

Bio-acrylic polyols for two pack polyurethane coating

J V Patel, S D Desai and V K Sinha*

Department of Industrial Chemistry, V P & R P T P Science College, Vallabh Vidyanagar 388 120

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The feasibility of starch and non-edible oil in liquid polyester polyol synthesis and their modification by using acrylic and vinyl monomers is studied. Polyurethane coatings are formulated by reacting synthesized polyols with aromatic isocyanate adduct. Performance properties of oil and bio-acrylic polyol based polyurethane coatings are compared. It is found that acrylation of polyol improves the overall performance of the coating. Synthesized polyols and polyurethane are characterized by Fourier transform infrared spectroscopy (FTIR), Gel permeation chromatography (GPC), and Differential scanning calorimetry (DSC).

Keywords: Bio-acrylic polyols, Polyols, Polyurethane, Coating

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Introduction

Polyurethanes are rapidly developing products of coating industry having a unique combination of performance and application properties¹. The wide commercial exploitation of polyurethane is restricted in India for various reasons, largely related to the poor availability of raw materials and their high price in the local market. To cut down the cost of polyurethane the use of biological²⁻⁷ material for the synthesis of polyols is already reported. Thus, one of the important areas of the present day research in the surface coating is to explore the potential utility of renewable and non-conventional raw materials for preparation of resins. The most common among these materials are starch, cellulose and various oils.

Attempt has been made to synthesize liquid polyols for polyurethanes by using starch and non-traditional oil, i.e., argemone oil and modification of this oil based polyol was done by free radical graft copolymerization by using acrylic and vinyl monomers viz., 2-hydroxyethylmethacrylate (HEMA) and styrene. Biomaterials are combined with acrylic and vinyl monomers with a view to obtain the tailor made surface coatings. Also, acrylic polyols are the most widely used polyol nowadays. With the increasing industrial use of polyurethane coatings; there has been an enormous growth in demand for acrylic polyols within the span of just few years⁸. Literature survey also shows that development of

acrylic based polymeric coating is a topic for research since last decade⁹⁻¹⁵.

These combined vehicles offer the possibility of uniting the cost-effectiveness, desirable application, and wetting properties of the oil moiety with the strength, chemical and solvent resistance of acrylic moiety. Two pack polyurethane coatings were formulated by using oil based and bio-acrylic polyols as a base component and aromatic isocyanate adduct as a hardener component. The performance properties of the different coating formulated were evaluated by standard test methods.

Materials and Methods

Starch was extracted from potatoes and freed from amylopectins by toluene extraction¹⁶. TDI used for the adduct formation, HEMA and styrene was supplied by marigold coatings Pvt. Ltd, Vithal Udyogagar, Gujarat. Argemone oil was extracted by using soxhlet extractor using hexane as a solvent. The chemical and solvents used for the work were of analytical reagent grade.

Glycosylation of Starch

Glycosylation of starch with ethylene glycol in the presence of sulphuric acid as a catalyst was carried out by the reported method in our earlier work¹⁷.

Alcoholysis of Argemone Oil with Glycol Glycoside

In a typical alcoholysis process the reactant ratio used was 1:10 (wt/vol) of glycol glycoside and argemone oil, respectively. The reaction was carried out under nitrogen blanket at 220-230 °C and 125 mm Hg pressure. In a three-neck flask 500 mL of oil and 1.4 g of lithium hydroxide catalyst were heated with constant stirring up to 150 °C and then 50 g of glycol glycoside was added to it at 125 mm Hg pressure. Reaction mixture was heated with constant stirring at 220-230 °C for 1h. After completion of reaction the mass was cooled to room temperature. The polyol thus obtained was analyzed for its hydroxyl value by acetic anhydride and pyridine method¹⁸. Hydroxyl value of the polyol was found to be 100 mg of KOH/g of sample. Polyol thus synthesized does not require any further purification as it was found to give transparent film.

