULTS AND DISCUSSION

A commercially available epoxy resin (diglycidyl ether of bisphenol A type, see 2.1 Materials) was converted into a vinyl ester resin by the addition of methacrylic acid to the epoxy group in the presence of imidazole as a catalyst. The reaction was followed by acid number, which was reduced to 8–9 mg KOH g^{-1}. The IR spectrum of the product showed absorptions at 3500 cm^{-1}

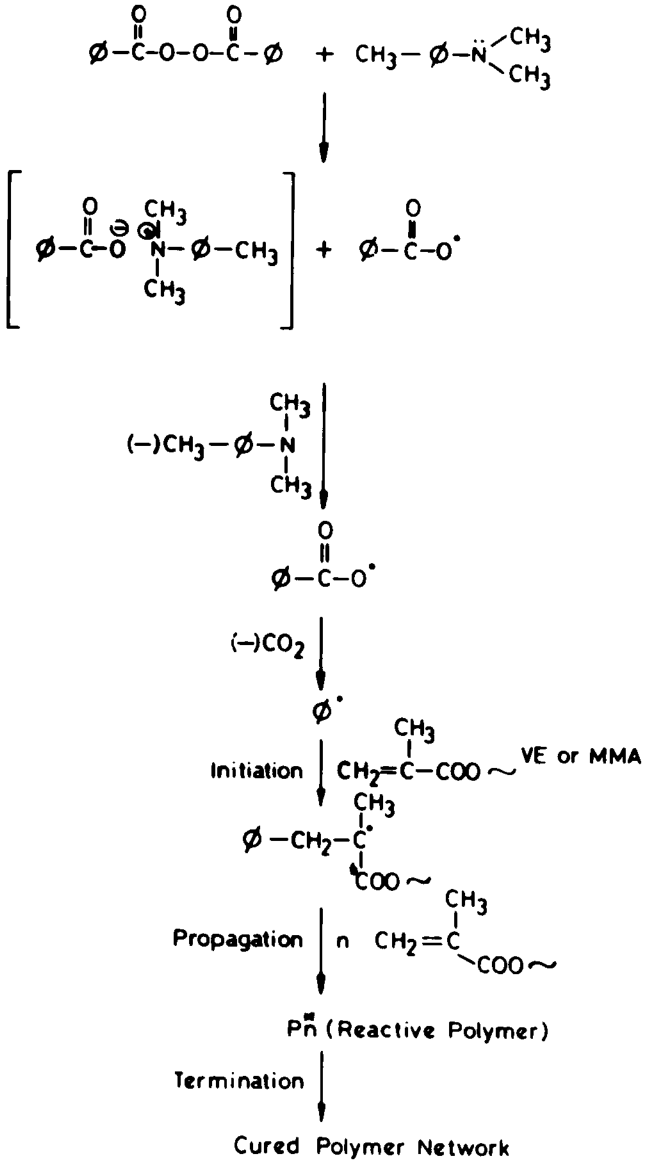
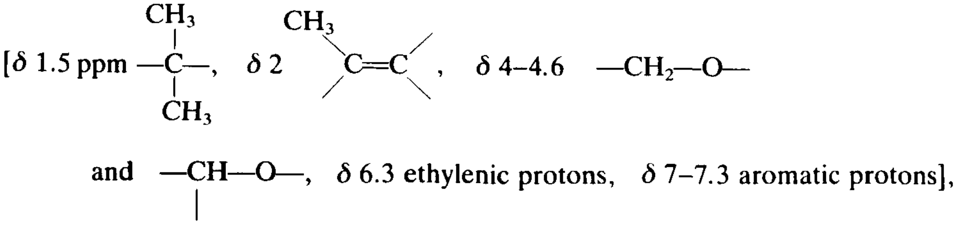


FIGURE 2 Cure reaction of the reactive acrylic adhesive.

