

Preparation of Novel CNSL-Based Urethane Polyol via Nonisocyanate Route: Curing with Melamine-Formaldehyde Resin and Structure-Property Relationship

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ABSTRACT: In this study, we report preparation of a novel cashew nut shell liquid (CNSL)-based polyol bearing urethane groups. The urethane group in the polyol was induced via isocyanate free route from the reaction of cyclic carbonate with primary amine. The polyol was characterized by determination of hydroxyl number, Fourier transform infrared spectroscopy, nuclear magnetic resonance spectroscopy, and so forth. The polyol was then used as coating component and cured with hexamethoxy methylene melamine (HMMM). Another CNSL-based polyol without urethane moiety from our earlier reported work was used for preparation of coating for comparative study to determine the effect of urethane group on the coating properties. The coating formulations based on these two polyols were cured with variable amounts of HMMM hardener to optimize coating properties. All the coatings were evaluated for mechanical properties such as adhesion, flexibility, pencil and scratch hardness, impact resistance, pull-off, and adhesion. The optimized coatings were also evaluated for chemical and thermal properties. It was observed that the urethane containing polyol resulted in better adhesion to the metal substrate at higher quantity of HMMM hardener compared to the other polyol providing significant improvement in various coating properties. The final coating properties were also compared with the acrylic polyurethane coatings. © 2014 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* **2015**, *132*, 41391.

KEYWORDS: coatings; polyurethanes; structure-property relations; thermogravimetric analysis

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INTRODUCTION

Polyols are typically used as comonomer for preparation of polyesters, alkyds, polyurethanes (PUs), and so forth. PUs, reaction products of polyols and isocyanates, are one of the most widely used classes of addition polymers resulting in excellent mechanical strength and chemical properties. Most commonly used polyols for this purpose include polyether polyols, polyester polyols, polycarbonate polyols, and monomeric polyols such as ethylene glycol, glycerol, and neopentyl glycol.^{1,2} In spite of producing some of the extraordinary properties, the PUs also attract negative attention due to application related issues and growing concern over production and handling of isocyanate raw materials. In this context, the nonisocyanate PU chemistry based on cyclic carbonates and amines is a promising alternative to conventional PU chemistry providing at par properties. Moreover, the chemistry does not include isocyanate as a reaction component and contribute to green environment through utilization of CO₂ as a medium and reactant for the reaction.^{3,4}

Nowadays, the synthesis of newer chemicals that are based on renewable resources has been accepted as a strategy to contribute to sustainable development due to anticipated depletion of fossil oil reserves and rising oil prices. In this regard, vegetable oil derived polyols, glycerol, mannitol, sorbitol, and so forth serve as monomeric components for preparation of various polymers.⁵⁻⁷ In our recent study, we reported a series of polyols derived from cashew nut shell liquid (CNSL) as a component for PU preparation.⁸ CNSL is extracted from cashew plant and contains four major ingredients viz. cardanol, cardol, 2-methylcardol, and anacardic acid. Cardanol contains a characteristic long unsaturated aliphatic chain at the meta position of phenolic ring influencing many chemical transformations introducing novel functionalities. Utilization of CNSL in polymer chemistry has been well experimented and commercialized in the past.⁹⁻¹²

In this investigation, we report a new polyol (CP-1) prepared via isocyanate free route from CNSL derived cyclic carbonate.

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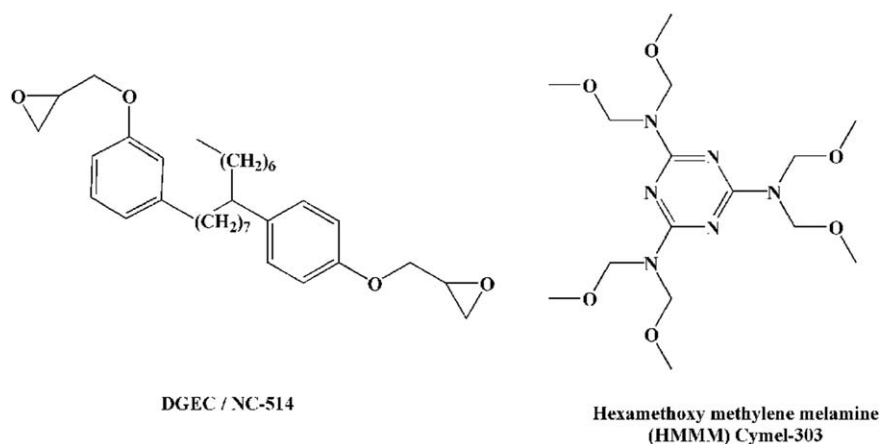


Figure 1. Typical structures of NC-514 epoxy resin and melamine-formaldehyde resin (Cymel 303).

This was used as a binder component and cured with hexamethoxy methylene melamine (HMMM). A polyol (CP-5) from our earlier study⁸ with equal number of hydroxyl groups as that of CP-1 was selected for comparison to study the effect of urethane groups on physical, mechanical, and chemical properties. The coating properties were further optimized by curing the polyols with lesser amount of HMMM hardener on equivalent basis and compared with acrylic PU coatings.

MATERIALS

Diglycidyl ether of cardanol (DGEC; NC-514) was procured from Cardolite Specialty Chemicals India, Mangalore. Monoethanolamine, tetrabutyl ammonium bromide, sodium sulphate, acetic anhydride, and pyridine were laboratory grade chemicals purchased from SD Fine Chemicals, Mumbai and were used as received. HMMM (Cymel 303) was obtained from Cytec India, Mumbai. Typical chemical structures of NC-514 and Cymel 303 are as shown in Figure 1.

