

In Situ Development of Zn/Cd-Incorporated Poly(esteramide-urethane) from Sustainable Resource

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ABSTRACT: It was for the first time we attempted to develop zinc and cadmium incorporated linseed oil based poly(esteramide-urethane) [Zn/Cd-LPEAUr], and investigated their structure, mechanism, and properties. The resin was synthesized *in situ* by the reaction of linseed oil derived fatty amide diol [HELA], divalent zinc/cadmium acetate and toluylene-2, 4 (6), diisocyanate [TDI; 2–12 wt %] with minimal solvent. The structural elucidation of Zn/Cd-LPEAUr was carried out by FTIR, ¹H-NMR, and ¹³C-NMR spectral techniques. TGA and DSC techniques were used to measure the thermal stability and curing behavior of these resins, respectively. The

physicomechanical and chemical/corrosion resistance properties were investigated by standard laboratory methods. The performance of Zn/Cd-LPEAUr coating was compared with reported oil based polyesteramide. Antibacterial test of the resins were performed by agar diffusion method against *E. coli* and *S. aureus*, and compared with those of petroleum-based metal containing polyurethanes. © 2008 Wiley Periodicals, Inc. *J Appl Polym Sci* 110: 584–593, 2008

Key words: renewable resource; poly(esteramide-urethane); anticorrosive; antimicrobial; coatings

INTRODUCTION

Polyurethanes (PUs) are the most versatile class of polymers, since they can be tailored according to their use.^{1,2} Generally, they contain urethane groups (NH—CO—O) in the main polymeric chain and may also contain other functional groups such as ester, ether, urea, and amide. The presence of these functional groups provide a wide spectrum of properties.^{3–6} PUs based materials have commercial significance in many areas, such as biomedical,^{5,7} adhesives,^{8–10} foams,^{11–13} plastics,^{14,15} elastomers,^{16,17} and coatings^{18–25} for their excellent properties like abrasion resistance, strength, adhesion, toughness, low temperature flexibility, good outdoor service along with their chemical resistance.^{24–28}

PU is formed by the polyaddition reaction of dior polyisocyanates and dior polyhydric alcohols and other compounds having a plurality of active hydrogen. The reaction is rapid even at room temperature, which takes place without the elimination of volatile products.²⁹ The polyurethane chains consist of alternating short sequences of soft (flexible) and hard (rigid) segments. The former originates from the

polyol and imparts elastomeric characteristics to the polymer, while the latter originates from isocyanate and acts as physical crosslinks. The physical, mechanical, and adhesive properties of PUs depend strongly on the composition and chemical structure of hard and soft segments.^{30,31}

The polyols have until now developed, from different sustainable resources^{32–34} but the seed oil based polyols have attracted much attention in recent years.^{15,25,28,35,36} They were developed from different edible and nonedible seed oils, which react with isocyanate to produce polyurethane.^{36–38} The oil-based PU systems have been found to exhibit good physicomechanical and chemical resistance properties.^{25,38} The incorporation of urethane linkages in the oil based monomers and polymers such as monoglyceride, diol fatty amide,³⁹ epoxies,⁴⁰ polyetheramides,² and polyesteramides⁴¹ through the reaction of isocyanate with the hydroxyl group of these resins leads to the formation of polyurethane. Such PUs have high adhesion, toughness, weather resistance, and chemical/solvent resistance properties, but have lower thermal stability that decreases their applicability in the field of anticorrosive surface coatings.^{38–42}

It is reported that the incorporation of metal in the polymer have drastically altered their thermal stability, electrical conductivity, fracture toughness, flame retardancy, catalytic and biocidal activities, gloss, protective efficiency as well as reduction in curing temperature, and have found applicable in many

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areas.^{3,43–52} Jayakumar et al.³ and Matsuda⁵³ have lately reviewed the work on metal incorporated-PU and their derivatives which are generally derived from petroleum resource. Scanty work is available in literature on metal/metalloid incorporated oil based polymers from different seed oils.^{41,54,55} However there is no reported work on the development of sustainable resource based divalent Zn and Cd metals incorporated in poly(esteramide-urethane).

In the present manuscript we report the development, characterization, antibacterial and anticorrosive properties of urethane modified divalent zinc and cadmium incorporated linseed oil polyesteramide [Zn/Cd-LPEAUr]. The syntheses of these polymers were done for the first time *in situ* by the reaction of zinc and cadmium incorporated polyesteramide [Cd-LPEA and Zn-LPEA]⁵⁵ with toluylene-2, 4⁶-diisocyanate [TDI] in different weight ratios (2–12 wt % of resin). Antibacterial activities of these polymers have also been analyzed by the agar diffusion method.