(—OH), 1630 cm^{-1} (—C=C—) and 1730 cm^{-1} (ester carbonyl). No evidence of the epoxy group at 910 cm^{-1} was found. The values of ^{1}HMR showed agreement with the structure,



$$[\delta\ 1.5\,\text{ppm}\ -\overset{CH_3}{\underset{CH_3}{\overset{|}{\underset{|}{C}}}}-,\quad \delta\ 2\ \ \overset{CH_3}{\gt C{=}C\lt},\quad \delta\ 4\text{–}4.6\ \ -CH_2-O-$$

$$\text{and}\ \ \underset{|}{-CH-O-},\quad \delta\ 6.3\ \text{ethylenic protons},\quad \delta\ 7\text{–}7.3\ \text{aromatic protons}],$$

but the number of protons calculated are not in good agreement with the theoretical values, which might be due to side polymerization reactions.[9]

A solution of vinyl ester resin in methyl methacrylate monomer was used for formulating the reactive acrylic adhesive (Table II). When benzoyl peroxide was added to the solution of VE in MMA containing *N,N* dimethyl *p*-toluidine, an exothermic cure reaction proceeds rapidly at room temperature and a brittle, crosslinked polymer network was obtained. The free radicals produced by the induced decomposition of benzoyl peroxide by *N,N* dimethyl *p*-toluidine, initiate the polymerization reactions as represented in Figure 2. The cured matrix is a homogeneous random copolymer of vinyl ester and methyl methacrylate. This system cannot dissipate the stress in an adhesive joint due to its brittleness, which limits its application as an adhesive.

Effect of modification with HTPB on the properties of the acrylic adhesive

Figure 3 gives the structure of HTPB.[9] HTPB has a low polarity and solubility parameter compared with VE resin and MMA monomer, but it is soluble in the VE/MMA blend due to its low molecular weight. As the cure reaction proceeds, the mixture becomes cloudy and the elastomer phase separates due to its insolubility. SEM examination of the cured sample confirmed that rubber particles had precipitated randomly throughout the matrix (Figure 4). The rubber particles precipitate during the cure reaction because the Gibbs' free energy of mixing, ΔGm, changes from negative to positive as the molecular weight of the polymer increases.

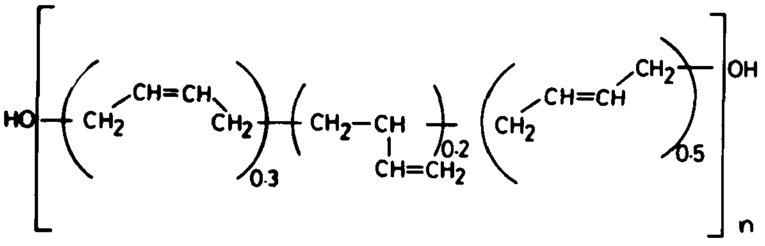


FIGURE 3 HTPB.

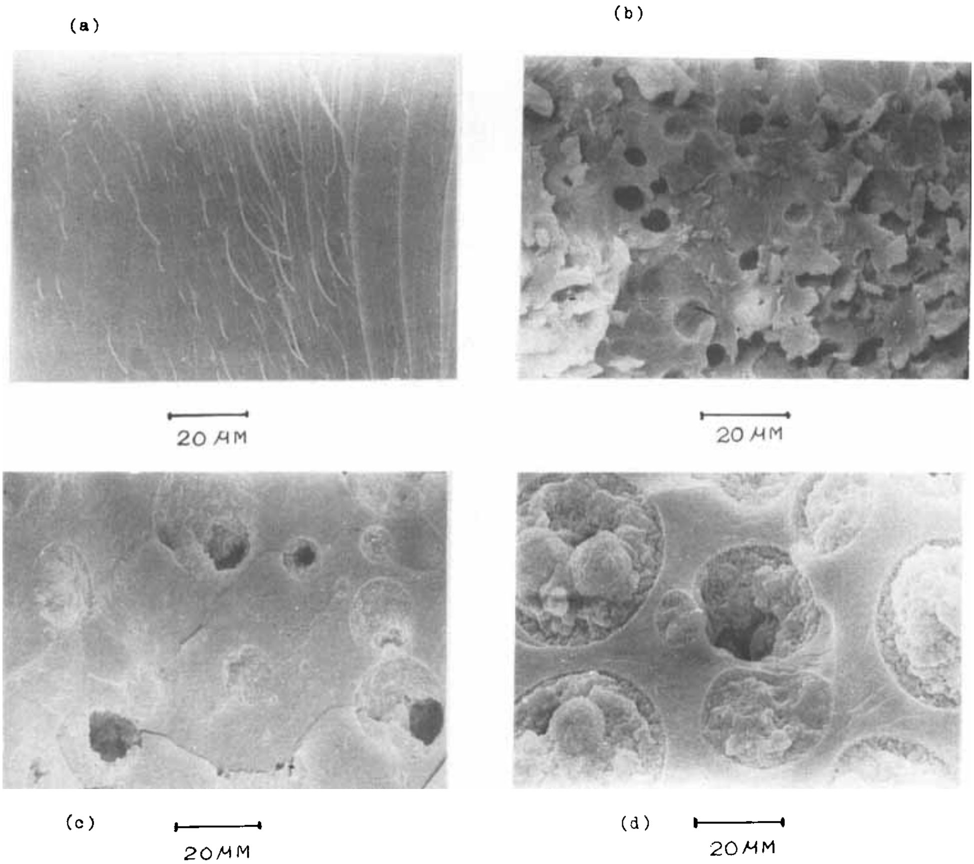


FIGURE 4 SEMs of tensile fractured surfaces of VE/MMA based reactive acrylic adhesive, (a) unmodified, (b), (c), (d), modified with 10, 20 and 30 wt% HTPB, respectively.