METHODS

The urethane containing polyol was prepared from cyclic carbonate derivative of DGEC with reaction of monoethanolamine. Polyol CP-5, was prepared from DGEC via ring opening reaction as reported in our earlier study.

Cyclic Carbonate of NC-514 (CC)

The cyclic carbonate derivative of DGEC was prepared by high pressure CO₂ addition reaction as described in our earlier study.¹³ The reaction was carried out in an autoclave reactor assembled with temperature and pressure controller. The structure of the product formed was confirmed by Fourier transform infrared spectroscopy (FTIR) and nuclear magnetic resonance spectroscopy (NMR) analysis.

Synthesis of Urethane Polyol (CP-1)

The cyclic carbonates react with primary amines typically producing urethane and hydroxyl groups. Moreover, position of attack of amine group on carbonate ring decides the type of hydroxyl group and can result in primary as well as secondary hydroxyl groups, wherein primary hydroxyl groups are formed predominantly.³ Here, ethanolamine was reacted with CC on mole basis to produce polyol. The reaction was carried out in a

three-necked flask assembled with thermometer, nitrogen inlet, water condenser, and magnetic stirrer. CC and ethanolamine were charged in the flask in molar ratio of 1 : 2 along with triethylamine catalyst. The mixture was mixed at room temperature for first 10 min and then the temperature was gradually raised to 120°C and maintained afterward. After 90 min, the reaction mixture was cooled down to room temperature; the product was washed with lukewarm water to remove any traces of unreacted monoethanolamine and dried over anhydrous sodium sulphate. The purified polyol was then characterized by FTIR and NMR spectroscopy and hydroxyl number. Figure 2 is the schematic representation of formation of CC and CP-1.

Preparation of Coatings

The polyols, CP-1 and CP-5 were cured with HMMM hardener in presence of 3% *p*-toluene sulphonic acid as a catalyst (on solid basis). In case of CP-1, a solvent mixture of xylene, methyl ethyl ketone, and dimethyl formamide (50 : 20 : 20 on volume basis) was used to attain application viscosity while in case of CP-5, xylene/MEK mixture (70 : 30 on volume basis) was used. Required quantity of HMMM was added to these mixtures and applied on surface pretreated mild steel substrates and cured at 150°C for 5 min. As the cured coatings with 1 : 1 equivalent ratio of hydroxyl : HMMM yielded brittle films, the coating properties were further optimized by lowering the quantity of HMMM (on equivalent basis) for curing. These coatings were also applied using identical solvent mixtures for respective polyols and cured at same conditions. All the coatings applied were then evaluated for physical, mechanical, chemical, and thermal properties.

CHARACTERIZATION

The hydroxyl value of the polyol sample was determined using acetic anhydride-pyridine method against standard alcoholic KOH solution as per ASTM E222. The hydroxyl value was calculated using the following equation:

$$\text{Hydroxyl value} = \frac{56.1 \times N \times (B-S)}{W} + \text{Acid Value}$$

where *N*, normality of alcoholic KOH solution; *B*, titrant consumption for blank solution (mL); *S*, titrant consumption for sample (mL); *W*, weight of sample (gm); in this case, acid value is zero.

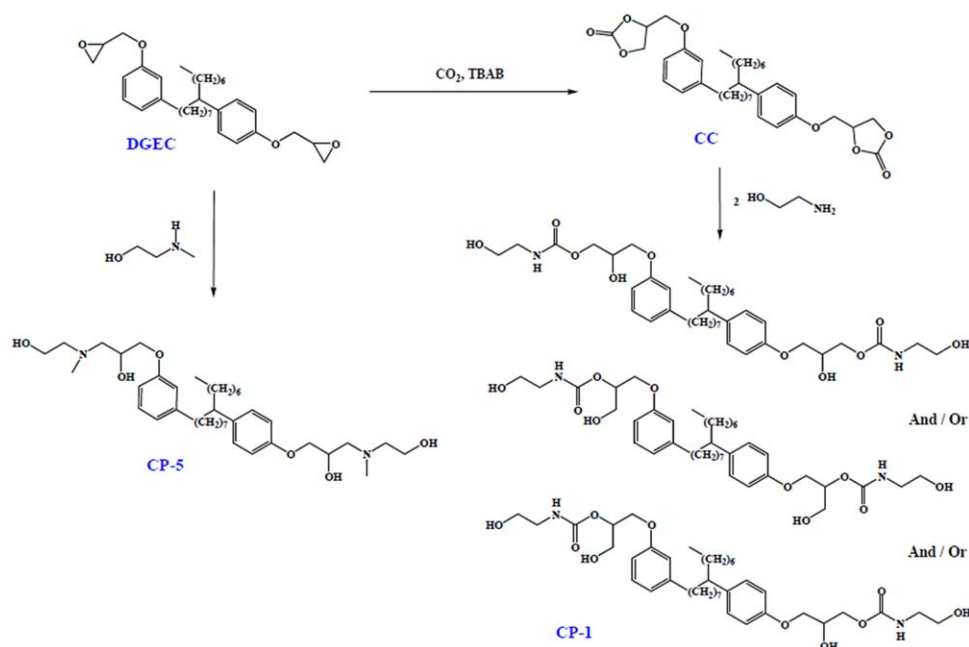


Figure 2. Schematic representation of preparation of CP-1 urethane polyol via nonisocyanate method showing polyol with both primary and hydroxyl groups. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

The adhesion properties of the applied coatings were evaluated by cross cut tape method as per ASTM D-3359. The hardness properties of the coatings were determined for pencil and scratch hardness according to ASTM D-3363 and IS-101, respectively. Flexibility and load distribution property of the coatings were evaluated by conical mandrel and impact tester as per ASTM D-522 and ASTM D-2794, respectively. Impact resistance was measured on the impact tester with maximum height of 23.6 inches and load of 3 lb. The abrasion resistance was measured by ASTM D-4060 using by CS-17 wheels for 1000 cycles and was reported in terms of weight loss. Pull-off adhesion strength of coatings was evaluated by portable adhesion tester as per ASTM D-4591. The solvent resistance was evaluated by ASTM D-4752 method. The alkali and acid resistance tests were conducted as per ASTM D-1308 method using 5% each of NaOH and HCl solutions, respectively.