EXPERIMENTAL

Materials

Linseed (obtained from local market) was air-dried, grounded into powder and further subjected to oil extraction in petroleum ether (a solvent, bp 60–80°C) through Soxhlet apparatus. The fatty acid composition of the oil was determined by gas chromatography (GC; 111/8s.s column, FID detector).⁴³ Metal acetate [M(OCOCH₃)₂ where M = Cd⁺² and Zn⁺²] of extra pure grade (Merck, India), sodium methoxide, xylene, diethanolamine, and phthalic anhydride [PA] (S.D Fine Chemicals, India), toluylene-2,4(6)-diisocyanate [TDI, 80/20](Merck; India) were of analytical grade. *N, N*-bis(2 hydroxyethyl) linseed fatty amide [HELA] and virgin linseed oil based poly(esteramide urethane) [LPEAUr] were developed as per reported methods.⁴¹

Synthesis of prepolymer [Zn/Cd-LPEA]

Prepolymer of Zn-LPEA and Cd-LPEA was prepared after applying a reported method.⁵⁶ HELA (0.2 mol) was taken in a four-necked flat bottom flask equipped with a condenser, nitrogen gas inlet, a thermometer, and temperature maintained 70 ± 5°C. At this temperature fine powdered PA (0.05 mol) was added in pinches over a period of 15 min under continuous stirring. The reacted mixture was further stirred for additional 15 min at this temperature, followed by very slow addition of different amount of fine powder of cadmium acetate (0.0325 mol)/zinc acetate (0.04 mol) over a period of next 15 min with continuous stirring under N₂ atmosphere. After the complete addition of cadmium/zinc

acetate, the temperature was raised up to 80 ± 5°C. TLC (Thin layer chromatography) and acid value determination was used to monitor the progress of the reaction. The reaction was conducted under vacuum and allowed to continue under the same conditions till the desired acid value was attained, followed by the addition of the rest of the PA (0.15 mol). TLC and acid value determination was further used to monitor the progress of the reaction. To obtain a desired acid value that is the completion of the reaction the product [Zn/Cd-LPEA] was transferred to a sample container.

Synthesis of Zn/Cd-LPEAUr

In the same aforementioned reaction setup containing prepolymer was allowed to cool up to 60°C, and added calculated amount of TDI (2–12 wt % of resin, dissolved in minimal xylene solvent) drop wise through a dropping funnel under continuous stirring condition at 60 ± 5°C. TLC and hydroxyl values were measured at regular intervals to monitor the progress of the reaction. The reaction was stopped on attaining the desired TLC and hydroxyl value. Repeatedly dissolving in xylene and filtering purified the final product. Finally, xylene was removed on the reaction mixture by vacuum rotary apparatus under reduced pressure to obtain pure Zn/Cd-LPEAUr resin.

Antibacterial Activity of Zn/Cd-LPEAUr

Zn/Cd-LPEAUr was screened for their antibacterial activity against Gram positive (*Staphylococcus aureus*) and Gram negative (*Escherichia coli*) bacteria. The antibacterial activity was evaluated with respect to Amekasin (amino glycoside) as a standard controlled drug in the nutrient agar diffusion method.⁵⁷ All the samples are soluble in xylene. The antibacterial tests were therefore carried out in xylene. It has no effect on the growth of microorganism.

One loopful of bacteria was inoculated in 10 mL of nutrient broth (peptone 5 g/L, pH 6.8) and incubated at 37°C for 28–30 h in a test tube shaker at 100 rpm. The actively growing bacterial cells were used for inhibition studies. The nutrient agar (20 mL) was poured into sterile petridishes and allowed to solidify at room temperature. After solidification 0.1 mL of the bacterial culture was spread on the nutrient agar. A circular well (9 mm, diameter) was made with a sterilized steel borer. The Zn/Cd-LPEAUr was prepared in xylene, as this solvent had no effect on growth of microorganisms. These test samples containing different wt % of metal was used to study the antibacterial activity. 0.1 mL of each Zn/Cd-LPEAUr resin test solution was added into the well and incubated at 37°C for 24 h. After incubation

TABLE I
Physico-Chemical Characterizations of Zn-LPEA, Cd-LPEA, LPEAUr, Zn-LPEAUr, and Cd-LPEAUr