Figure 5 demonstrates the effect of HTPB content on the lap shear strength and peel strength of the reactive acrylic adhesive formulation. As shown, both peel strength and lap shear strength increased initially with HTPB content, reached a maximum and then began to decrease with further increase in HTPB. At about 10 wt% HTPB content, the material exhibits the best combination of shear and peel strength. The explanation for the influence of HTPB concentration on the adhesive joint strength is found in the morphology and chemistry of the system. The adhesive joint strength variation is related to the change in morphology as indicated in Figure 4. The cured VE/MMA blend is homogeneous and the failure is brittle in nature as is evident from the cracks seen as a river pattern (Figure 4a). The 10 wt% HTPB added formulation gave a heterogeneous phase containing a dispersion of rubber particles ranging in diameter from 3 μm to 8 μm (Figure 4b). These rubber particles enhance the resistance to brittle fracture by dissipating the stress, hence they improve the adhesive joint strength. On increasing the HTPB concentration, the rubber particles become larger and

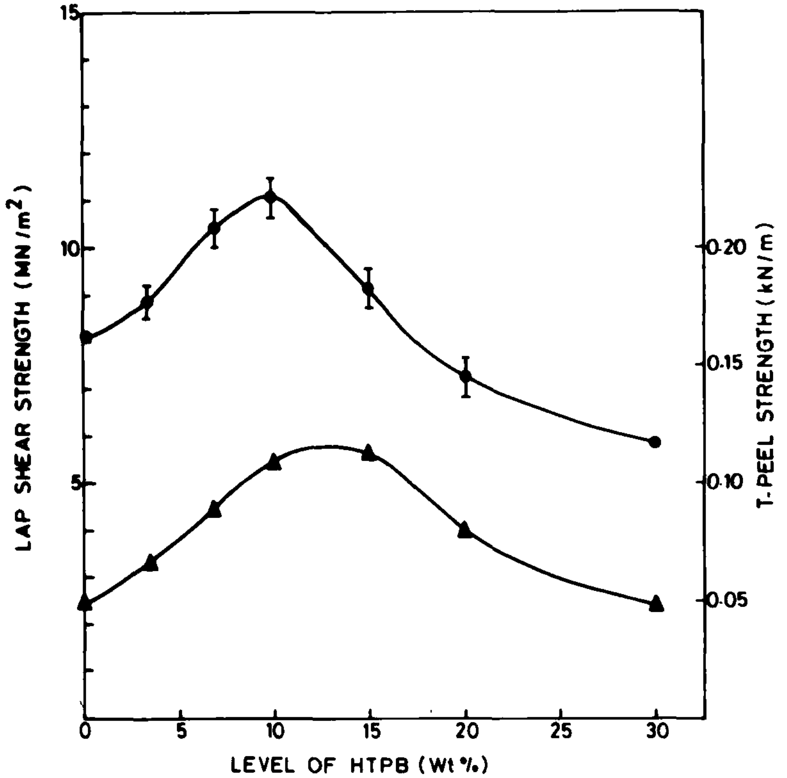


FIGURE 5 Effect of HTPB content on the lap shear strength (●) and T-peel strength (▲) of the VE/MMA based reactive acrylic adhesive.

irregular. The particle size ranges in diameter from 10 μm to 25 μm at 20 wt% HTPB and from 15 μm to 40 μm at 30 wt% HTPB (see Figure 4c and 4d). The larger particles are formed due to aggregation and may have a deleterious effect on the toughness. For the compositions containing 10, 20 and 30 wt% HTPB (respective volume fractions calculated from wt fraction and specific gravity are 11.04%, 22.08% and 33.1%), the volume fractions of the precipitated particles estimated from the area fractions of the micrographs are 12.4%, 29.5% and 47.6% respectively, which indicates that the precipitated particles are mixtures of HTPB and methacrylate.