INSTRUMENTATION

Fourier Transform Infrared Spectroscopy

The FTIR spectra were collected on Perkin-Elmer Spectrum 100 Instrument (Perkin-Elmer) at 40 scans and 2 cm^{-1} of resolution. The spectra obtained in the frequency range of the middle infrared were monitored particularly in the region of —OH stretching ($4000\text{—}3000$ and $1000\text{—}400\text{ cm}^{-1}$), —C=O ($1800\text{—}1600\text{ cm}^{-1}$), carbonyl asymmetric and alcohol linkages ($1400\text{—}1000\text{ cm}^{-1}$) for evaluating the chemical structure of the end products.

Nuclear Magnetic Resonance Spectroscopy

NMR spectra were recorded on Mercury Plus NMR spectrometer (400 MHz, Varian) using CDCl_3 solvent. The chemical shifts in the discussion are reported in parts per million.

X-ray Diffraction Spectroscopy

The wide angle X-ray diffraction (XRD) patterns were evaluated using X-ray diffractometer Miniflex Rigaku (Rigaku Europe, Germany). The 2θ diffraction was scanned from 2° to 60° at interval of 0.05° . The percentage crystallinity was calculated as reported earlier.¹⁴

Differential Scanning Calorimetry

Differential scanning calorimetry (DSC) analysis was performed under nitrogen atmosphere with DSC Q-100 equipment (TA Instrument) calibrated with *n*-octane and indium. All the samples were heated from -50 to 100°C at a heating rate of $10^\circ\text{C}/\text{min}$.

Thermogravimetric Analysis

Thermogravimetric analysis (TGA) was performed under nitrogen atmosphere on DSC Q-100 instrument for the temperature range of $100\text{—}650^\circ\text{C}$ at heating rate of $10^\circ\text{C}/\text{min}$. For analysis, sample of coating was removed from coated substrates and used for characterization.

RESULT AND DISCUSSION

This investigation deals with structure–property relationship of the coatings based on two different polyols derived from CNSL of which one contains urethane linkages obtained via nonisocyanate route. Two polyols, CP-1 and CP-5 with equal number of hydroxyl groups, were cured with variable concentrations (on equivalent basis) of melamine formaldehyde resin until satisfactory coating properties in terms of adhesion to metal substrate and flexibility were achieved. The physicochemical properties of both these polyols are as given in Table I. The structures of these polyols were also confirmed by FTIR and NMR

Table I. Physicochemical Properties of the Polyols

	CP-1	CP-5
Pendant hydroxyl groups present	4	4
Molecular weight (g/mol)	718	658
Color (Gardener scale; hugh)	11→12	9→10
Viscosity (Pa.s @25°C)	113	122
Hydroxyl value (mgKOH/g)	322	341

spectroscopic techniques. We have earlier reported the detailed analysis of CP-5 polyol with the help of FTIR and NMR spectroscopy.⁸

The FTIR spectra of the DGEC, CC, and CP-1 product are as shown in Figure 3. CC is a result of addition of CO₂ molecule across the epoxy ring resulting in heterocyclic five membered cyclic carbonates. The epoxy to cyclic carbonate conversion producing CC can be confirmed by appearance of peak at 1801 cm⁻¹ attributed to C=O from carbonate group and disappearance of peak at 938 cm⁻¹ representing epoxy group from DGEC. Moreover, other transmission bands at 2929 and 2854 cm⁻¹ represented the aliphatic C—C linkages in the structure. Transmission band at 1608 cm⁻¹ was observed due to the C=C— from the C15 aliphatic chain. Peaks observed at 3014 and 1457 cm⁻¹ showed presence of aromatic C—C linkages. Further, the reaction of CC with ethanolamine resulted in formation of urethane and hydroxyl groups which can be confirmed with transmission bands observed at 1706 and 3384 cm⁻¹, respectively, while other characteristic peaks were retained. This confirmed that the nucleophilic ring opening reaction of cyclic carbonate occurred producing urethane polyol.

The structure of CP-1 polyol was further confirmed with ¹H-NMR and C¹³-NMR as presented in Figures 4 and 5. As shown in Figure 4, the hydroxyl groups from the polyol can be confirmed by the signal obtained at 1.9–2.0 ppm. Further protons from urethane linkage could be assigned to the peak

obtained at 8.0 ppm. The protons from monoethanolamine moiety were confirmed by the presence of strong signals at 3.3 and 3.7 ppm. The presence of these peaks in the ¹H-NMR spectra confirmed that the ring opening reaction of the cyclic carbonate moiety with amine was successfully achieved. Further, the protons from the aromatic rings and the characteristic long aliphatic chain of CNSL were assigned as shown in the figure. In addition, the C¹³-NMR also confirmed all the chemical changes as discussed above. The carbonyl group from urethane moiety was assigned to the signals observed at 158 ppm. The carbons from the ethanolamine moiety and the carbon adjacent to urethane group were confirmed by signals obtained between 42 and 72 ppm. All the aromatic carbons were also assigned to the signals seen in the range of 110–162 ppm as shown in the figure. Thus, it was confirmed, from the FTIR and NMR results, that the urethane formation from CC and monoethanolamine was successful generating a polyol with four pendant hydroxyl groups.