Resin code ^a	Hydroxyl value (%)	Saponification value (mg KOH/g)	Iodine value (g I ₂ /100 g)	Specific gravity (g/mL)	Refractive index	Inherent viscosity (dl/g)
Zn-LPEA	7.67	89	45.0	1.2105	1.5322	0.712
Cd-LPEA	7.65	86	44.3	1.2124	1.5380	0.723
LPEAUr-6	4.86	103	39	0.960	1.5200	0.697
Zn-LPEAUr-4	3.92	71	42	1.2145	1.5570	0.762
Zn-LPEAUr-6	3.78	65	41	1.2153	1.5652	0.768
Zn-LPEAUr-8	3.66	63	40	1.2172	1.5701	0.776
Zn-LPEAUr-10	3.56	61	37	1.2190	1.5770	0.788
Cd-LPEAUr-4	3.52	66	38	1.2149	1.5631	0.775
Cd-LPEAUr-6	3.38	60	37	1.2158	1.5704	0.779
Cd-LPEAUr-8	3.27	58	36	1.2179	1.5753	0.787
Cd-LPEAUr-10	3.17	56	34	1.2203	1.5812	0.799

^a The numerals given along with the resin codes indicate the wt % of TDI.

the zone of inhibition was measured in millimeter and represented as inactive (–), mild (+), moderate (++), and highly active (+++) depending upon the diameter and clarity of zone (Table IV).

Test methods

FTIR, ¹H-NMR, and ¹³C-NMR characterized the chemical structure of Zn/Cd-LPEAUr. FTIR spectra of these resins were taken on Perkin-Elmer 1750 FTIR spectrophotometer (Perkin-Elmer Instruments, Norwalk, CT) using a NaCl cell. ¹H-NMR and ¹³C-NMR spectra were recorded on JEOL GSX 300MHZ FX-1000 spectrometer using deuterated chloroform as a solvent, and tetramethylsilane (TMS) as an internal standard. The thermogravimetric analysis (TGA) was done with thermogravimetric analyzer, TA-51 (T.A. Instruments USA) at 20°C/min in nitrogen atmosphere. Differential scanning calorimetric analysis (DSC) was done in Dupont 910 model at 10°C/min in nitrogen atmosphere. Solubility of these resins were tested in various polar and nonpolar solvents by taking 25 mg of each resin in 5 mL of different solvents in a closed test tube and set aside for a day. Iodine value, hydroxyl value, saponification value, inherent viscosity, specific gravity, and refractive index were determined by standard laboratory methods (Table I).

Preparation of coatings

The coatings were prepared by brush technique using solution containing 60% resin in xylene applied on mild steel strips. The strips were polished on various grade of silicon carbide papers and then washed with water and degreased with alcohol and carbon tetrachloride. They were dried under vacuum for several hours. The standard sizes of strips of 30 × 10 × 1 mm³ size were taken for chemical/corrosion resistance test in water, acid (5 wt % HCl), alkali (5 wt %), xylene solvent by placing

them in 3-in. diameter porcelain dishes. Salt spray test (ASTM B177-94) in 3.5-wt % NaCl solutions was also carried out for a period of 10 days in a salt mist chamber. The coated panels were dipped in the aforementioned media and periodic examination was conducted until coatings showed visual evidence of softening, deterioration in gloss, discoloration or weight loss (Table II). The strips of 70 × 25 × 1 mm³ size to evaluate their physicochemical properties such as scratch hardness (BS 3900), bending (ASTM D3281-84), impact resistance (IS: 101 part 5/s.3, 1988) and specular gloss at 45° by gloss meter (model RSPT 20; Digital Instrument, Santa Barbara, CA) (Table III). The thickness of the coating was found to be between 75 and 100 μm as measured by Elcometer (Model 345; Elcometer Instrument, Manchester, UK).

RESULTS AND DISCUSSION

Synthesis

In situ synthesis of Zn/Cd-LPEA and their Zn/Cd-LPEAUr were carried out through the condensation polymerization reaction between hydroxyl groups of HELA and anhydride group of PA followed by addition polymerization reaction between residual free hydroxyl groups of Zn/Cd-LPEA and isocyanate groups of TDI. The reaction proceeds via addition-elimination mechanism at the carbonyl double bond of the carboxylic group of the LPEA chains, the acyl substitution involving in the same set up. While urethane formed through the addition reaction without any catalyst. In this reaction hydroxyl terminated Zn/Cd-LPEA itself acts catalytically. Since Zn/Cd-LPEA contain divalent zinc and cadmium in a chain. Therefore, it is assumed, that the reaction is also catalyzed through these metals.²⁶ Generally the TDI used in the development of Zn/Cd-LPEAUr is available in two isomeric forms, toluylene-2, 4-diisocyanate and toluylene-2, 6-diisocyanate

