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Synthesis and Characterization of Non-Isocyanate Polyurethanes using Diglycidyl Ether of Bisphenol Acetone (DGEBPA) Epoxy Resin

D.K. SONI*, A. MAITHANI and P.K. KAMANI

Department of Paint Technology, School of Chemical Technology, Harcourt Butler Technical University, Kanpur-208002, India

*Corresponding author: E-mail: durgeshkrsoni@gmail.com

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Present work focuses on synthesis of non-isocyanate polyurethane (NIPU) using the conventional epoxy resin, diglycidyl ether of bisphenol acetone (DGEBPA). The conventional polyurethanes (PUs) are prepared by reaction of the toxic diisocyanates and polyols. The epoxy resin contains two epoxy groups which are converted to cyclic carbonate groups when reacted with carbon dioxide. In this work, the epoxy resin (ER) was converted into the cyclocarbonated epoxy resin (CCER) using methyltriphenylphosphonium iodide (MePh.I) as the catalyst and ethyl cellsuolve as the reaction medium. The reaction was carried out in a carbon dioxide atmosphere, slightly above the atmospheric pressure, for 20 h. The progress of reaction was monitored by percent oxirane oxygen content (%OOC). The FTIR study confirms the disappearance of epoxy groups at 910 cm^{-1} and appearance of cyclic carbonate groups at 1800 cm^{-1}. The films of the resulting resin were prepared by curing with diethylamine (DEA), ethylene diamine (EDA) and reactive polyamide resin (70% NV). The formation of urethane linkage was confirmed by FTIR spectrum. The mechanical, chemical and appearance properties of the resulting NIPU were studied. The results were satisfactory, like improvement in adhesion and alkali resistance, but reduction in gloss and colour retention was observed. This eco-friendly route for synthesis of polyurethane can be used easily and variation in properties can be obtained by selecting the suitable epoxy compound as well as curing agent.

Keywords: Amine, Cyclic carbonate, Epoxy, Urethane.

INTRODUCTION

Polyurethanes are a versatile class of synthetic polymers that are produced when a diisocyanate reacts with a polyol. The repeating unit of polymer contains urethane linkage, also called carbamate linkage [1-4]. Polyurethane-based coatings comprise about 13% of the global market, and due to their extraordinary properties, find their uses in the normal atmosphere to highly corrosive atmospheres, like underground pipelines, seashore refineries, marine coatings, *etc*. The epoxy resin is another versatile class of polymer that is normally used in undercoats and primers. These are prepared by reaction of bisphenol acetone and epichlorohydrin under an alkaline medium. The epoxy resins are almost available in all types of coatings [5,6]. In two-component or baking systems, the epoxy resins react with multiple kinds of curing agents to suit the application requirements.

The monomers of polyurethanes (PUs) *i.e.* diisocyanates are very difficult to manufacture without sophisticated safety equipment and large investment, as poisonous phosgene due to use of the raw material. Isocyanates are quite toxic and sensitive to moisture [7,8]. The environmental changes taking place currently force us to think beyond the conventional and eco-harming methods of synthesis of materials. It is very important to ensure the health, safety and well-being of the people in the industry as well as the consumers. One of the most popular methods for preparing PU without using the isocyanates is the development of polyurethanes *via* an isocyanate-free route by the reaction of cyclic carbonate groups and primary diamines. The cyclic carbonate groups are produced by the carbonation reaction of the epoxy group and carbon dioxide. The performance of non-isocyanate polyurethane (NIPU) depends upon the molecular structure of cyclic carbonate oligomers, as well as the crosslinking agent [9,10]. Asemani *et al.* [11] used different epoxy group containing monomers and molecules to synthesize cyclic carbonates. Those cyclic carbonates were reacted with various diamines by step growth polymerization reaction to synthesize polyurethane polyamines. 2K-NIPU was made by 1:1 equivalent ration of epoxy compound and polyurethane polyamine. The same authors [11] aslo used three different epoxy compounds. The multifunctional cyclic carbonate thus formed was reacted with different amines and polyols to generate NIPU polyamine, NIU polyol, NIPU polyol. These were crosslinked with amino resin made from HMMM in different ratios. Wu *et al*. [12] synthesized a series of water soluble NIPU by the reaction of glycerine carbonate and trimellitic anhydride, pyromellitic anhydride and benzophenone-3,3′,4,4′-tetracarb-oxylic dianhydride under atmospheric pressure at 170 ºC, 3 h. The mixture thus obtained was dispersed in water and various amines were mixed according to molar ratio of carbonate to primary amine [13-15]. This opens a door for new possibilities of structure property variation in the NIPU [16-20]. The epoxide equivalent weight/epoxy value is defined as the weight of resin in grams, which contain one gram equivalent of epoxide. When ‘n’ value is nearly zero, the glycidyl ether formed is called diglycidyl ether of bisphenol acetone (DGEBPA) [21-25].