COATING PROPERTIES

The polyols CP-1 and CP-5 possessed two secondary and two primary hydroxyl groups with hydroxyl numbers in the range of 320–340 mgKOH/g. In our earlier study, we demonstrated a series of such polyols as precursor for PU coatings. Herein, we investigated the application of such polyol cured with HMMM for coating application. CP-1 polyol with additional chemical constituent, urethane moiety, was prepared from CC and cured with HMMM hardener. In both the cases, the quantity of hardener (on equivalent basis) for curing of the film was varied until optimized coating properties were achieved. Table II elaborates various physical and mechanical performance properties for coatings based on both the polyols.

All the coatings cured on metal substrates were clear and light red in color with typical dry film thickness in the range of 40–60 μm. The curing reaction of polyols with HMMM was evaluated with FTIR analysis. Figure 6 shows FTIR spectra of the

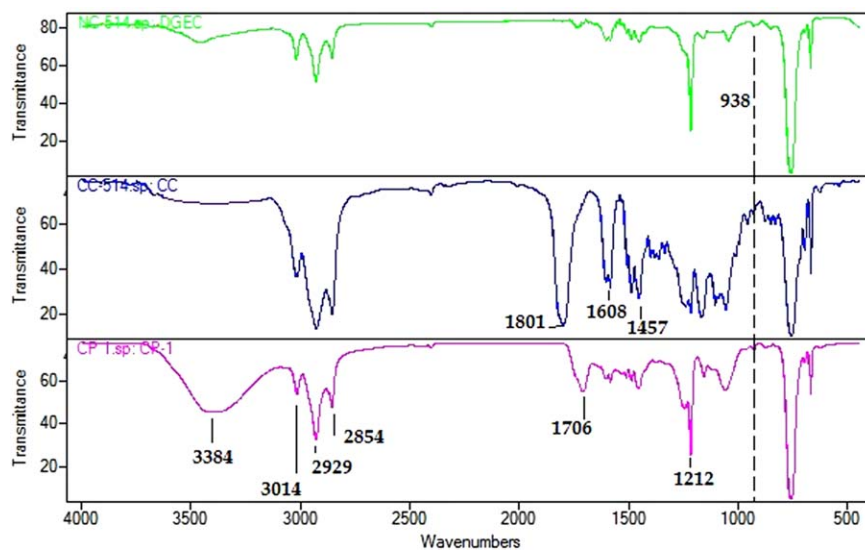


Figure 3. FTIR spectra of DGEC, CC, and CP-1 polyol. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

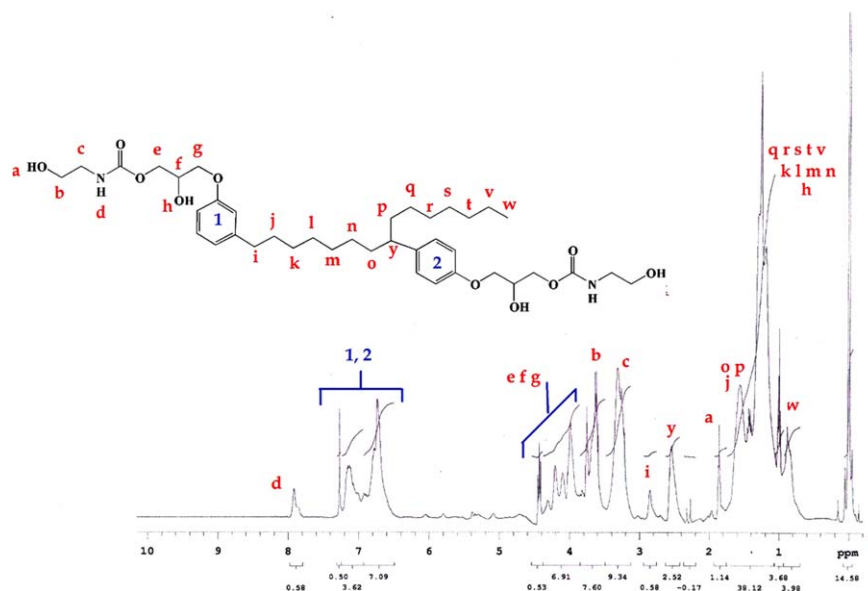


Figure 4. ^1H NMR of urethane polyol CP-1 evaluated in CDCl_3 solvent. (Structure of polyol with only primary hydroxyl groups is correlated for representation purpose). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

cured CP-1 (70% HMMM) coating with detailed structural elaboration. Broad transmission band at 3336 cm^{-1} showed unreacted hydroxyl groups after the curing reaction. Peaks at 1242 cm^{-1} confirmed Ph-O-C etheric linkages from DGEC structure. Moreover, C-O-C etheric linkages formed after condensation reaction were confirmed by strong peaks present at 1035 cm^{-1} . Additionally, -C-N- linkages from melamine component were confirmed by peaks present at 1546 and 1359 cm^{-1} . All the peaks obtained in the FTIR spectrum suggest that the curing reaction successfully proceeds through condensation reaction. Further, the 100% HMMM-based cured

samples and the optimized coating samples were evaluated with XRD analysis to measure the crystallinity of the samples. HMMM, being crystalline in nature, would directly affect crystallinity of the cross-linked network as it also affects the cross-link density when used in lower concentrations. The XRD diffractogram is as shown in Figure 7 and tabulated in Table III. The percentage crystallinity was calculated from the area under crystalline peaks and total area of all the peaks.¹⁴ For 100% HMMM cured CP-1- and CP-5-based coatings the crystallinity was observed to be higher than that of CP-1 (70% HMMM) and CP-5 (55% HMMM) coatings. Moreover, crystallinity of