Acrylation of Argemone Oil Based Polyol

Acrylation of argemone oil based polyol was done by using different amount of HEMA along with styrene. Table 1 shows the amounts of various raw materials used in the reaction.

Argemone oil based polyol and xylene were taken in a 250 mL four-neck flask fitted with an addition funnel, thermometer, nitrogen gas inlet and mechanical stirrer. Temperature was raised to 100 °C with stirring and required amount of previously purified monomers along with dissolved benzoyl peroxide initiator (0.5 per cent by wt of monomer) were added slowly from the addition funnel for 2h at 100 °C. After completion of addition the reaction was continued for further 2h. The mass was then cooled to room temperature and acrylated polyols were tested for viscosity, colour and hydroxyl value.

Isocyanate Adduct Formation

Isocyanate adduct of TDI with TMP and isooctanol was prepared by the method reported in our earlier work¹⁷. Percentage NCO content of adduct was found to be 12 per cent by butyl amine method.

Table 1— Batch formulation for different polyols

Set no	Weight of AOP g	Weight of HEMA g	Weight of styrene g	Total g
I	75	20	05	100
II	75	15	10	100
III	75	10	15	100

Polyurethane Coating Formulation

Two pack polyurethane coating system was formulated by using bio-acrylic polyol and oil based polyol as a base component and isocyanate adduct as a hardener component. Isocyanate adduct was mixed with previously weighed polyol component on the basis of equivalent weight in different proportion (NCO : OH) to obtain various coating formulations. The mass was thoroughly mixed with the help of glass rod and then it was applied with the help of 38 mm nylon brush on the pre-treated¹⁹ MS (mild steel) panels. MS panels were left at room temperature for complete curing (72 h) before testing their performance properties.

Results and Discussion

Acrylation Process

All the samples of bio-acrylic polyols were found to be clear when tested by taking a drop of sample on a glass plate. Addition of monomer takes place at the unsaturation present in the polyol. It was found that some homopolymer was also formed when HEMA concentration was high; it was removed by skimming off as it is in the form of thin solid film. Also up to some degree homopolymer formation is tolerable as copolymer formed in sufficient amount solubilises it²⁰. In the case of excessive or complete homopolymerization of acrylic monomers the product would have resulted in to a hazy mass because of non-compatibility of polystyrene and poly-HEMA with the oil based polyols²¹.

Acrylation was confirmed by measuring hydroxyl value, which increases with the increase in the content of HEMA. In some cases the hydroxyl value was found to be lower than their theoretical values; it was due to homopolymer formation (poly-HEMA), which was removed from the polyol as it is of no use for the end application as polyurethane coating.

Acrylation was also confirmed by gel permeation chromatography which indicates increase in molecular weight of the argemone oil based polyol after acrylation. Table 2 indicates the results for the hydroxyl value and the molecular weight of the polyols.

Performance Properties

The performance properties were evaluated for all the bio-acrylic polyol based polyurethane resins by Indian standard test methods²² and were compared with non-acrylated polyurethane resins from the argemone oil based polyols. All the samples were

Table 2 — Hydroxyl value and molecular weight of various polyols

Set no	Hydroxyl value	Molecular weight
AOP	100	1436
I	186	3170
II	164	—
III	143	—

tested for gel time, impact hardness, scratch hardness, flexibility, percentage adhesion, chemical and solvent resistance. Results obtained are discussed subsequently.

Drying Time and Gel Time

It was found that drying time and gel time of the acrylated polyurethane resin were less than that of non-acrylated polyurethane resin. Also it was found that it decreases with increase in acrylic percentage. This should be due to incorporation of acrylic and vinyl monomers in the polyols. Acrylic monomers increase the molecular weight²³, and therefore fewer crosslinks are required to form a coherent film²⁴ or to reach the dry stage²⁵. Table 3 shows the results for gel time and drying time of acrylated (Set I, II and III) and non-acrylated polyurethane (AOPU) coatings.