The present work describes the synthesis of cyclocarbonated epoxy resin using DGEBPA epoxy resin. When cured with diamines, hydroxyurethane linkages were formed after baking. Methyltriphenylphosphonium iodide (MePh.I) catalyst is used and known to show a very good conversion. Both the cyclic carbonate and the unconverted epoxy group react with amines, and thus creates with the hydroxyurethane linkages as well as epoxy amine reaction. Fig. 1 summarizes the scheme of the chemical reactions of carbonation stages [26-31].

EXPERIMENTAL

Liquid diglycidyl ether of bisphenol acetone (DGEBPA), epoxy resin of epoxy equivalent weight 180 g/eqiv. was procured from Kumar Rotoflex, India. 2-Methoxyethanol (Qualigens Fine Chemicals, India) was used as a solvent for epoxy resin. Methyltriphenylphosphonium iodide (MePh.I, Simson, India) was used as a catalyst for the carbonation of epoxy groups to cyclic carbonate groups. Diethylamine (DEA) and ethylenediamine (EDA), used for curing were purchased from Qualigens, India. Other reagents like acetic acid, perchloric acid, tetraethylammonium bromide, crystal violet indicator for percent oxirane oxygen content (%OOC) were all purchased from Thomas Baker, India. Solvents like methyl ethyl ketone and xylene, were purchased from Qualigens, India. The aqueous solutions of acid/alkali were made in deionized water.

Synthesis of cyclocarbonated DGEBPA resin: In the first step, cyclocarbonated epoxy resin was prepared by reacting carbon dioxide with the epoxy groups of DGEBPA epoxy resin. For this, 100 g of liquid epoxy resin (DGEBPA) was dissolved in 150 g of 2-methoxy ethanol (ethyl cellosolve). A 1.2 g of Me.Ph.I (3 mol% of epoxy compound) was dissolved in the resulting solution. Three-necked glass flask was flushed with dry CO_2 gas for 1 min to replace air with CO_2. The epoxy resin solution was kept in the reactor and put on a heater with a magnetic stirrer. The reflux condenser and thermometer were attached to the reactor. A balloon was filled with dry CO_2 gas and attached with the help of a rubber pipe directly to the neck of the flask. The mixture was heated at 70 ºC for 20 h, with intermittent refilling of the balloon using a CO_2 cylinder. After 20 h of reaction, the mixture was cooled to room temper-ature. The progress of the reaction was checked by the percent oxirane oxygen content (%OOC) titration method as per ASTM D1652 and by FTIR and NMR spectral analysis.

Aminolysis of coating application and curing: The next step was the development of urethane linkages which were produced during the curing of films *i.e.* the reaction of five-membered cyclic carbonate and primary amine groups. The cyclocarbonated DGEBPA epoxy resin (CCER) was mixed with ethylenediamine (EDA) and diethylamine (DEA) and reactive polyamide resin (70% NV) in different ratios (Table-1). The reaction mixture was stirred for the 30 s and applied to MS panels. Coating was applied on MS Panels (6 inch × 4 inch × 0.1 inch) and on Tin panels (6 cm × 4 cm × 0.1 cm). A Uniform film thickness of 50 µm was applied using a bar film applicator. The panels were kept at room temperature for 30 min for flash-off, and then at 160 ºC for 30 min in a box-type oven with a cooling air facility. The curing schedule was optimized by several trials. The separate panels in the given ratio of CCER and curing agents were applied and kept for air drying for 24 h to allow room temperature reaction. These were then subjected to forced stoving at 100 ºC for 40 min. Then, the temperature was incre-ased to 120, 140, 160, 180 ºC for different time intervals for optimization.

Instrumentation: The spectrum of ^1H NMR was recorded by a 400 MHz FT-NMR Spectrometer (JOEL, Model ECS), multiple nucleus spectrometer at room temperature using

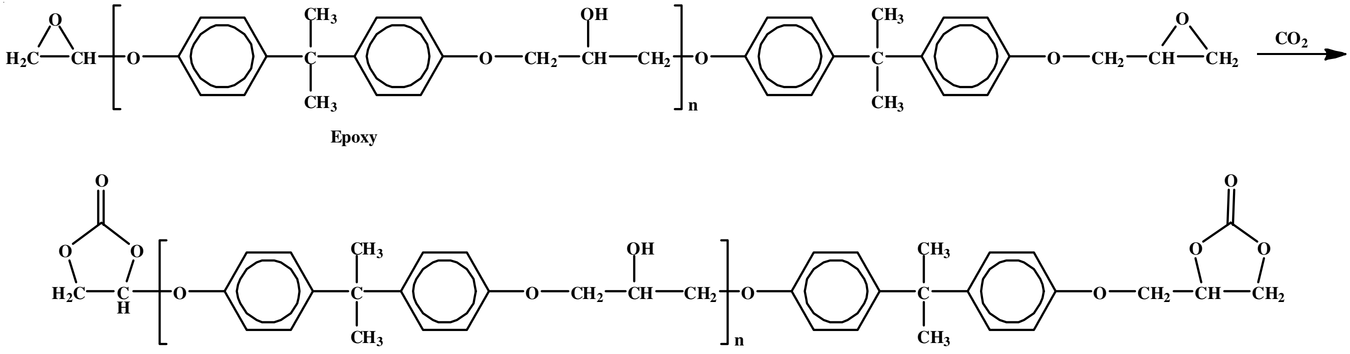

Fig. 1. Typical structure of epoxy resin (reactant) and cyclocarbonated epoxy resin (product)

TABLE-1
EFFECT OF CATALYST AND SOLVENT ON CARBONATION

Exp. No.	Cyclo carbonated epoxy resin (CCER)	Solvent	Catalyst	Temperature (°C)	Reaction time (min)	Conversion (%)
1	CCER1	Butanol	Me.Ph.I	60	15	20
2	CCER2	Xylene	Me.Ph.I	60	15	40
3	CCER3	Methoxy ethanol	Me.Ph.I	70	15	50
4	CCER4	Butanol	TEAB	70	20	30
5	CCER5	Xylene	TEAB	70	20	10
6	CCER6	2-Methoxyethanol	TEAB	70	20	25
7	CCER7	2-Methoxyethanol	LiBr	80	20	15

internal standards as TMS and DMSO-d_6 as a solvent. Fourier Transform Infrared (FTIR) spectroscopy was used for structure identification of the reactants and products. The ABB laboratory spectrometer MB3000 instrument, which was equipped with a DTGS detector and KBr crystal for beam splitting was used for the analysis in the frequency range of 4000-600 cm^{-1}.

Adhesion of cured coatings was evaluated by the cross-cut tape method as per ASTM D3359. A flexibility test was performed by conical mandrel tester at diameter ranging from 20 mm to 5mm. The resistance of samples to methyl ethyl ketone (MEK) double rubs was evaluated according to the ASTM D 4752 method. Finally, the resistance of the coatings to chemicals, acids, alkali and water Was checked by immersion test, as per ASTM standards. For all tests, at least three replicates were used to validate the reproducibility of the generated data.

RESULTS AND DISCUSSION

The carbonation reaction involves the conversion of the oxirane ring to the five-membered cyclic carbonate groups. The type of solvent and the catalyst plays an important role in the conversion of epoxy groups to cyclic carbonate groups. Different solvents and catalysts were used, and the conversion was studied. The protic solvents, like butanol and 2-methoxy ethanol, were helpful in the activation of the epoxy ring when the methyl triphenylphosphonium ion interacts with the oxygen of epoxy group. This may be due to hydrogen bonding between the hydroxyl group of solvent and the oxygen of epoxy group. The nucleophilic part of the catalyst *i.e.* iodide ion also helps parallel the ring-opening of epoxy group. Although bromide ion has better nucleophilic character than iodide ion, tetraethylammonium bromide (TEAB) did not show desirable conversion. Apart from this the epoxy group content is also responsible for the % conversion. The concentration of the catalyst to be used was also optimized using the reaction conditions and conversion studies.

FTIR studies: Carbonation reactions of epoxy groups were carried out using a polar solvent 2-methoxyethanol and the catalyst methyl triphenylphosphonium iodide was used here (CCER3). The progress of the reaction was tracked by FTIR spectroscopic technique by testing a sample at a regular interval of time. Figs. 2 and 3 shows the spectra of the carbonation batch of DGEBPA resin at the initial stage and after 20 h of reaction time. It is clear from the spectrum that the absorption peak at 909 cm^{-1}, which is attributed to the oxirane ring of epoxy resin was completely diminished after 20 h of reaction. As expected, the sharp peak corresponding to the C-O vibration of the cyclic carbonate group, emerged at 1800 cm^{-1}.

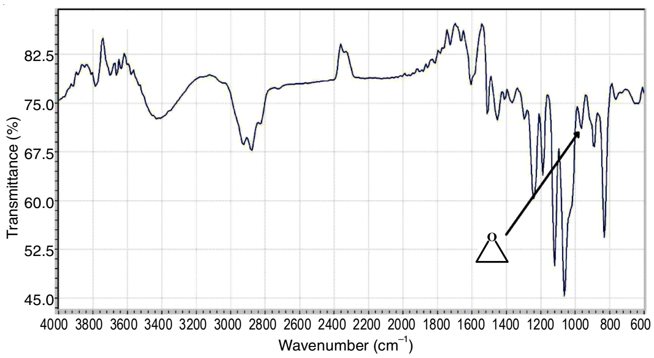

Fig. 2. FTIR spectrum of DGEBPA epoxy resin before reaction

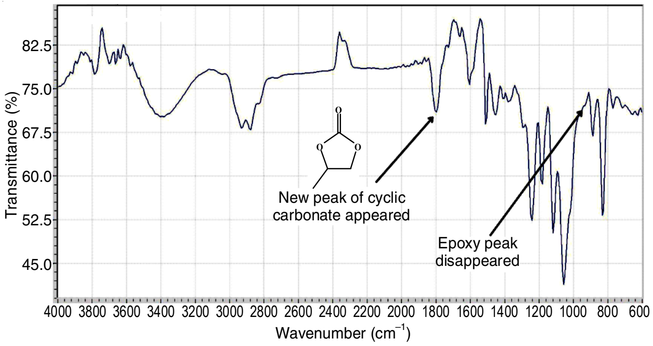

Fig. 3. FTIR spectra of DGEBPA liquid epoxy resin after 20 h of reaction with CO_2

Mechanism of carbonation: The FTIR results were found to be consistent with %OOC indicating the conversion of up to 50%. The conversion was measured based on the reduction of OOC% from its initial value and has been given in Table-1. This conversion requires some specific catalysts which activate the oxygen atom of epoxy groups. The catalysts used for carbonation contain Lewis acid as an electrophile responsible for activation of oxirane ring, and a Lewis base act as a nucleophile. MePh.I consists of the carbonation of epoxy groups, in which the nucleophilic part temporarily opens the epoxy group which is stabilized by polar protic solvents, a mechanism is shown in Fig. 4a. The rate of reaction of epoxide group and CO_2 follows first-order kinetics. The variation of % oxygen oxirane content with time is shown in Fig. 4b. The rate of reaction is expressed by the equation:

$$\frac{-d[\text{epoxide}]}{DT} = k[\text{epoxide}][\text{catalyst}]^m$$

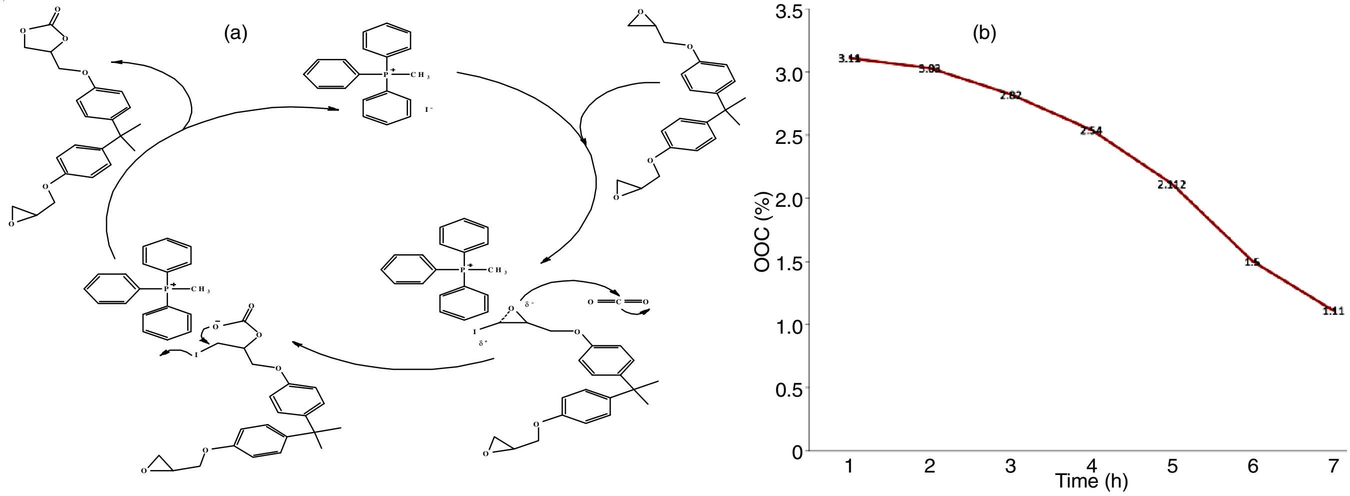

Fig. 4. (a) Mechanism of carbonation by CO_2 insertion and (b) variation of %OOC with time

^{1}H NMR studies: The ^{1}H NMR results also supported the FTIR spectra. The absence of peaks at δ 2.6-2.87 ppm is attributed to the protons of the oxirane ring $-CH_2$ (Fig. 5). The appearance of new peaks at δ 4.62 and 4.80 ppm are related to the protons in $OCHCH_2O$ of the cyclic carbonate ring. The peak at δ 1.5 ppm is attributed to two methyl groups between the two benzene rings. The $-CH_2-$ (δ 4.206 ppm) near the epoxy group is present in both the spectra. Triplets at δ 6.808 ppm and 7.046 ppm are present in both which are attributed to two $-CH_2-$ groups of 2-methoxyethanol. The singlet at δ 2.495 ppm represents the $-CH_3$ group of the solvent. Peaks at δ 4.206 and 3.799 ppm are attributed to two different hydrogens at the *ortho*- and *meta*-position of the benzene ring (Fig. 6).

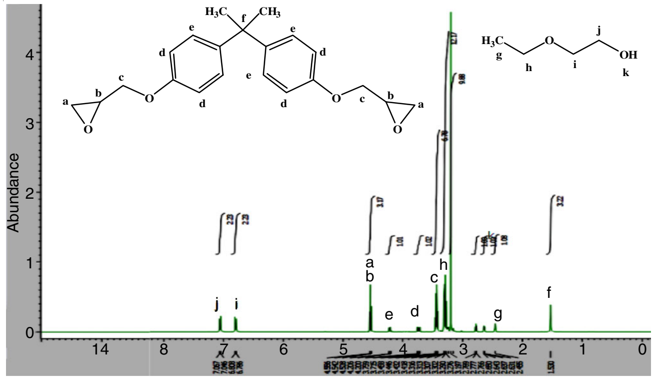

Fig. 5. ^{1}H NMR spectrum of epoxy resin before reaction

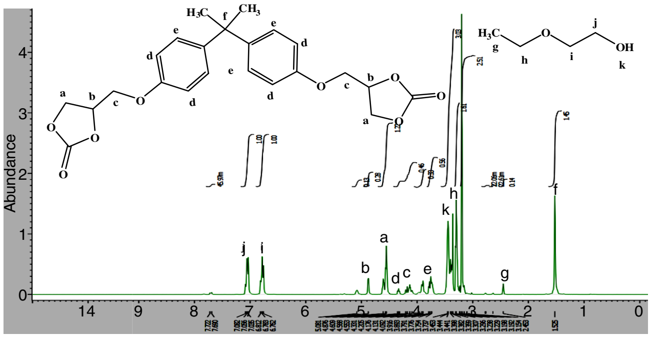

Fig. 6. ^{1}H NMR spectrum of epoxy resin after 20 h of reaction with CO_2

Development of hydroxyurethane linkage and its characterization: The cyclocarbonated DGEBPA epoxy resin was reacted with diethylamine, which has only one reactive hydrogen. Ethylenediamine has two primary amino groups which will take part considerably in curing. Similarly, reactive polyamide resin, which is a resinous polymer has also -an NH_2 group at terminals and helps in crosslinking. The reaction of amines with cyclic carbonate involves the attack of amine on the carbonyl carbon of CC, which forms a tetrahedral intermediate. On another attack of amine, the ring gets opened up and two different urethane linkages are created. The primary and secondary hydroxyl groups near urethane linkages are important, as certain properties, will change. As shown in the Fig. 7, the IR spectrum of NIPU1 was compared with CCER. At 1800 cm^{-1} no peak was observed in NIPU1, which confirmed the cyclic carbonate groups have reacted. The absorption peaks around 3323 cm^{-1} are due to the OH stretching of hydroxyl group. A peak at 1697 cm^{-1} is due to C=O stretching of urethane group and the broad peaks between 3400 to 3200 cm^{-1} are attributed to -NH of the urethane linkage.

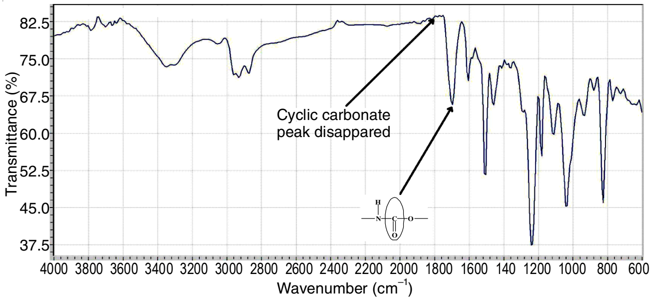

Fig. 7. FTIR spectrum of CCER cured with EDA

Reactive polyamides cover a range of polyamide, polyamine and cycloaliphatic amine curing agents, all capable of undergoing crosslinking reactions with compounds containing an epoxy ring or cyclic carbonate group. In CCER, both these groups are present, which are crosslinked to give the tough and resistant film. The quantity of reactive polyamide was taken slightly higher than the stoichiometric requirement for the film formation. The general reaction between the cyclic carbonate group and diamines is shown in Fig. 8.

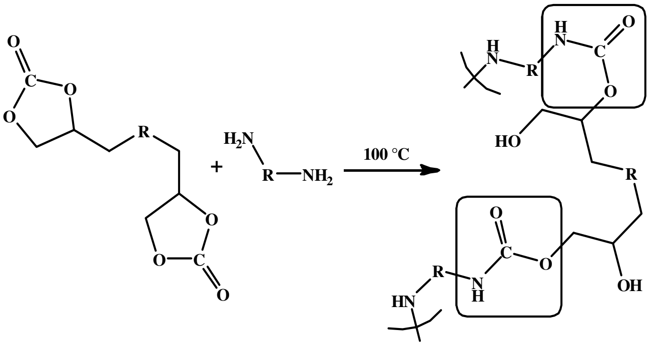

Fig. 8. Reaction between di cyclic carbonate and diamine to form hydroxy-urethane

Properties of cured film: The chemical and mechanical properties of different coatings samples prepared by curing CCER with three different crosslinkers were checked after baking at 160 ºC for 20 min, REF sample was taken as the liquid DGEBPA epoxy resin. Adhesion of the coatings was satisfactory for almost all the panels except NIPU1. Also, adhesion was best for NIPU3 and NIPU4, both of these show that reactive polyamide is a good curing agent for the cyclic carbonate group (Table-2). The reason behind this is the composition of reactive polyamide, which consists of a mixture of multifunctional amines like diethylene triamine, triethylene triamine, tetraethylenepentamine, *etc*. Diethylene triamine has only one active hydrogen due to which it cannot link the two molecules during the curing of the film. DM30 was used as a catalyst for curing with reactive polyamide.

The adhesion of coating to metal substrates depends upon the polar groups present in the polymer structure. The reason for the improvement in adhesion in CCER can be assigned to the formation of secondary and primary hydroxyl groups besides the urethane linkage, as well as the increased XLD. The unconverted epoxy groups also react with amine and help in crosslinking. The optimum adhesion is observed by a good balance between crosslink density and polar groups of the cured film. With the increase in the content of reactive polyamide as a crosslinker, the adhesion decreased and at a 1:1.2 ratio, it was observed at maximum. The small molecular weight of ethylenediamine cures the film but the adhesion is not as good as reactive polyamide. Diethylamine consists one hydrogen only, which is not able to react with the cyclic carbonate group. It was taken to observe the reaction with a cyclic carbonate group.

The hardness and flexibility properties of the coatings showed improvement when compared with REF, it is because the crosslink density has increased and the amines react with the cyclic carbonate group. Also in the case of reactive polyamide, the molecular weight increases considerably as compared to small molecules of ethylenediamine. The hardness and flexibility of coatings were compared on the basis of different curing agents, a general trend of decreasing flexibility and increasing hardness was observed. Again this is also attributed to increasing in XLD with an increase in the content of -NH_2 groups.

The impact resistance, which represents a measure of hardness, modulus of elasticity, compression, extension, is a complex property. As shown in Table-3, all the coatings showed good direct impact resistance except those based on diethylamine as a curing agent.

The resistance of epoxy resin (ER) and non-isocyanate polyurethane (NIPU) coating samples to different chemicals is shown in Table-3. Samples were checked for loss of adhesion, blistering, colour retention, *etc*. and rated from 1 to 5. A rating of 5 means no defect was found and *vice-versa*. In general and as observed, the samples with a higher level of crosslinking agent showed superior performance. The reference epoxy samples showed similar to slightly inferior performance as compared to NIPU 3 and NIPU 4. The NIPU now contains hydrolytically stable bonds and chemical resistant linkages. All the samples failed under extremely acidic conditions due to the sensitivity of linkages produced by the reaction of epoxy and amine groups.

Conclusion

The conversion of the epoxy group into cyclic carbonate group can be easily carried out by reaction with carbon dioxide

TABLE-2
COATING PROPERTIES RESULTED FROM CURING OF ER AND CCER

Sample name	Ratio of CCER and amine	Adhesion	Mandrel flexibility	Pencil hardness	Impact resistance (lb-in)
REF	ER + RP (100%) + DM30	4B	Pass	3H	40
NIPU1	CCER + DEA (25%)	2B	Fail	2H	30
NIPU2	CCER + EDA (25%)	4B	Fail	2H	60
NIPU3	CCER + RP + DM30 (1:1.2:0.1)	3B	Pass	3H	140
NIPU4	CCER + RP (1:1.5)	5B	Pass	4H	150

*DFT of the coating 30 ± 2 μm

TABLE-3
RESISTANCE OF COATINGS AGAINST CHEMICALS

Sample name	Coating sample/resistance to chemicals	Water	Alkali (5 wt%)	Acid (5 wt%)
REF	ER + RP (100%) + DM30	5	5	2
NIPU1	CCER + DEA (25%)	3	2	1
NIPU2	CCER + EDA (25%)	4	3	1
NIPU3	CCER + RP (10%) + DM30	5	4	3
NIPU4	CCER + RP (20%) + DM30	3	2	2

in a polar protic solvent in presence of suitable catalysts like methyl triphenylphosphonium iodide. The reaction takes place at slightly above atmospheric pressure. The disappearance of epoxy peaks at 909 cm^{-1} and emergence of cyclic carbonate peaks at 1800 cm^{-1} can be easily checked out along with %OOC titration, which reduced from 3.44 to 1.11 after 20 h of reaction. The reaction of cyclic carbonate and amine makes urethane linkage with a secondary hydroxyl group, which is responsible for the improvement in adhesion. The best results were obtained in sample NIPU4 in which reactive polyamide was used as a curing agent. This method was optimized in terms of catalysts and solvents and methyltriphenylphosphonium iodide (MePh.I) as catalyst and ethyl cellosolve as solvent showed the highest% conversion up to 50%. This is an eco-friendly route for the synthesis of polyurethane and by using the epoxy resins of different molecular weights, the NIPU technology may find use in those applications of epoxy resin, like powder coating, radiation-curable coating, *etc*.

CONFLICT OF INTEREST

The authors declare that there is no conflict of interests regarding the publication of this article.

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