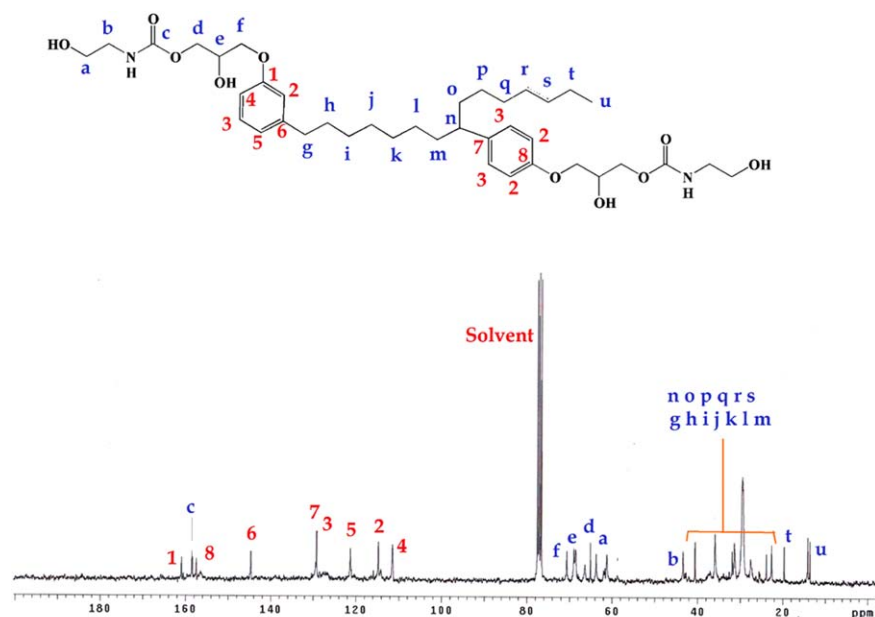


Figure 5. ^{13}C NMR spectrum of urethane polyol CP-1 evaluated in CDCl_3 solvent. (Structure of polyol with only primary hydroxyl groups is correlated for representation purpose). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Table II. Physical and Mechanical Performance of the Optimized Coatings Based on CP-1 and CP-5 Polyols

Hardener quantity (%)	Gloss (60°) ±2	Adhesion	Flexibility	Pencil hardness	Scratch hardness (Kg)	Impact (lb.in)	
						Intrusion	Extrusion
CP-5							
100	115.1	0	Failed	1 H	<0.5	23.6	23.6
80	111.7	0	Failed	2 H	<0.5	35.4	23.6
60	108.9	0	Failed	2 H	1.0	59.0	47.4
55	104.5	4B	Passed	4 H	1.3	70.2	70.2
CP-1							
100	123.2	0	Failed	1 H	0.7	23.6	23.6
90	120.4	0	Failed	2 H	1.1	47.4	35.4
80	114.2	2B	Failed	4 H	1.9	70.2	59.0
70	112.1	5B	Passed	4 H	2.3	70.2	70.2

CP-1 (70% HMMM) coating was higher than that of CP-5 (55% HMMM) which could be attributed to higher loading of HMMM in CP-1 system. The results obtained confirmed that the HMMM concentration controlled the crystallinity of the cross-linked network.

MECHANICAL PROPERTIES

The cured coatings exhibited less adhesion to metal substrate at 100% hardener loading due to high cross-link density and absence of pendant polar groups. However, reduction in HMMM quantity resulted in improved adhesion, wherein 55% HMMM produced satisfactory adhesion in case of CP-5 polyol. In contrast, CP-1 cured with 70% HMMM resulted in excellent adhesion while CP-5 polyol cured with 60% HMMM possessed inferior adhesion. The results obtained were largely due to presence of urethane groups in CP-1 polyol which balanced the high crystallinity of HMMM cured cross-linked structure (Figure 8). The flexibility of coatings was influenced in the same way. The lower quantity hardener resulted in improved flexibility, wherein presence of urethane moiety in CP-1 contributed to

better flexibility of the coatings. Gloss of the coatings measured at 60° was observed to be higher in case of CP-1 polyol as compared to CP-5 polyol which can be attributed to presence of urethane group. It further reduced in both cases as the hardener quantity was lowered which in turn reduced the content of heterocyclic ring from HMMM which largely affects the gloss. We have earlier reported properties of the conventional acrylic polyurethane (CPU) coatings prepared from acrylic polyol resin and polyisocyanate hardener.¹⁴ The CPU resulted in excellent adhesion to the metal substrate with 7-mm crack developed during the conical mandrel flexibility test. In comparison to CPU, CP-1 produced superior flexibility with excellent adhesion.

The surface hardness properties of the cured coatings measured by pencil and scratch hardness methods complement the fact that the excessive crystallinity of the cured structure due to high loading of HMMM hardener resulted in poor adhesion to metal substrate leading to inferior properties. The optimized coating formulations cured with 70% HMMM in case of CP-1 exhibited better scratch hardness as compared to those cured with 55% HMMM cured CP-5 coating. This can be attributed to the

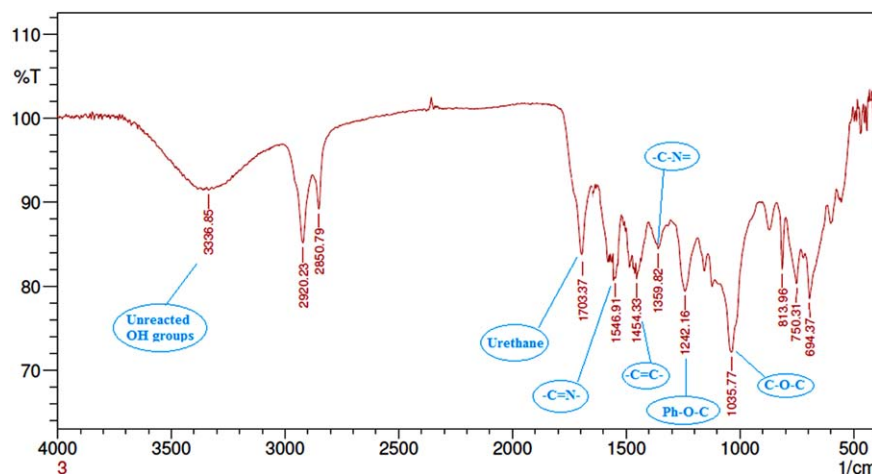


Figure 6. FTIR spectrum for CP-1 polyol cured with 70% HMMM showing formation formation urethane network. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

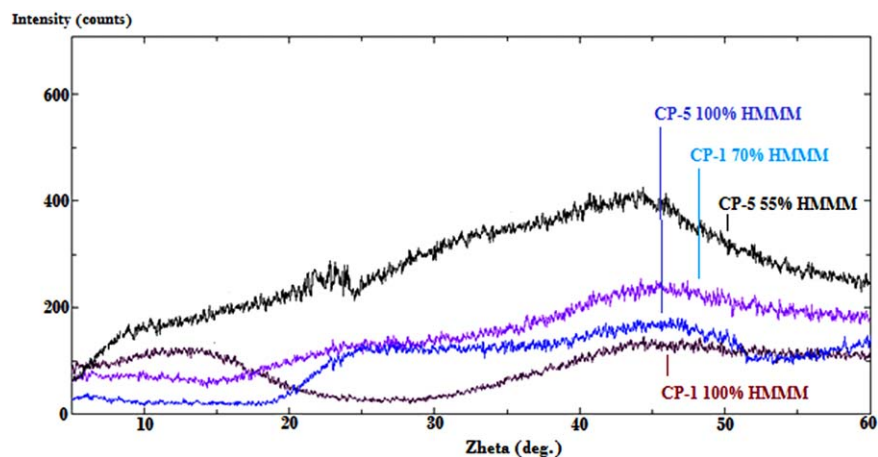


Figure 7. XRD diffractogram of the various coating films evaluated to measure the percent crystallinity. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

presence of urethane moiety which led to formation of intermolecular hydrogen bonding. The inferior adhesion at high HMMM loading also affected the impact resistance of the coatings. The results obtained revealed that the impact resistance improved as the hardener quantity was lowered. The maximum impact resistance measured (70.2 lbs.in) with the falling dart impact tester was obtained with 70% HMMM in case of CP-1 and 55% HMMM in case of CP-5 formulation. Overall, it was observed that curing of both the polyols with equivalent amount of HMMM hardener resulted in excessive crystallinity and high cross-link density. Curing of such polyols with lower amount of hardener led to reduced cross-link density keeping few pendant hydroxyl groups free/unreacted which in turn helped in improving adhesion to metal substrate. Therefore, presence of urethane moiety in CP-1 structure also provided sufficient polarity and compensated for the high cross-link density resulting in improved adhesion to metal substrate at over 15% higher loading of HMMM as compared to that required for CP-5 polyol. In comparison, CPU exhibited higher scratch resistance (3.7 kg) but inferior impact resistance (intrusion = 53.1 lbs.in; extrusion = 47.4 lbs.in) as compared to the CP-1-based coating system due to high cross-link density imparted by heterocyclic polyisocyanate curing agent.

PU structures are well known to provide better abrasion resistance as compared to other chemistries due to intermolecular hydrogen bonding. The abrasion resistance of the optimized

coatings was evaluated using CS-17 type wheels for 500 and 1000 cycles and the results are as furnished in Figure 9. The weight loss after 500 and 1000 cycles was observed to be higher in case coatings made up of CP-5 polyol than those made of CP-1 polyol. The difference in weight loss after 1000 cycles was observed to be more than 2.5% which confirmed that presence of urethane linkage in polyol contributed to better abrasion resistance even at higher loading of the hardener. The CPU coating resulted in 7.8 mg weight loss after 1000 abrasion cycles which was higher than the CP-1 system by a small margin. The difference can be attributed to presence of the long aliphatic chain of CNSL derivative and reduced cross-link density as compared to that in the CPU coatings.