Percentage Adhesion and Flexibility

In general, percentage adhesion was found to increase in acrylated polyurethane than in the non-acrylated polyurethane. This is due to increase in molecular weight and increase in cross-linking site (hydroxyl value) in acrylated polyol than that of non-acrylated. Flexibility of the film was found to be excellent in all type of polyurethane resins. Oil based compound showed good flexibility which improves by the addition of acrylates and vinyls as they form flexible thermoplastic polymers. All the resins were found to pass successfully 1/8" and 1/4" mandrel bend for flexibility test and cross-hatch adhesion test.

Impact and Scratch Hardness

In general, impact and scratch resistance were improved in acrylated polyurethane resins than the non-acrylated polyurethane resins. The scratch resistance test was performed manually by using scratch hardness tester and impact resistance was carried out with impact resistance tester with the indenter of 4.77 kg.

The scratch resistance increases with increase in acrylic monomer loading. This is due to inclusion of

Table 3 — Drying and Gel time of different polyurethane systems

PU	NCO/OH	Drying time, min	Gel time, h
AOP	1.0	180	6.0
	1.1	140	5.5
	1.3	120	5.0
	1.5	100	4.5
	1.0	30	3.5
Set I	1.1	25	3.3
	1.3	20	2.7
	1.5	20	2.3
	1.0	37	3.6
	1.1	35	3.4
Set II	1.3	25	2.8
	1.5	20	2.5
	1.0	40	3.1
	1.1	35	2.3
	1.3	30	2.1
Set III	1.5	30	2.0

monomer styrene, which is known for increase in hardness property of resin²⁶ also with inclusion of HEMA in polyol backbone hydroxyl value of polyol increases which will produce highly cross-linked polymer network which contributes to the increase in hardness.

The impact of hardness decreases with increase in styrene content and decreases in HEMA content; because increase in styrene content incorporates the brittleness in the film which is responsible for decrease in an impact hardness. Table 4 shows results of impact hardness and scratch hardness of acrylated and non-acrylated polyurethane coating.

Chemical and Solvent Resistance

The acid, alkali, water, and xylene resistance of various polyurethane films of acrylated resins and non-acrylated resins were studied by immersion method for specific length of time. The results revealed that alkali resistance of acrylated polyurethane was better than that of non-acrylated polyurethane resins. Since, acrylic monomer is known to give better resistance against alkali and acids²⁷. Acrylic and vinyl monomers add the non-polar characteristic to the resins, making them more resistant to alkali and water. The increase in the alkali and acid resistance is also due to increase in molecular weight and increase in cross-link in acrylated polyurethane resins. Table 5 shows the

Table 4 — Impact hardness and Scratch hardness of polyurethane coatings

Set no	NCO/OH	Scratch hardness in kg	Impact hardness lb in	
			Forward	Reverse
AOPU	1.0	0.5	225	250
	1.1	0.7	250	205
	1.3	0.8	275	300
	1.5	1.0	200	300
Set I	1.0	3.0	300	275
	1.1	3.1	275	250
	1.3	3.5	250	275
	1.5	3.5	225	250
Set II	1.0	2.5	275	275
	1.1	2.8	250	275
	1.3	2.8	225	250
	1.5	3.0	200	225
Set III	1.0	1.8	250	250
	1.1	2.0	250	225
	1.3	2.5	225	225
	1.5	2.5	200	200

results of solvent and chemical resistance of acrylated and non-acrylated polyurethanes.

Instrumental Analysis

FTIR Spectral Analysis

Acrylation of argemone oil based polyol was confirmed by FTIR spectral analysis. Representative FTIR spectra of non-acrylated polyol, acrylated polyol and polyurethane are shown in Figure 1.

Band around 3450 cm^{-1} attributed to free hydroxyl group in the polyol is found to become sharper in acrylated polyols due to more hydroxyls present in them than the non-acrylated polyol. A strong absorption band around 1750 cm^{-1} is attributed to $\text{C}=\text{O}$ of ester group present in the polyol and also due to ester linkage of acrylic monomer. The presence of aromatic moiety at 700 cm^{-1} confirms the inclusion of styrene monomer in the polyol. Formation of polyurethane was also established by using FTIR analysis. Band at 1602 cm^{-1} and 1536 cm^{-1} confirms formation of urethane linkages; they are attributed to *tertiary*-amide carbonyl and $-\text{N}-\text{H}$ bending. The band at 1727 cm^{-1} is due to polyester moiety present in the polyurethane formed from the polyester polyol. The

Table 5 — Chemical resistance of polyurethane coating

PU code	NCO/OH	2 per cent NaOH	2 per cent HCl	Benzene	Xylene	Wat
APOU	1.0	f	g	a	a	a
	1.1	f	b	a	a	a
	1.3	b	b	a	a	a
	1.5	b	b	a	a	a
Set I	1.0	b	b	a	a	a
	1.1	b	b	a	a	a
	1.3	a	b	a	a	a
	1.5	a	a	a	a	a
Set II	1.0	c	b	b	a	a
	1.1	c	b	b	a	a
	1.3	b	b	b	a	a
	1.5	a	a	b	a	a
Set III	1.0	f	c	b	b	a
	1.1	c	d	a	b	a
	1.3	b	c	a	a	a
	1.5	b	b	a	a	a

a=no effect, b=loss in gloss, c=loss in adhesion, g=swelling and blistering, f= failure

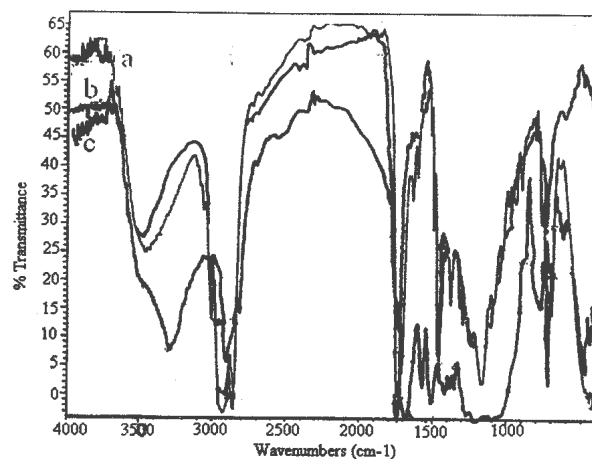


Figure 1 — IR spectrum of (a) non-acrylated polyol (b) acrylated polyol and (c) polyurethane

band at 3351 cm^{-1} is due to NH deformation. Further the absence of any band at 2270 cm^{-1} in the spectrum indicates that no unreacted isocyanate is present.

Gel Permeation Chromatography (GPC)

The data obtained from GPC shows that there is significant increase in molecular weight on acrylation of polyol which establishes the inclusion of acrylic monomers in the polyol. The molecular weight was found to increase by more than double of the molecular weight of non-acrylated argemone oil based polyol. Table 2 shows the result of GPC for acrylated and non-acrylated polyol.

Thermal Stability

DSC thermograms of non-acrylated and acrylated polyurethanes are shown in Figure 2 and 3 (a, b and c). DSC analysis is carried out to establish mechanical and thermal stability. For this purpose, glass transition temperature was measured by using Perkin Elmer Pyris-1, USA instrument. Heating range was 100 to 400 °C. The heating rate was kept 1°C/min. All the properties decrease above glass transition temperature except impact resistance, so Tg measurement is one of the important parameter in evaluation of overall stability of coating material. The results revealed that there is an increase in glass

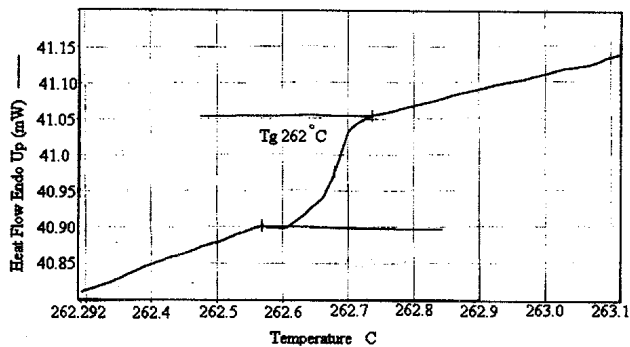


Figure 2 — DSC thermogram of oil based polyurethane

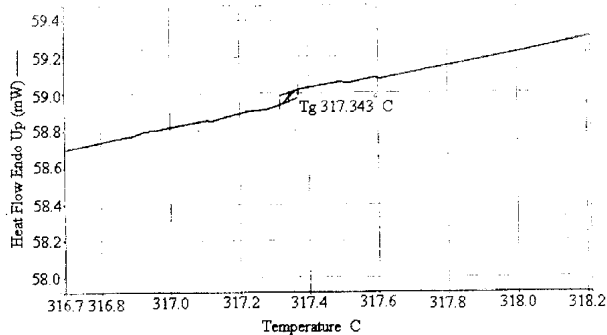


Figure 3(a) — DSC thermogram of acrylated polyol based polyurethane

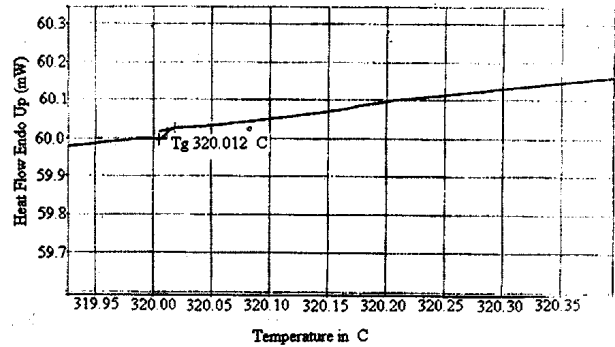


Figure 3(b) — DSC thermogram of acrylated polyol based polyurethane

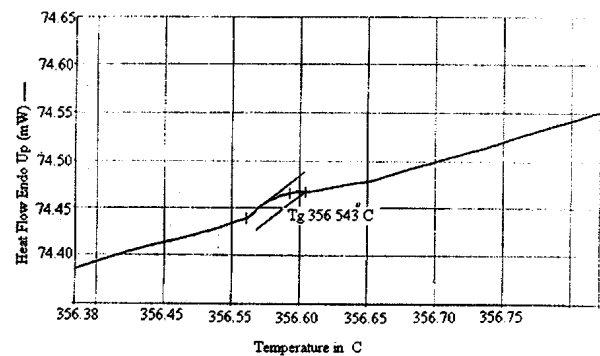


Figure 3(c) — DSC thermogram of acrylated polyol based polyurethane

Table 6 — Tg of acrylated non-acrylated polyols based polyurethanes

Sl No.	PU code	Tg1 °C	Tg2 °C	Tg3 °C
1	AOPU	262	—	—
2	Acrylated	317	320	356

transition temperature (Tg) on acrylation which increases the thermal stability of the resin. Also the presence of more than one Tg in acrylated polyurethane confirms the presence of more than one polymeric moiety in it. While, only one Tg was gained in non-acrylated polyurethane due to the presence of only urethane moiety. Table 6 shows the data of Tg for various polyurethanes.

Conclusions

Acrylation of argemone oil based polyols can be successfully carried out by using acrylic monomer (HEMA) and vinyl monomer (styrene). Polyurethane resins can be successfully formulated from argemone

oil based polyol and bio-acrylic polyols. Polyurethane coatings prepared from the acrylated polyols have better performance properties than the non-acrylated polyurethane coatings. Also, it was observed that there is considerable effect of amount of monomers present in polyol on the coating quality.

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*Author for correspondence

E-mail: sdd7677@rediffmail.com