The DSC curve of the room-temperature-cured adhesive sample indicated a Tg (~60°C) and residual cure exotherm (RCE). On post curing the sample at 120°C for 10 min, the Tg shifted to a higher temperature and no RCE peak was seen (Figure 6). The DSC analysis of the post-cured samples of the HTPB-modified acrylic adhesive (Figure 7) showed two distinct Tgs, a characteristic of an immiscible blend. We found no significant softening effect due to the addition of low concentrations of HTPB. But incorporation of high concentrations of HTPB shifted the matrix Tg (138°C) to slightly lower temperature and the rubber Tg

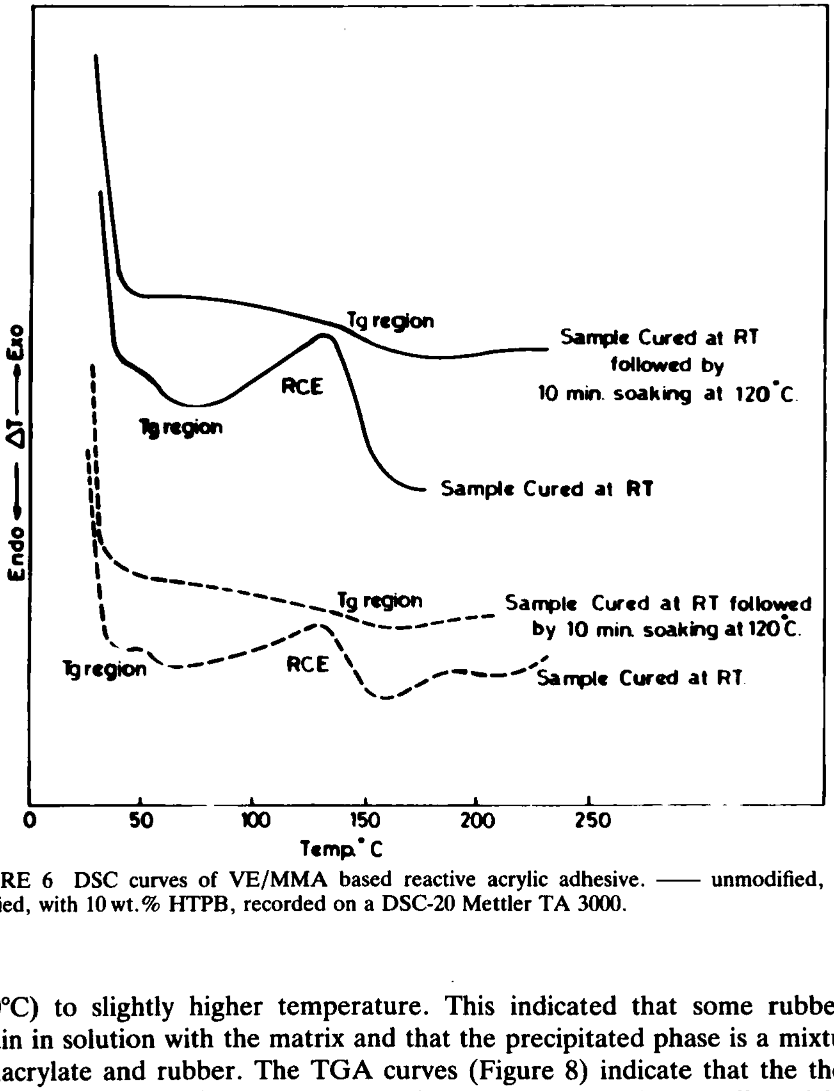


FIGURE 6 DSC curves of VE/MMA based reactive acrylic adhesive. —— unmodified, ---- modified, with 10 wt.% HTPB, recorded on a DSC-20 Mettler TA 3000.

(−80°C) to slightly higher temperature. This indicated that some rubber can remain in solution with the matrix and that the precipitated phase is a mixture of methacrylate and rubber. The TGA curves (Figure 8) indicate that the thermo-degradative stability (in N_2 atmosphere) of the adhesive is not affected by the incorporation of 10 wt% HTPB.

