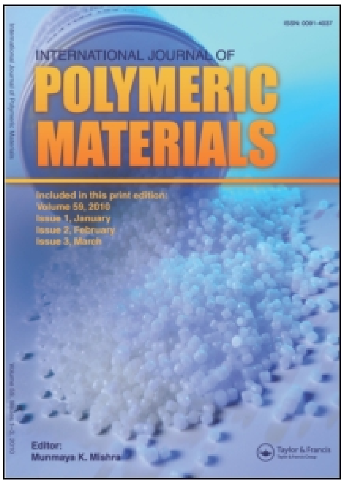

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BOND STRENGTH IMPROVEMENT OF POLYURETHANE ADHESIVE BY GRAFTING 2-HYDROXYETHYL METHACRYLATE ON POLYOL BACKBONE

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A series of acrylated polyols were prepared by grafting 2-hydroxyethyl methacrylate (HEMA) on to polyol backbone prepared from vegetable oil fatty acid and epoxy resin. Grafting was carried out by free radical mechanism on conjugated double bond present in the polyol using benzoyl peroxide (BPO) as an initiator. Polyols and polyurethane adhesives were characterized by IR spectroscopy. Polyurethane adhesive synthesized from the modified polyols were found to provide better peel strength to styrene butadiene rubber (SBR) joints. Mode of failure was studied using Scanning Electron Microscopy (SEM). Improvement in cohesive strength of the adhesives resulted in high bonding strength. Comparative study has been carried out to determine the effect of acrylation on polyurethane adhesive by Green strength, Curing behavior, and Chemical resistance studies. Loading of 20% HEMA gave significant results. However, 15% loading of HEMA resulted in a sample with highest peel strength.

Keywords: acrylated polyol, two-pack polyurethane adhesive, peel strength

INTRODUCTION

Polyurethane is a class of adhesive material that over 40 years have developed a reputation for reliability and high performance in many applications including the footwear industry, packaging, furniture assembly, and plastic bonding [1]. Due to the segmented nature of polyurethane, it can be tailor-made to fit the application. For many years great effort has been put on synthesizing and modifying polyols

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from renewable resources [2–4]. One of the important areas of work was to modify polyols using acrylic monomer on the double bond present in the backbone of oil/oil derived material [5–8]. The advantages of polyurethane derived from such modified polyols are fast drying with improved durability and chemical resistance.

Many attempts have been made to modify polyols using various acrylic monomers to improve their characteristics in coating application [9–12]. Much less attention has been paid to study the effect of polyol modification by acrylic monomer on two pack polyurethane adhesive [13].

The aim of this work is to improve the bonding strength of polyester polyol synthesized using epoxy resin and oleic acid as raw materials. Modification of polyol was done by incorporation of an acrylic monomer, that is, 2-hydroxyethyl methacrylate (HEMA), by generating free radicals at the unsaturation available in the polyol. Incorporation of HEMA in polyol structure not only increases the molecular weight of the polyol but also provides hydroxyl functional group to form cross-linked polyurethane structure. The effect was studied of the amount of HEMA on the adhesion of polyurethane adhesive to rubber substrate.

EXPERIMENTAL

Materials

Epoxy resin (DGEBA type) of average molecular weight 400 gm/mole was supplied by SYNPOL, Ahmedabad, India. Oleic acid was purchased from s.d. fine chemical, Bombay, India. Triethylamine and benzoyl peroxide were procured from Merck, USA and used directly. Toluene Diisocyanate (TDI) adduct (13.5% free NCO content) and 2-hydroxyethyl methacrylate were received from Marrygold Industries, Vallabh Vidyanagar, India. Prior to use, HEMA was made inhibitor free with 2% solution of sodium hydroxide followed by washing with distilled water till it became free from alkali. Commercial adhesives and Styrene Butadiene Rubber (SBR) were purchased from local traders.

The chemical reagents and solvents used for experimental procedure were of laboratory grade.