Pull-off adhesion test measures the force required to pull a specified diameter of a coating away from its substrate which provides a direct indication of the adhesive strength for the bond between the coating with the substrate. The pull-off strength of the CP-1 coating was measured to be 4.9 MPa and resulted in cohesive failure, whereas that of CP-5 coatings was observed to be 3.4 MPa resulting in adhesive failure. The cohesive failure is due to the delamination of the aluminum pulley from the surface without removing the coating film during the test, whereas the adhesive failure is due to delamination of coating film from the metal surface along with the pulley. The results obtained revealed that the CP-1 coatings exhibited superior adhesion to metal substrate as compared to CP-5 coating due to presence of urethane group in the polyol structure. (Figure S1 showing real images of the tested substrates are attached as Supporting Information)

Table III. Crystalline and Thermal Properties of the CP-1 and CP-5 Cured Samples

Sample	% Crystallinity	T_g (°C)	$T_{5\%}$ (°C)	$T_{10\%}$ (°C)
CP-1 100% HMMM	11.17	56.72	-	-
CP-1 90% HMMM	-	52.93	-	-
CP-1 80% HMMM	-	50.66	-	-
CP-1 70% HMMM	7.1	47.43	170	255
CP-5 100% HMMM	11.74	-	-	-
CP-5 55% HMMM	5.3	31.02	200	240

CHEMICAL PROPERTIES

The chemical properties of the optimized coating formulations were evaluated by acid, alkali, and water immersion method. The coated samples were immersed in water, 5% HCl and 5% NaOH solutions each for a period of 24 h and observed for any visible damages. The immersion tests did not produce any visible damages other than loss in gloss in case of alkali test for both the polyol systems. The greater chemical stability was attributed to the sufficient curing of the formulation leading to

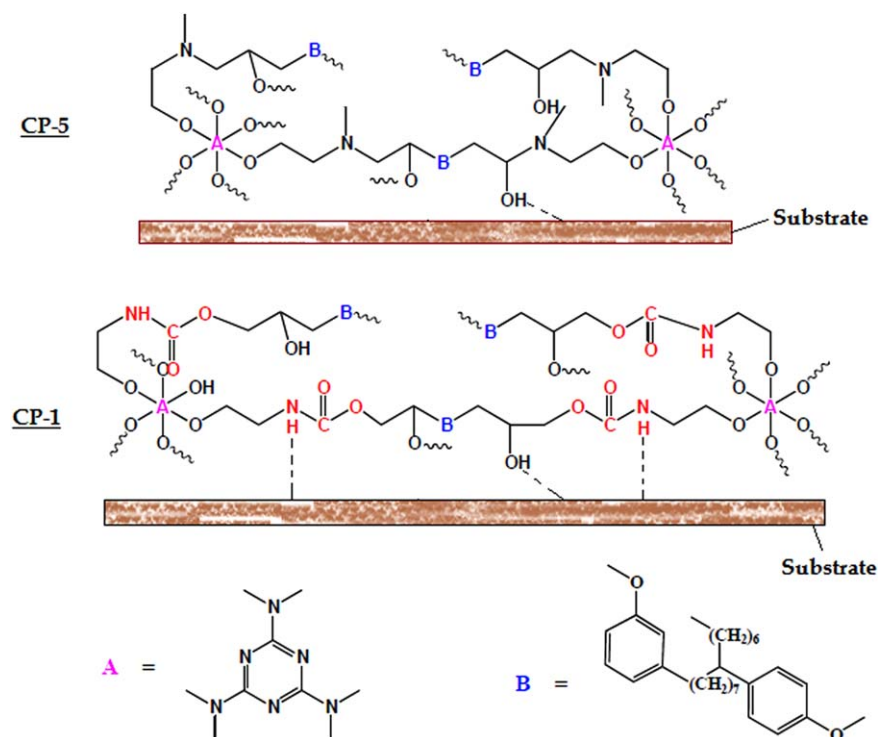


Figure 8. Schematic representation showing interaction of cross-linked structure with the metal substrate. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

the significantly chemically stable cross-linked network. However, when the acid immersion test was extended for 5 days, severe blistering was observed in case of CP-5-based coating while CP-1-based coating was observed to be unaffected. The extended alkali test for 5 days increased in brittleness of CP-5 polyol coating reducing secondary adhesion to the metal substrate while in case of CP-1 coating, the adhesion to the metal substrate was still significantly better.

Further, the solvent resistance was evaluated by rub method. The coating systems based on CP-1 provided more resistance to

the polar solvent (>200 rubs), methyl ethyl ketone, whereas CP-5 led to film removal after 140 rub cycles. However, both the coating systems provided excellent resistance to nonpolar solvent (xylene), wherein no damages were observed after 200 rub cycles.

THERMAL PROPERTIES

The glass transition temperature (T_g) is generally dependent on the cross-linked density along with structure of the binder and hardener. The aromatic or cycloaliphatic cross-linkers result in higher T_g as compared to aliphatic counterparts. In this study, the variable quantity of HMMM hardener used would decide

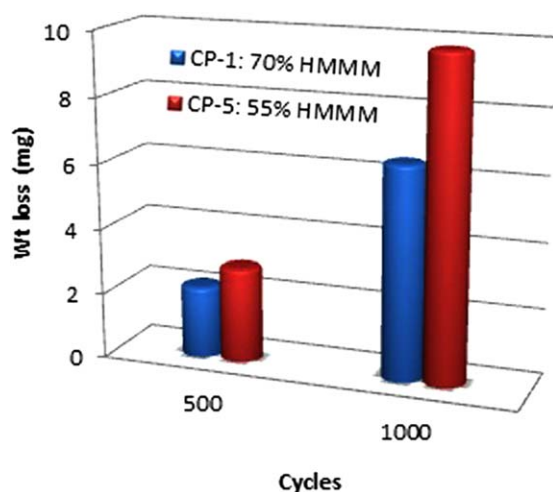


Figure 9. Abrasion resistance of cured coatings in terms of weight loss after 500 and 1000 cycles. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

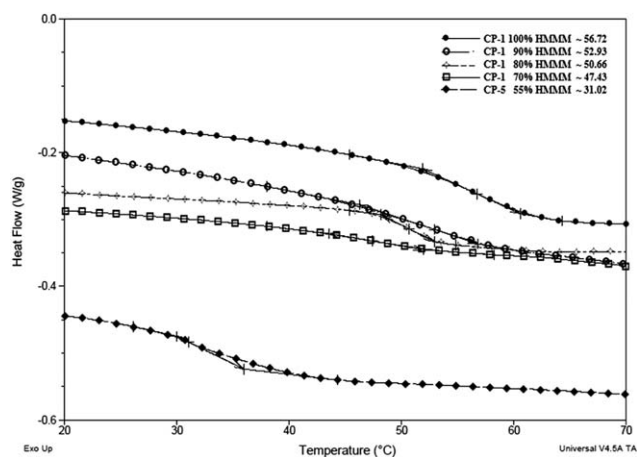


Figure 10. DSC thermogram of the various cured coatings plotted as heat flow vs. temperature.