TABLE II
Physico-Mechanical and Anticorrosive/Chemical Resistance Properties of Zn-LPEA, Cd-LPEA, LPEAUr, Zn-LPEAUr, and Cd-LPEAUr

Resin code	Scratch hardness (kg)	Impact resistance (lb/in.) passes	Gloss at 45°	Bending test, inch passes	Corrosion resistance				
					H ₂ O 10 days	NaOH (5%) 2 h	HCl (5%) 15 days	NaCl (3.5%) 15 days	Xylene 15 days
Zn -LPEA	3.20	150	130	1/8	e	a*	c	c	e
Cd-LPEA	3.50	150	155	1/8	e	a*	c	c	e
LPEAUr-6	2.10	100	130 ¹	1/8	e	a ²	c ³	c ³	e ³
Zn-LPEAUr-4	4.00	150	150	1/8	e	b	e	e	e
Zn-LPEAUr-6	4.30	150	152	1/8	e	b	e	e	e
Zn -LPEAUr-8	4.50	150	152	1/8	e	b	e	e	e
Zn -LPEAUr-10	4.90	150	154	1/8	c	c	e	e	e
Cd-LPEAUr-4	4.10	150	175	1/8	e	b	e	e	e
Cd-LPEAUr-6	4.40	150	177	1/8	e	b	e	e	e
Cd-LPEAUr-8	4.90	150	178	1/8	e	b	e	e	e
Cd-LPEAUr-10	5.20	150	180	1/8	e	c	e	e	e

The coating passes adhesion test with no visible damage. a-film completely removed, b-film cracked and partially removed, c- slight loss in gloss, d- loss in gloss, e- unaffected, f-film slightly swell, 1-gloss at 60°, 2- after 3 h, 3- after 10 days and * Film completely removed in one h.

in the weight ratio 80 : 20. The former isomeric form is more reactive than the latter.^{26,29} Therefore, all the reactions are based on former isomer. It is observed during the synthesis that beyond 10-wt % loading of TDI the resins become highly viscous and no gel formation occurs. At this stage the resin becomes unbrushable. This can be attributed to the reaction of isocyanate groups of TDI with active hydrogen of hydroxy terminated Zn/Cd-LPEA to form a linear urethane chain (primary reaction) leading to the increase in molar mass and viscosity.^{29,38,41}

Spectral analysis

FTIR spectral analysis of Zn/Cd-LPEA⁵⁶ and Zn/Cd-LPEAUr show the following additional characteristic absorption bands: 3420–3200 cm⁻¹ (broad band of —NH stretching of urethane linkage with contribution of hydrogen bonding in the system),

TABLE III
Thermal Stability of Zn-LPEA, Cd-LPEA, LPEAUr-6, Zn-LPEAUr, and Cd-LPEAUr

Polymer	T ₅ (°C)	T ₂₀ (°C)	T ₅₀ (°C)	T ₈₀ (°C)
Zn-LPEA	320	375	455	655
Cd-LPEA	330	395	475	675
LPEAUr-6	235	330	395	500
Zn-LPEAUr-4	306	360	450	635
Zn-LPEAUr-6	301	354	440	630
Zn-LPEAUr-8	296	354	435	630
Zn-LPEAUr-10	291	352	430	625
Cd-LPEAUr-4	315	387	470	665
Cd-LPEAUr-6	310	382	470	665
Cd-LPEAUr-8	305	382	475	660
Cd-LPEAUr-10	300	380	465	670

T₅, T₂₀, T₅₀ and T₈₀ are temperatures at 5 wt %, 20 wt %, 50 wt %, and 80 wt % decomposition, respectively.

3600–3400 cm⁻¹ (lower intensity, residual hydroxyl groups), 1684 cm⁻¹ (>C=O stretching of urethane groups), 2272 cm⁻¹ (free —NCO groups), 1540.4 and 1240 cm⁻¹ (due to the interaction of C—N stretching and N—H bending), 668.2 cm⁻¹ (N—H wagging of urethane group), and shifting towards lower values was also observed in bands such as those of >C=O (ester) stretching (7–10 cm⁻¹) and C—N stretching (5–6 cm⁻¹). These shifting are also correlated to the hydrogen bonding, which occurs between the hydrogen of urethane groups and carbonyl groups of urethane and polyesteramide chains. ¹H-NMR spectra (Fig. 1) of Zn/Cd-LPEAUr shows the characteristic bands at δ = 2.14–2.12 ppm (CH₃ of TDI), δ = 7.98–7.80 ppm (hydrogen bonded —NH of urethane), δ = 6.6–6.90 ppm (non hydrogen bonded —NH of urethane) and δ = 4.0–3.98 ppm (CH₂ attached to —OOCNH). ