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Synthesis, characterization and application of soya fatty acid based blend polyol in polyurethane acrylate surface coating by UV curing

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Abstract

Acrylated Polyols were synthesized by reacting PEG-200 and soya-fatty acid by esterification, epoxydation and acrylation process respectively. Epoxyester Polyol was synthesized by reported method as per literature. Acrylated Polyols & epoxy ester were blended in different weight ratio. Acrylated Polyols were characterized by FT-IR analysis. Polyurethane acrylate oligomer was prepared from blend polyols with Hexamethylene diisocyanate by taking 1:1 and 1:2 NCO/OH ratios. They show exceptional combination of properties. UV curable coating compositions were prepared by simple blending by Polyurethane acrylate oligomer, reactive diluents with photo initiator and were coated on MS penal. Coated Penal is cured by UV light and monitoring by FT-IR analysis. This UV coating films were evaluated by mechanical, chemical and thermal properties. As the epoxy ester ratio increase the thermal degradation decrease also mechanical properties increase. Aromatic diisocyanate give harder film properties.

Keywords: Soya Fatty acid, Epoxy ester, Acrylated Polyols, polyurethane-acrylate, UV- curing

1. Introduction

Growing concerns about environmental protection have driven industry toward the use of solvent-free polymerization systems, and UV curing has become a viable alternative to the conventional thermal curing of solvent-containing polymer formulations.

UV-curable coatings offer various advantages such as: instant drying, low VOC, reduced energy consumption and less space and capital requirement for curing equipment compared to thermally cured coatings [1]. It is well known that polyurethane acrylates are widely used as oligomers for UV-curable coatings, which provide excellent physical and mechanical properties such as adhesion, flexibility and impact strength [2, 6]. During use, a low viscosity and a high curing speed are two important properties pursued for UV-curable oligomers. Acrylate oligomers are some of the most important UV-curable resins. However, traditional acrylate oligomers are commonly linear molecules containing two double bonds; their viscosity is usually higher, and this causes difficulties in use, so reactive diluents must be used [7, 12].

Johansson and Hult [13]. have suggests that the acrylated hyperbranched polymers have lower viscosities and higher curing rates as compared to conventional UV-curable resins of similar molecular weight. Schwalm *et al.* [14]. have synthesized hard or flexible coatings by varying the molecular weight, functionality and chemical structure of the polymer. Asif *et al.* [15]. studied physical and thermal properties of UV-curable waterborne polyurethane dispersions by incorporating hyperbranched aliphatic polyester of varying generation number and suggests that there is no appreciable weight loss occurs up to a temperature of 200 ^{0}C. Xu *et al.* [16]. studied the properties and morphologies of UV-cured epoxy acrylate blend films containing hyperbranched polyurethane acrylate.

Epoxy ester have good chemical resistance but their brittleness and long elongation restrict their use in high performance application so to improve property the acrylated polyol from polyethylene glycol are blend with epoxy ester. A systematic and detail study required to obtain a combination of property suitable for high performance coating.

In this study Acrylated Polyols synthesized from polyethylene glycol (mol. wt 200) & soya fatty acid. Epoxy ester Polyol was synthesized by reported method as per literature. Acrylated Polyols & epoxy ester were blended in different weight ratio. Polyurethane acrylate oligomer was prepared from blend polyols in different weight ratio with aromatic & aliphatic diisocyanate by taking various NCO/OH ratio. They show exceptional combination of properties from flexibility to toughness. UV curable coating compositions were obtained by blending these oligomers with reactive diluents (cross-linking monomer), Photo-initiator and other additives. These compositions were cured under UV light at (200 Watt/inch) (280-360nm) medium pressure mercury vapor lamp of UV-2KW-2-35 intensity on UV light and monitoring by FT-IR analysis. This UV coating films were evaluated by mechanical, chemical and thermal properties. Aim of this study is to fast curing with better properties.

2. Materials and Methods

2.1 Reagents

Oleic acid, Diglycidyl ether of bisphenol-A, Triethyl amine was procured from Chitichem Corporation, Baroda. Polyethylene glycol with molecular weight 200, Formic acid, Hydrogen peroxide, Acrylic acid. Merck, USA) were used as received. Hexamethylene diisocyanate, were supplied by Bayer material science, Bombay, India. Photo initiator (Benzophenone) and Reactive diluents like Trimethylol propane triacrylate and DBTDL (Di butyl tin di-laureate) were obtained from Merck, USA.

2.2 Synthesis of Acrylate Polyol

2.2.1 First step: (Esterification)

In 3N-RBF equipped with mechanical stirrer, nitrogen inlet, thermometer pocket & water condenser charge oleic acid (2-mole) & polyethylene glycol-200 (1-mole) in presence of catalyst. Initially reaction was carried out at 160˚C & then raised the temp. at 190-200˚C. The progress of reaction was monitored by measuring acid value. The reaction was complete when acid value reaches near to zero. Calculate the iodine value of liquid material for epoxydation. FT-IR analysis was shown in Figure: 1.

2.2.2 Second step: (Epoxydation)

In 3N-RBF depending upon the iodine value of above materials (iodine value-48) & formic acid (0.5 mole of unsaturation) mix well & stir well and maintain the temp. at 0 to 5˚C. Start the drop wise addition of hydrogen peroxide (2-mole of unsaturation) at below 5˚C. [17, 19]. After completion of addition stir the reaction mixture to room temp., till iodine value reach to zero value or epoxy value to height value then separation was done by diethyl ether as solvent extraction. FT-IR analysis was shown in Figure: 1.

2.2.3 Third step: (Acrylation)

In round bottom flask Epoxidised viscous materials (E.E.Wt-499) stir well with reflux condenser, mechanical stirrer & thermometer pocket. Add acrylic acid (1-mole to epoxy value). Heat the flask up to 110˚C. Monitored the reaction by acid value till it reaches to zero value. Acrylate Polyol was characterized in Table: 1. FT-IR analysis was shown in Figure: 1. The reaction scheme of Acrylated Polyol is shown Scheme-1

Table 1: Characterization of Acrylated Polyols

S. No.	Properties	Result
1	Acid Value	≈ 1
2	Hydroxyl Value	120
3	Viscosity @ 25^0 C (10 rpm) cP	5200
4	Non Volatile Content	99.35
5	Average Molecular Weight	540

2.3 Synthesis of epoxy ester

Epoxy ester was prepared using soya fatty acid as per reported method. The calculated amount of above epoxy resin & soya fatty acid were taken in three neck flask & heated at 120-130˚C until the content became liquid the agitation was start & temp. Was raised to 240˚C. Reaction was continued until the esters of desired acid value were obtained [20]. Reaction was carried out in inert atmosphere. Epoxy ester was characterized in Table: 2.

Table 2: Specification of Epoxy Ester

Sr. No.	Properties	Result
1	Acid Value	≈ 0
2	Hydroxyl Value	115
3	Epoxy Equivalent Weight	≈ 0
4	Iodine Value	49.3
5	Viscosity @ 25^0 C (10 rpm) cP	7260
6	Non Volatile Content	99.62
7	Average Molecular Weight	975

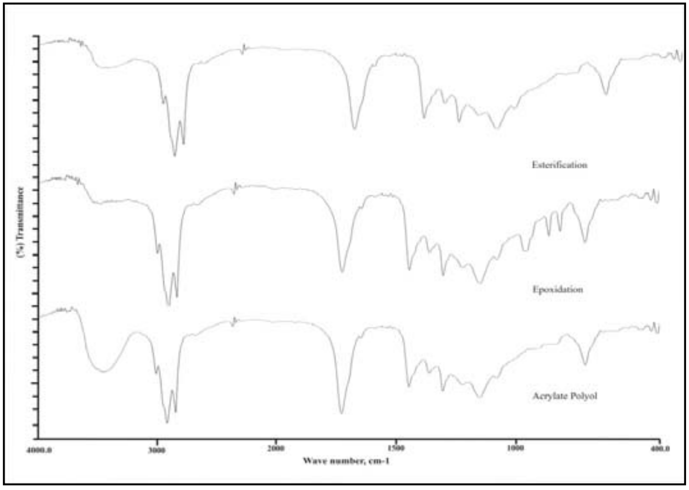

Fig 1: FT-IR Analysis of Acrylated Polyol

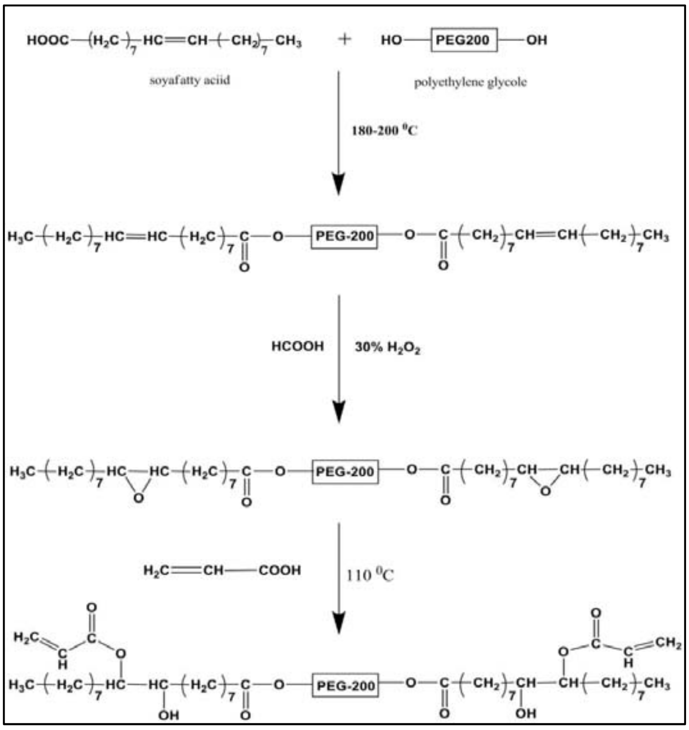

Fig 2: Preparation of Acrylated Polyol

2.4 Synthesis of blends Polyol

Polyol Blends were prepared by simply blending of above prepared acrylate Polyol: epoxy ester in % ratio of 100:00, 80:20, 60:40, 40:60, and 20:80 at room temperature is A1, A2, A3, A4, and A5 respectively.

2.5 Synthesis of Acrylate Polyurethane oligomer

In 3N-RBF equipped with mechanical stirrer, condenser, thermometer pocket & nitrogen inlets charge Acrylate Novel Polyol stir well & followed by the drop wise addition of diisocyanate in stoichiometrically proportion at 40 ^{0}C through separating funnel. As the reaction is exothermic in nature so temp. Raise up to 60 ^{0}C stir it. After dropping temperature to 40 ^{0}C stir it for an hour. Collect the clear viscous liquid to air tight bottle. Composition of Acrylate Polyurethane was oligomer Table: 3. FT-IR analysis was shown in Figure: 2.

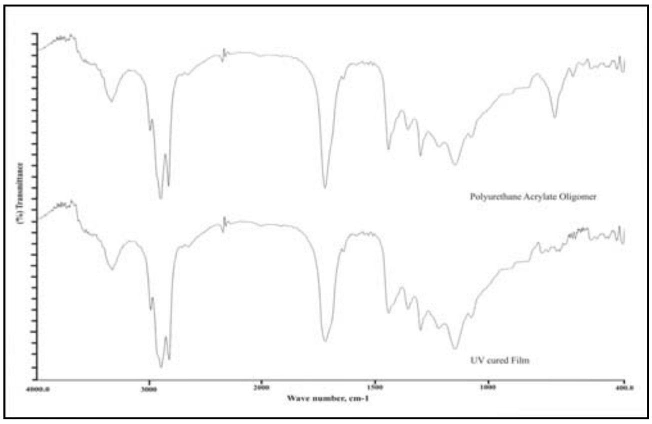

Fig 2: FT-IR of Polyurethane Acrylate oligomer and UV cured Film

2.6 Synthesis of UV curable Coating composition

UV curable coating composition was prepared by using above acrylate polyurethane with reactive diluents (TMPTMA), photoinitiator (Benzophenone) with additives.

3. Application and curing of coating composition

Sample to be tested for UV-curing was coated onto Mild steel panel (15cm X 5cm) as follows. An excess of the sample was placed at one end of the test panel and using a rod applicator (K-Bar No.5) drawn across the substrate with even pressure pushing excess material off the edge. [21] The coated panel was exposed to a (200 Watt/inch) (280-360nm) medium pressure mercury vapor lamp of UV-2KW-2-35 curing system for 1.5-2.0 min. This method produced coating with average wet film thickness of 23-35 um.