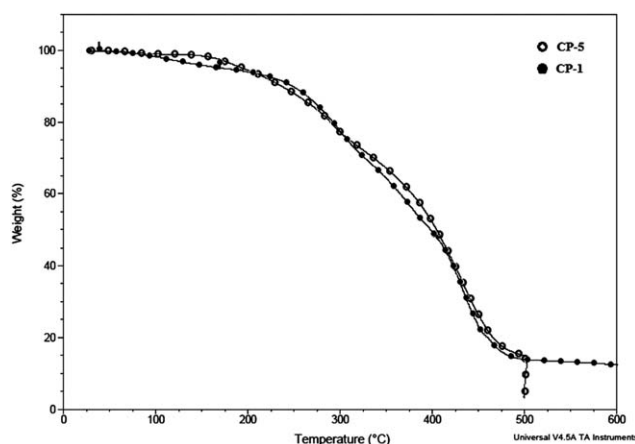


Figure 11. TGA thermogram of the optimized coating formulations plotted as weight loss vs. temperature.

the cross-link density further altering the T_g value. Figure 10 shows DSC thermogram of both the samples evaluated. The T_g s of the CP-1-based cured samples and CP-5 (55% HMMM) sample are as given in Table III. It was observed that the polyols cured with higher quantity of HMMM resulted in higher T_g . This confirmed that higher quantity of HMMM resulted in highly cross-linked network thereby producing higher T_g in case of CP-1 coating. Whereas the optimized coating using CP-5 showed the lowest T_g value at 31.02°C. This was due to lower concentration of HMMM used for curing which would have resulted in less cross-linked network.

Thermal stability of these optimized coatings was evaluated with the TGA analysis as shown in Figure 11 and Table III. It was observed that the CP-1-based coating resulted initial 5% degradation at about 170°C, whereas CP-5-based sample resulted in 5% degradation at about 200°C. This was probably due to degradation of urethane linkages forming CO, CO₂, and ammonia. Moreover, further degradation occurred after 240°C in both the cases which was due to breakdown of aliphatic C—C linkages present in the cross-linked structure. Hereafter, rapid degradation of the coating sample occurred. The study revealed that both the coating systems provided significant thermal stability which was also a result of presence of heterocyclic melamine ring in the cross-linked structure.

CONCLUSION

The preparation of CNSL-based polyol bearing urethane group is a novel approach towards development of versatile sustainable

functional materials. The urethane polyol when used as coating component results in greater adhesion to metal substrate as compared to the structurally similar polyol without urethane groups. Further, the presence of urethane group also enhances flexibility, scratch hardness, impact resistance, and abrasion resistance even with high T_g values. The study demonstrates extensive scope to prepare and utilize these kinds of polyol from renewable materials to replace the petroleum-based costly monomers and polymers.

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REFERENCES

- Kong, X.; Liu, G.; Curtis, J. *Eur. Polym. J.* **2012**, *48*, 2097.
- Malshe, V.; Sikchi, M. *Basics of Paint Technology Part-I*; Antar Prakash Centre for Yoga: Uttarakhand, India, **2008**.
- Kathalewar, M.; Joshi, P.; Sabnis, A.; Malshe, V. *RSC Adv.* **2013**, *3*, 4110.
- Guan, J.; Song, Y.; Lin, Y.; Yin, X.; Zua, M.; Zhao, Y.; Tao, X. *Ind. Eng. Chem. Res.* **2013**, *50*, 6517.
- Raquez, J.; Deleglise, M.; Lacrampe, M.; Krawczak, P. *Prog. Polym. Sci.* **2010**, *35*, 487.
- Miao, S.; Wang, P.; Su, Z.; Zhang, S. *Acta Biomater.* **2014**, *10*, 1692.
- Meier, M.; Metzger, J.; Schubert, U. *Chem. Soc. Rev.* **2007**, *36*, 1788.
- Kathalewar, M.; Sabnis, A.; D'Mello, D. *Prog. Org. Coat.* **2014**, *77*, 616.
- Balgude, D.; Sabnis, A. *J. Coat. Technol. Res.* **2014**, *11*, 169.
- Kathalewar, M.; Sabnis, A. *J. Coat. Technol. Res.* **2014**, *11*, 601.
- Voirin, C.; Caillol, S.; Sadavarte, N.; Tawade, B.; Boutevin, B.; Wadgaonkar, P. *Polym. Chem.* **2014**, *5*, 3142.
- Huang, K.; Zhang, Y.; Li, M.; Lian, J.; Yang, X.; Xia, J. *Prog. Org. Coat.* **2012**, *74*, 240.
- Kathalewar, M.; Sabnis, S.; D'Mello, D. *Eur. Polym. J.* **2014**, *57*, 99.
- Kathalewar, M.; Sabnis, A.; Waghoo, G. *Prog. Org. Coat.* **2013**, *76*, 1215.