The variation of mechanical properties of the acrylic adhesive with HTPB concentration is illustrated in Table III. The cause of the lowering of tensile strength with increasing HTPB level may be inadequate bonding of the rubber particles. The polymerization of HTPB with benzoyl peroxide and *N,N* dimethyl *p*-toluidine is sluggish at room temperature and the mixture remained as a liquid even after 24 hrs. Comparison of the relative peak intensity at 1640 cm^{-1} ($>$C=C$<$) of the spectra of the samples immediately after mixing and after 24 hrs., showed a decrease of only 4% in the total concentration of double bonds. Based on this, it seems logical to assume that the double bonds in HTPB are not

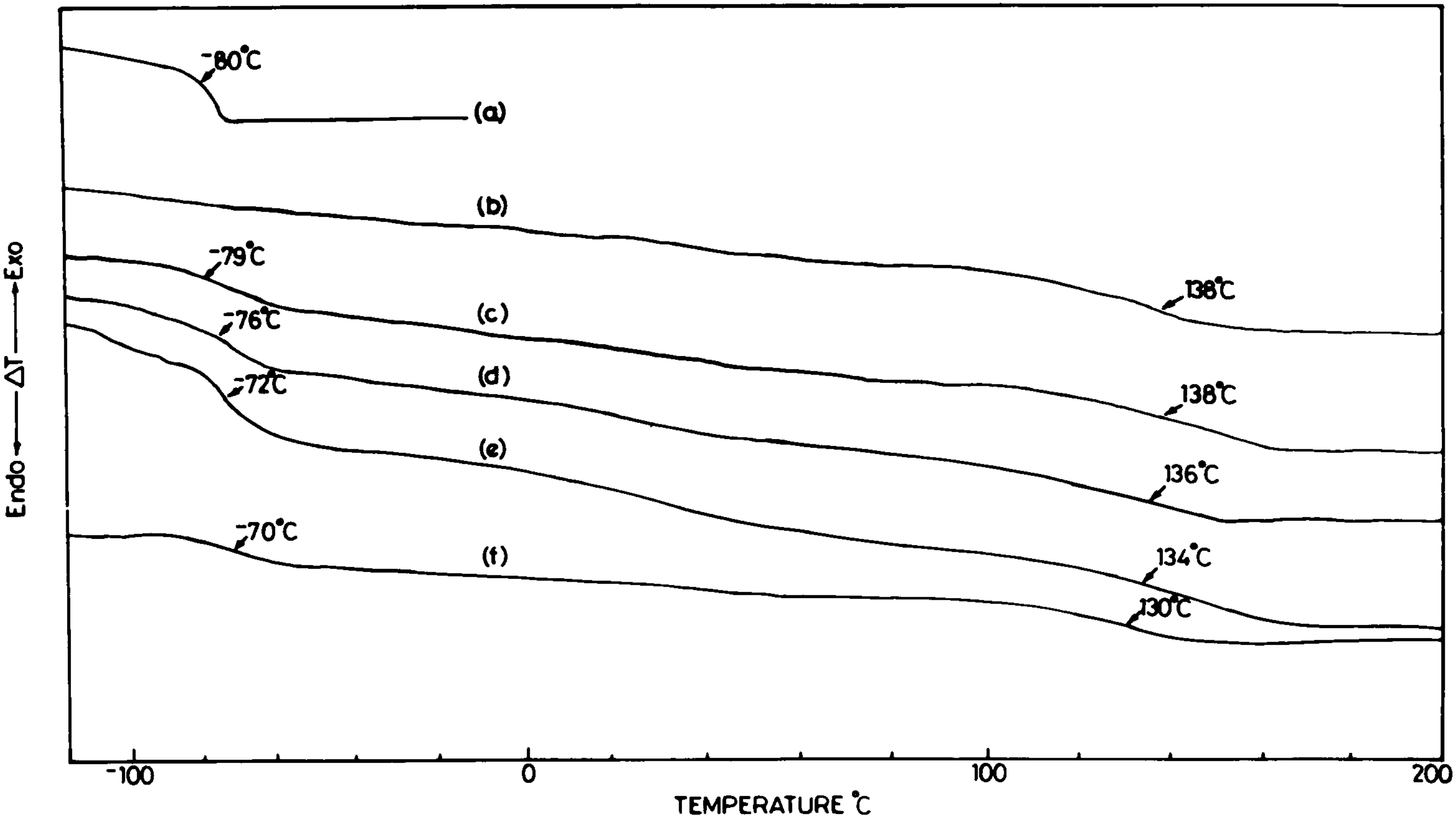


FIGURE 7 DSC thermograms of (a) HTPB, (b) cured $\overline{\text{VE}}$/MMA (unmodified), (c), (d), (e) cured VE/MMA modified with 10, 20 and 30 wt% HTPB, respectively (f) cured VE/MMA modified with —NCO terminated prepolymer of HTPB and TDI (rubber content 10 wt%).

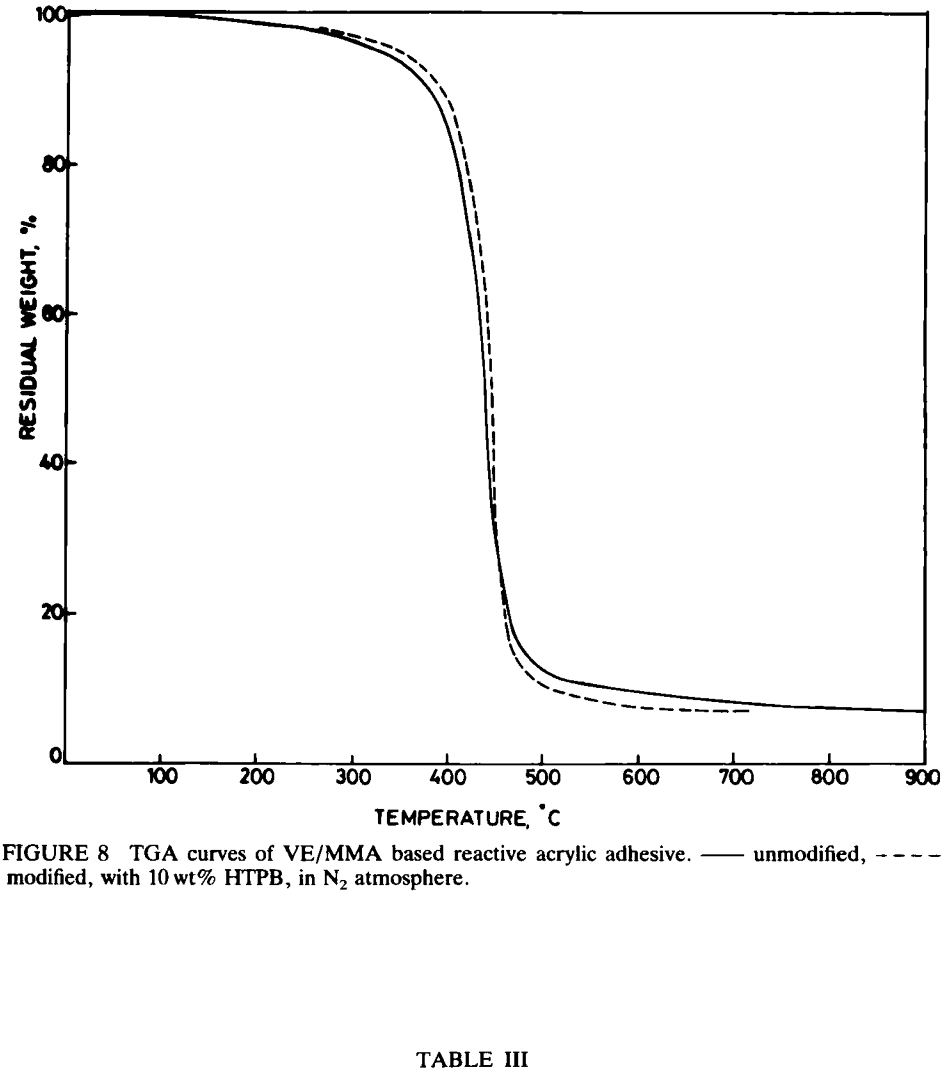


FIGURE 8 TGA curves of VE/MMA based reactive acrylic adhesive. —— unmodified, - - - - - modified, with 10 wt% HTPB, in N_2 atmosphere.

TABLE III
Effect of variation of concentration of HTPB on the mechanical properties of the VE/MMA based reactive acrylic adhesive

HTPB (wt%)	Tensile strength (MN/m^2)	Elongation at break (%)
0	39	3.5
3.5	38.2	3.7
7	32.1	2.7
10	30.8	2.9
15	27.9	2.7
20	14.9	2.9
30	8.9	2.9

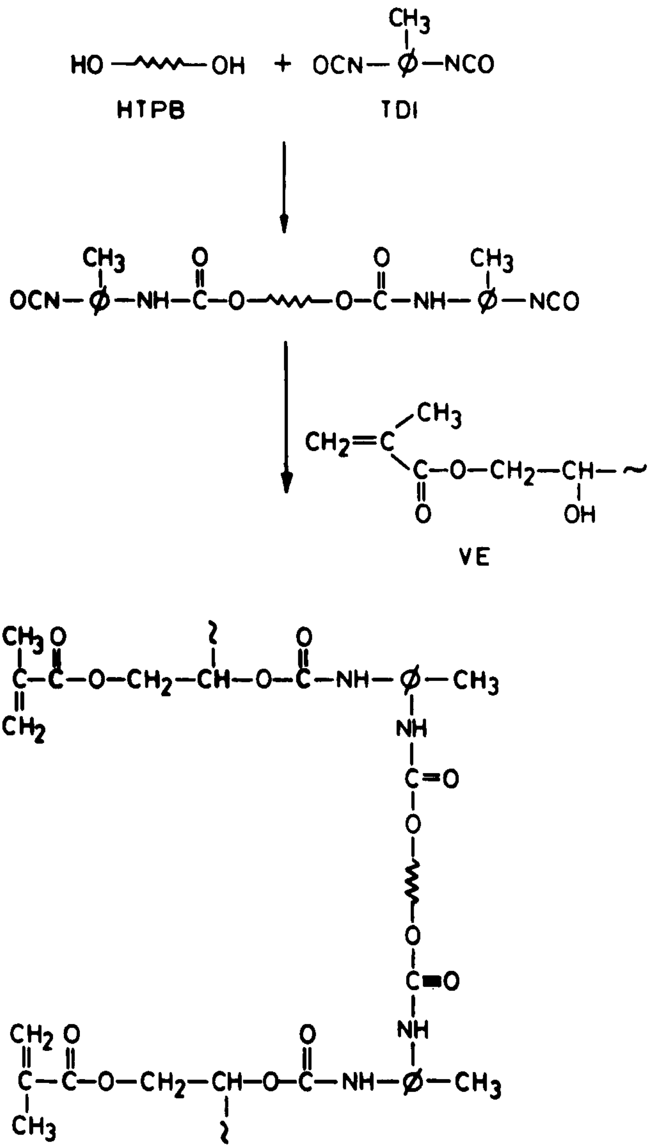


FIGURE 9 Coupling reaction of HTPB with VE resin.

capable of undergoing co-polymerization under the specified conditions and hence a decrease in strength with HTPB level results.

To improve the bonding between the rubber and the matrix, —NCO terminals were introduced into HTPB by reacting it with excess toluene diisocyanate so that it could couple with VE (Figure 9). The completion of the coupling reaction was indicated by the absence of the isocyanate peak (2270 cm^{-1}) in the infrared

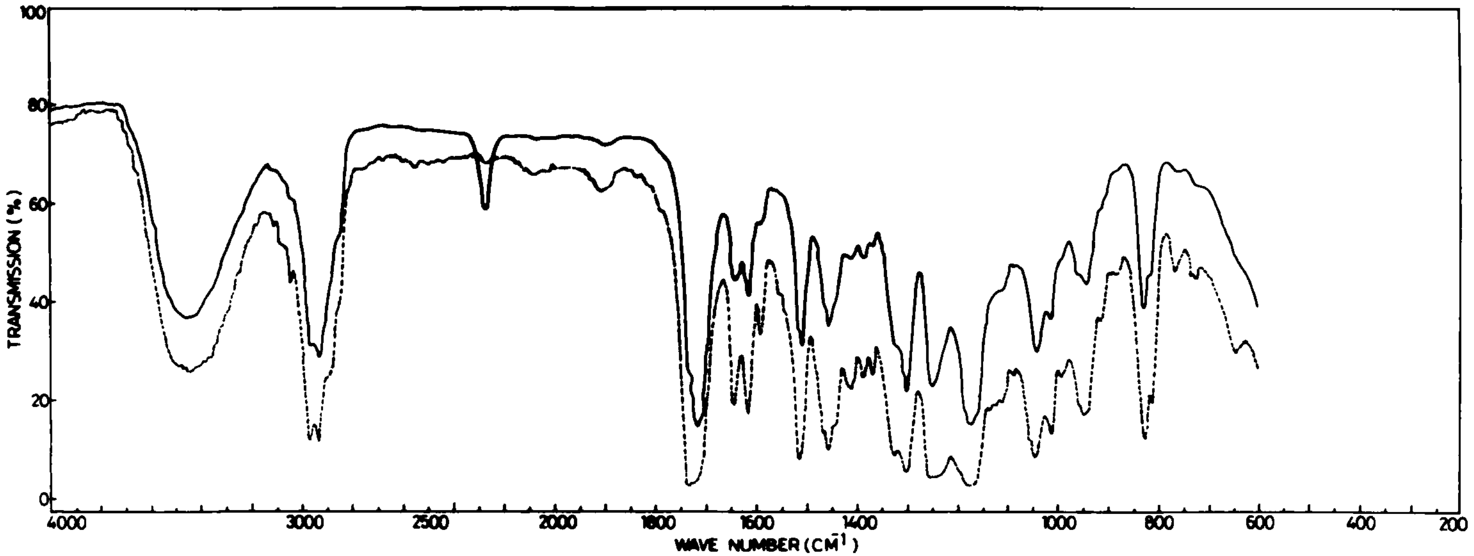


FIGURE 10 Infra red spectrum during the coupling reaction of VE with —NCO terminated prepolymer of HTPB and TDI. —— beginning, - - - - end, of the reaction.

TABLE IV
Effect of modification of the liquid rubber with reactive end group (—NCO)

Properties of VE/MMA based reactive acrylic formulation	Lap shear strength MN/m^2	Peel strength kN/m	Tensile strength MN/m^2	Elongation (%)	IDT[a] °C	Tmx[b] °C	Tf[c] °C
i. Modified with 10 wt% HTPB	12	0.11	30.8	2.9	410	455	525
ii. Modified with NCO terminated liquid rubber obtained from HTPB and TDI (rubber content 10 wt%)	15	0.14	40.2	4.8	426	490	550

[a] Initial decomposition temperature.
[b] Temperature at which rate of decomposition is maximum.
[c] Temperature at which decomposition almost complete.

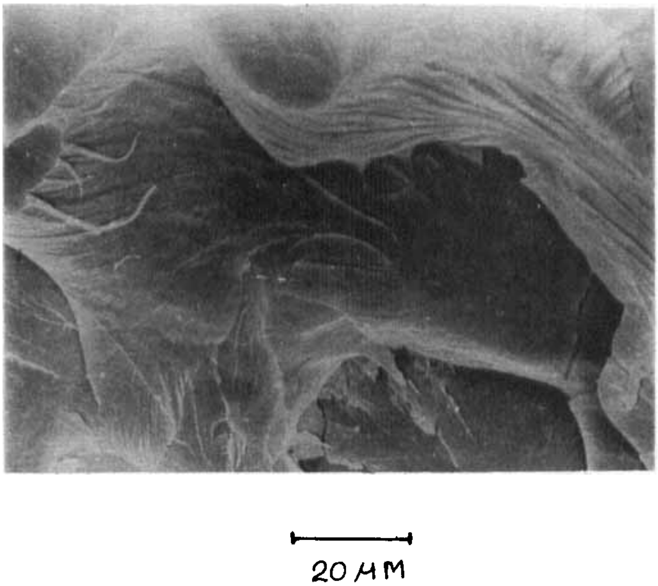


FIGURE 11 SEM of tensile fractured surface of VE/MMA based reactive acrylic adhesive containing 10 wt% HTPB modified with isocyanate.

spectrum (Figure 10). The effect of isocyanate (—NCO) modification on the properties of the acrylic adhesive formulation containing 10 wt% HTPB was studied. The adhesive strength, tensile strength, elongation at break and thermal degradative stability (in N_2 atmosphere) all were increased by the —NCO modification, as seen in Table IV. The increase in adhesive and mechanical strength can be attributed to the increase in chemical reaction between the rubber and the matrix through the urethane linkage, and to the increased miscibility of the rubber into the matrix. A SEM micrograph of the tensile fractured surface of the —NCO prepolymer modified acrylic adhesive (Figure 11) showed no phase separated particles, indicating better homogeneity. The DSC curve [Figure 7f] indicated two Tgs (two phases) and calculation from the decrease of Tg of the matrix using the Fox equation[11,12] indicated the presence of approximately 4.4 wt% phase-separated rubber (added rubber 10 wt%). The flexibilization of the adhesive by the —NCO prepolymer could be due to the increased miscibility of the rubber in the matrix, probably due to the presence of the better-interacting urethane group.

CONCLUSIONS

Improvements in adhesive properties were observed by the incorporation of low levels of HTPB to a vinyl ester/methyl methylacrylate (VE/MMA) based reactive acrylic adhesive, without altering its glass transition temperature. A maximum in adhesive strength was observed at about 10 wt% HTPB content and the system contains small rubber particles dispersed in the VE/MMA matrix. The lap shear strength of the VE/MMA containing 10 wt% HTPB was markedly enhanced when HTPB was reacted with toluene diisocyanate and coupled with VE. The isocyanate modification decreased the Tg of the system probably due to the increased miscibility of the rubber in the matrix.

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