3.1 Evaluation of coating

The coatings were evaluated within one hour after irradiation. The coatings were examined for various mechanical properties like adhesion, flexibility, impact resistance and scratch hardness as per ASTM D 3359-97, ASTM D0522-93 and ASTM 2197 respectively. The impact resistance of dried film was checked by Tubular impact tester. Film thickness was measured by using micro test Magnetic coating thickness gauze. Each panel had an average of three measurements to determine the thickness of panels. Flexibility of the UV cured film was estimated by using conical mandrel Bending tester. Scratch hardness of the films was measured under specified load on a UV cured film of coating by a mechanized apparatus. The films were also evaluated for their chemical, corrosion and solvent resistance as per methods of their characterization described in the literature [22]. The results of the film characterization are shown in the Table-4 and 5.

4. Result and Discussion

4.1 FT-IR Analysis

In FT-IR spectra was shown in Figure 1. The bands are shown in the region 2950-2850cm^{-1} & 1485-1445cm^{-1} indicates C-Hstretching and bending (deformation) of the alkane chains. The spectrum shows C=O stretching band of acid at 1710cm^{-1}, bands at about 1050-1300cm^{-1} are C-O stretching of acid ester. Finger print region at 650cm^{-1} to 1055cm^{-1} indicates presence of unsaturation in long chain hydrocarbon of fatty acid and PEG.

In FT-IR spectra was shown in Figure 1. Epoxy groups are clearly observed at about 920cm^{-1}

In FT-IR spectra was shown in Figure 1. Novel polyols indicates that the band at about 3400cm^{-1} is due to –OH stretching. The strong and broad band indicates presence of the hydroxyl group associate to long chain and/or polymeric compound. The bands at about 1050 and 1350cm^{-1} indicate the O-H banding of alcohol and C-O stretching of ester group respectively.

IR spectra of Polyurethane acrylate oligomer and UV cured film as shown in Figure 2, respectively. The –N-H stretching and bending vibration of urethane linkage is observed at 3380-3300cm^{-1} and 1550-1500cm^{-1}, respectively. In the spectrum bands at 2950-2850cm^{-1} and 1470-1430cm^{-1} are observed due to –C-H stretching and bending vibration of alkane group. The sharp bands at 1710-1730cm^{-1} reveal the presence of ester group. The additional band at 770-815cm^{-1} confirms the presence of double bonds (-C=C-). A & B also reveals to formation of urethane acrylate adduct and urethane acrylate oligomers. In Fig.2 the disappearance of 770-815cm^{-1} band at this frequency region was monitored for the extent of curing.

Table 3: Mechanical properties for UV-PU coating

Different UV-PU coating	Scratch Hardness(gms)	Impact Hardness(lbinch)	Pencil Hardness	Flexibility 1/8”mandrel	Crosshatch Adhesion (%)
PUA1-H1	1100	P	2H	P	P
PUA2-H1	1150	F	3H	P	F
PUA3-H1	1200	P	3H	P	P
PUA4-H1	1250	P	3H	P	P
PUA5-H1	1300	P	4H	P	P
PUA1-H2	1200	P	2H	P	F
PUA2-H2	1250	P	2H	P	F
PUA3-H2	1200	P	4H	P	P
PUA4-H2	1350	P	4H	P	P
PUA5-H2	1350	P	4H	P	P

P- Pass & F-Fail

4.2 Mechanical & Chemical Properties

4.2.1 Adhesion

The high functionality of Epoxy Ester is reflected as failure in adhesion of coating composition. This may be argued in terms of shrinkage and aromaticity. The higher extent of adhesion observed in higher content of Acrylate Polyol can be argued in two senses. First, the aliphatic character of PEG decreases somewhat shrinkage and secondly, chemical nature of reactive diluents. The results of the film characterization are shown in Table-3.

4.2.2 Flexibility

The term ‘cross- link density’ here refers to the average number of cross-links per unit volume of cured film. This shows failure in flexibility of the cured film. The results of flexibility for coating composition of higher content of Acrylated polyols increases, the flexibility of film increases. Thus, the observed flexibility can be explained in two senses, first, increased aliphatic chain length and secondly, aliphatic diisocyanate. The results of the film characterization are shown in Table-3.