Synthesis of Epoxy Ester Polyol

141 gm oleic acid and 100 gm epoxy resin (molar ratio 2:1) were taken into 500 ml three neck flask along with 75 ml of 1,4-dioxane as solvent. The flask was equipped with mechanical stirrer, nitrogen inlet, thermometer pocket, and water condenser. Nitrogen was dried and

purified before use by passing through pyrogallol solution and $CaCl_2$. 1 gm triethylamine was added into the reaction kettle as a catalyst. Temperature was raised slowly and maintained at 100–102°C by means of solvent reflux. The reaction yielded epoxy ester polyol by ring opening of epoxide functional group with carboxylic acid. The formation of product was confirmed by measuring acid value (which tends to decrease to the final value of zero) of the reaction mass. The reaction was completed within four hours. The solvent was distilled off by vacuum. The reddish brown transparent product was stored in airtight container.

Synthesis of Acrylated Polyol

100 gm of epoxy ester polyol was taken into a three-necked flask equipped with an efficient water condenser, mechanical stirrer, and a thermometer pocket. The reaction mixture was heated and brought to reaction temperature 90°C. BPO (0.05% by wt. of monomer) was previously dissolved in HEMA. This HEMS solution was added dropwise to the reaction flask over a period of three hours. During this time, the temperature was maintained at 90–95°C. After completion of the addition of HEMA, the reaction was stirred at the same temperature for three hours. The product was stored in an airtight container.

A series of acrylated polyols was synthesized using different weight ratios of Polyol:HEMA under identical reaction conditions. Hydroxyl value of the synthesized polyols was measured by acetic anhydride and pyridine method [14]. Hydroxyl value of different acrylated polyols is tabulated in Table 1.

Rubber Strips Preparation

SBR rubber strips for lap shear strength measurement were cut into pieces of 6”×12” as per ASTM D 1876. The rubber surface was treated

TABLE 1 Hydroxyl Value of HEMA Grafted Polyols

% HEMA (by wt. polyol) loaded on polyol	Hydroxyl value mg of KOH/gm
0%	120
5%	132
10%	151
15%	160
20%	230

with sulphuric acid followed by wash with cold water. It was then treated with 15% ammonium hydroxide solution to remove traces of sulphuric acid. Improvement in surface wettablility of rubber was measured by contact angle measurement by *Ram'e Hart* Goniometer. Untreated rubber (SEM photograph-M) showed high contact angle 94 and 80 for water and ethane diol respectively whereas for the treated rubber the contact angle was 30 and 23, respectively. The improvement in surface wettability was, in part, because of formation of microcraks on the rubber surface (SEM photograph-N).

Adhesive Preparation

The adhesive was prepared in clean and dry 150 ml beaker. TDI based adduct was added in the required amount (on the basis of NCO/OH = 1.0) to previously weighed polyol component. The mixture was well mixed using glass rod for about one minute and used thereafter.

Bonding of Substrates [ASTM D 1876]

The adhesive was applied with the help of a brush on both rubber substrates uniformly. The area of application was 6" × 9" and it was adhered immediately. Fixed load of 5 kg was placed on the rubber joints for 24 h. After that, the rubber joints were kept at room temperature (30°C) and relative humidity (RH) of 50 ± 5 for 7 days. The rubber sheets were cut into 1" × 12" to carry out the tests.

Peel Strength

180° peel strength of rubber joints was measured by Universal Testing Machine at a peel rate 0.1 m/minute. At least five tests have been carried out for each test and average values are given in Table 2.

Study of Green Strength and Curing Time

Green strength is one of the important aspects for adhesives as it shows the ability of an adhesive to hold the substrates together when brought into contact and before the adhesive develops ultimate bond properties when fully cured.

For this purpose PU adhesive synthesized using normal polyol and polyol grafted with 15% HEMA were lap joined and tested at a regular interval of days till the lap shear strength showed no significant difference. The data are tabulated in Table 3.