4.2.3 Impact resistance

The result of impact resistance of the cured films followed the same trend as that of adhesion and flexibility. For satisfactory impact resistance, UV coated film must have sufficient flexibility. The results of the film characterization are shown in Table-3.

4.2.4 Scratch resistance

The coating compositions based on Epoxy Ester and Acrylated polyol give surprising result in the present work. The poor results of scratch hardness in higher content of Acrylated polyol based coating composition can be due to the aliphatic nature. The results of the film characterization are shown in Table-3.

Table 4: Chemical properties for UV-PU coating

Different UV-PU Coating	Acid Resistance 5%HCL	Alkali resistance 5% NaOH	Corrosion resistance 5% NaCl
PUA1-H1	2	2	2
PUA2-H1	3	2	3
PUA3-H1	4	4	3
PUA4-H1	3	3	4
PUA5-H1	4	4	4
PUA1-H2	3	2	3
PUA2-H2	3	3	3
PUA3-H2	3	3	3
PUA4-H2	4	4	4
PUA5-H2	4	4	4

4.2.5 Chemical resistance

High acid and alkali resistance of the cured film for almost all coating compositions can be explained in terms of higher urethane linkage content in the film network, as, the urethane linkages are well known for their better stability against chemicals and at the same time higher cross link density of the network in the film.

The high polarity of urethane acrylate oligomer impart hydrogen bonding in the cross linked network which, also decrease the ability of the polymer to dissolve or even swell in solvents. The solvent resistance of the film can also be argued on the same ground. As the epoxy ester contain increase, resistance to solvent increase also polyurethane acrylate from higher diisocyanate give better resistance to acid and alkali. The results of the film characterization are shown in Table-4.

5. Thermo gravimetric Analysis (TGA)

The TGA thermograms in Figure 3 shows clearly indicate good thermal stability of cured film. Graph indicated by negligible weight loss shows that all the UV coating films are stable up to 150-250 ^{0}C irrespective of types and amount of polyol and urethane linkage. Thermograms indicate that all the UV coating films degraded as not well-distinguished three stages. The degradation in the first stage of polyurethanes may correspond to the breaking of urethane bond and leading the formation of CO_2, alcohols, amines carbon monoxide etc.

To second stage at about 250-350 ^{0}C may be due to the decomposition of ether and ester links. In the case of UV coating films from different types of Polyols, the main chain degradation may occur with the formation of as evidenced by the thermal degradation of fatty acid. In the third step finally this cured product degrades completely at slow rate.

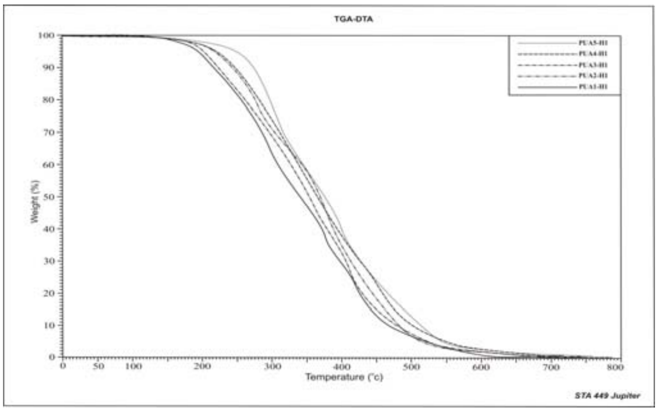

Fig 3: TG-Thermogram of PUA-H1

6. Conclusion

A series of urethane acrylates derived from different hydroxyl group containing blend polyols was prepared. These materials were used as oligomers in radiation curable compositions. Coatings obtained from these oligomers were characterized by mechanical analysis, chemical analysis, thermo gravimetric analysis. The UV cured samples from Acrylate polyurethane exhibit satisfactory mechanical and thermal properties, their mechanical properties are more dependent on weight ratio of the epoxy ester group, as the epoxy ester increase the hardness increase and flexibility, adhesion decrease and decomposition temperature also increases. It leads to a formation of new cross-links and additional improvement in the properties of the UV cured samples from soft to tough polymeric film.

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