TABLE 2 Peel Strength and Mode of Failure Data

% HEMA grafted on polyol	Peel strength KN/m	Mode of failure
0%	3.1	Cohesive
5%	3.9	Cohesive + Adhesive
10%	4.7	Cohesive + Adhesive
15%	7.2	Interfacial + Cohesive failure of rubber
20%	5.3	Mainly cohesive
Desmocoll 510–based PU adhesive	6.4	Adhesive

Effect of Chemical Resistance

Rubber pieces bonded with the adhesives prepared from normal polyol, acrylated polyols, and commercial polyol were kept in cold water (30°C) for one day. Then they were taken out, dried at room temperature (30°C and RH 50 ± 5) for one day and the lap shear strength was determined. Similarly, bonded pieces were immersed in hot water at 100°C, in acid pH 2 and alkali pH 10 both at 80°C for one hour [15]. After that, the lap shear strength was determined as described earlier. The resulting data are presented in Table 4.

Gel Permeation Chromatography

Molecular weight of the polyol and acrylated polyol were determined by Gel permeation chromatography using the Perkin Elmer Series 200.

TABLE 3 Green Strength and Curing Time

No. of days	0% HEMA based PU adhesive KN/m	15% HEMA based PU adhesive KN/m
1	0.4	2.4
2	0.7	4.7
3	1.3	5.9
4	1.9	7.2
5	1.9	7.1
6	2.7	7.2
7	2.9	—
8	3.1	—
9	3.2	7.3
10	3.1	7.2

TABLE 4 Chemical Resistance

	Average lap shear strength KN/m (After treatment)			
PU adhesive	Cold water	Hot water	Acid pH 2	Alkali pH 10
0% HEMA based	2.6	1.8	1.1	0.9
15% HEMA based	6.8	6.0	5.8	5.5
Desmocoll® 510 based	6.5	5.2	5.4	5.8

The molecular weight of the epoxy ester polyol was 1011 and that of acrylated polyol 1440. The conclusive evidence of the formation of the graft polymer of HEMA with liquid polyol is attained by sharp chromatogram. Also, the polydispersity of the liquid polyol, which was found to be 1.2 and 1.3 in grafted polyol, showed good homogeneity in the polyol and acrylated polyol.

FTIR Spectroscopy

In Figure 1 the IR spectrum of epoxy ester polyol synthesized from oleic acid and epoxy resin shows the presence of aromatic ether at 1250 cm^{-1}. Large amount of methylene groups showing its presence by strong band at 1450 cm^{-1} and medium band at 730 cm^{-1}. The Band at 1710 cm^{-1} is attributed to ester linkage, which forms by the reaction between carboxylic group and epoxy ring. Also, the absence of a band at 980 cm^{-1} confirms the formation of epoxy ester polyol. Ring opening of epoxy group yields hydroxyl group showing a band around 3500 cm^{-1} in the yielded product.

Comparative IR spectra of epoxy ester polyol and acrylated polyol are shown in Figure 2. The intensity of the characteristic band of vinyl system at 1620 cm^{-1} decreased in the acrylated polyol, confirming the grafting at the conjugated double bond. The strength and broadness of the peak around 3500 cm^{-1} confirms the increase of hydroxyl functional group due to incorporation of HEMA. The broadness of the band around 1700 cm^{-1} increased due to an increased ester linkage concentration. This increment is because of the presence of ester linkage in the HEMA structure.

Figure 3 shows the IR spectrum of the polyurethane synthesized from acrylated epoxy ester polyol. The characteristic carbonyl stretching of urethane linkage was observed at 1735 cm^{-1}. The absorptions resulting from NH stretching and bending vibrations are observed at 3330 cm^{-1} and 1560 cm^{-1} respectively. IR spectra of polyols and PU clearly indicate the formation of PU by the absence of OH

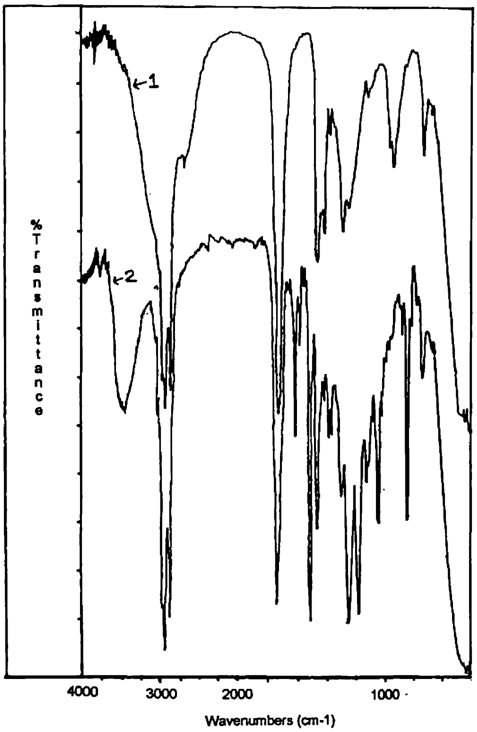

FIGURE 1 IR spectrum of Oleic acid (1) and Epoxy ester polyol (2).

frequency of polyol and presence of NH frequency. The bands at 883 cm^{-1} and 762 cm^{-1} are due to substituted aromatic ring of TDI.

Table 2 shows peel strength data of polyurethane adhesive synthesized from epoxy ester polyol having different amount of HEMA grafted on polyol backbone. The data reveal that the amount of HEMA directly affect the final bonding strength of polyurethane adhesive. As the amount of HEMA in the polyol increases the peel strength increases significantly up to a point. The mode of bond failure is mainly Cohesive + Adhesive type (Figure 4, SEM photograph-P) in the epoxy ester polyol based adhesive. It suggests that the low peel strength value is mainly due to low cohesive strength of the bulk adhesive material. The mode of failure changed to cohesive failure + interfacial failure of rubber surface (SEM – photograph-Q) when HEMA grafted polyol was used. This increase in peel strength and change in mode of failure is attributed to change in polyol structure by grafting with HEMA. Grafting with HEMA on the conjugated double bonds not only increased the molecular weight of the polyol but

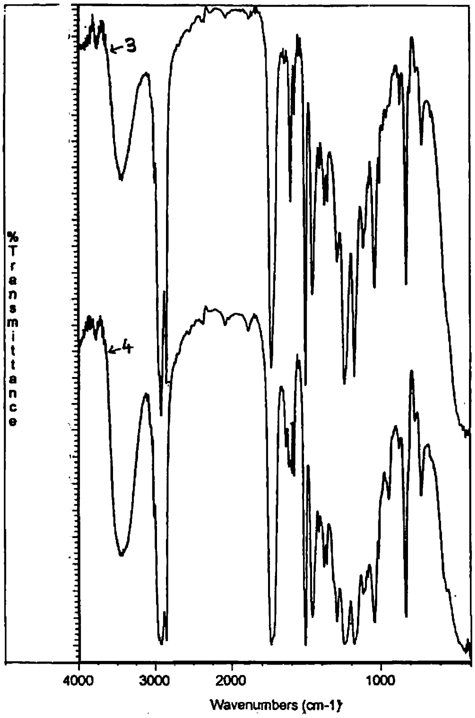

FIGURE 2 IR spectrum of Epoxy ester polycol (3) and HEMA grafted polyol (4).

also increased the crosslinking density (as grafted HEMA provide hydroxyl group to the polyol structure), which in turn provided a polyurethane network having high cohesive strength. Increase in the cohesive strength of the polymer network improved the mode of failure and the bond strength.

After a significant increase in the bond strength, the trend reversed for the PU adhesive synthesized using polyol grafted with 20% HEMA. This is because the high amount of acrylic present in the polyol structure produces a brittle adhesive that tends to fail at lower peel strength. So, polyurethane adhesive prepared from polyol grafted with 15% HEMA by weight of polyol was found to give the best bonding strength.

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FIGURE 4 SEM photograph of SBR rubber surface (M), Sulphuric acid–treated rubber (N), mixed failure (P) for non-acrylated polyol–based adhesive and Interfacial failure (Q) for acrylated polyol based adhesive.

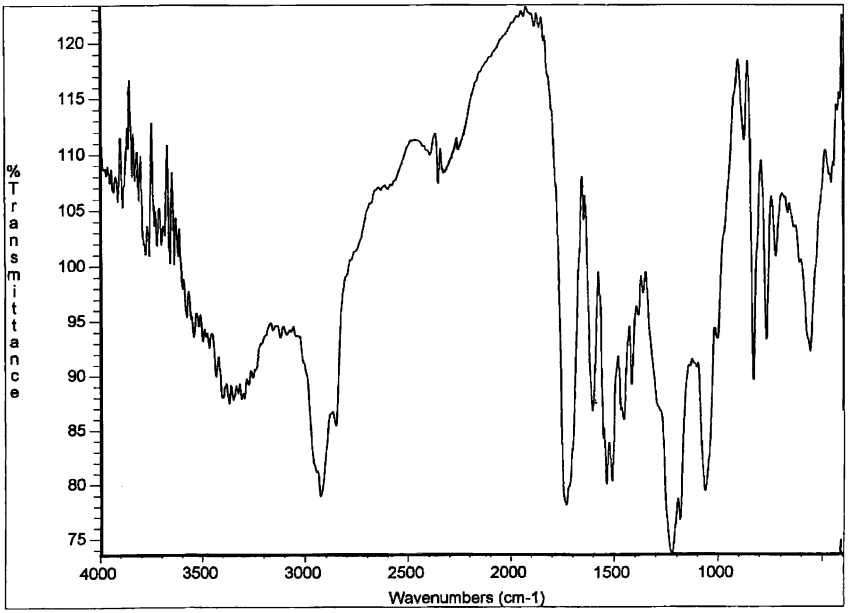

FIGURE 3 IR spectrum of Polyurethane based on acrylated polyol.

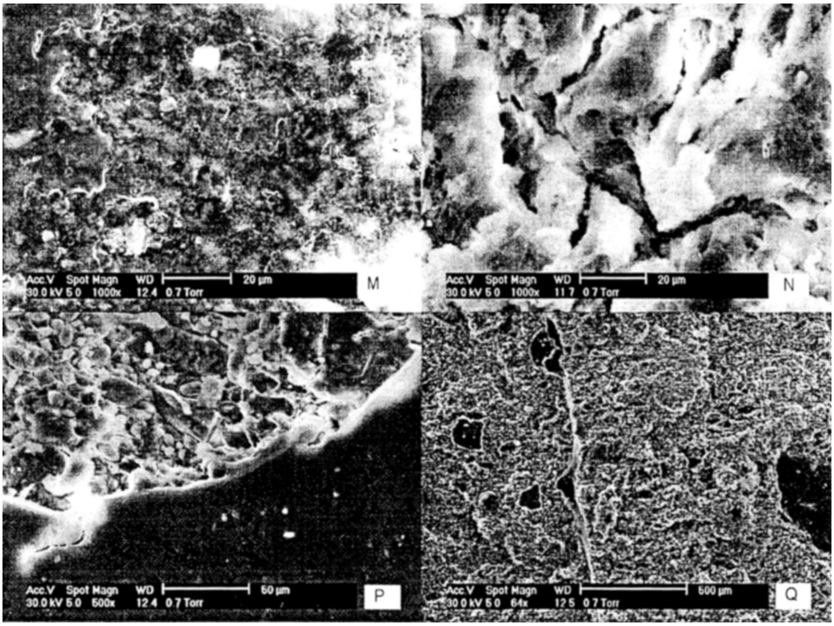

Table 3 shows Green strength and time required for an adhesive to get fully cured. PU adhesive based on acrylated polyol have better green strength than the normal polyol. Also, the time required for an adhesive to get completely cured is decreased for polyol grafted with HEMA. This is because of the fast drying property of acrylics.

Table 4 shows data of chemical resistance of PU adhesive based on polyol, grafted polyol, and commercial polyol. The data suggest that acrylic based adhesive has a very high chemical resistance compared to normal polyol-based adhesive. This might be because a higher crosslinked polyurethane network any more efficiently resist a chemical attack.

A commercial polyol, desmocoll 510 (Bayer AG, Germany), was compared with the synthesized polyol for the adhesive strength. Lap shear value of the synthesized adhesive is almost near the commercial one and has a better chemical resistance than the commercial adhesive.

CONCLUSION

Acrylation of polyol was found to be one of the possible ways to improve the cohesive strength of polyurethane adhesive, which improves bonding strength. Incorporation of hydroxyl group containing acrylic monomer improves the chemical resistance, green strength, and curing time. The amount of acrylic monomer directly affects the cohesive strength and final bonding strength and a too high amount of grafting may produce an adverse effect.

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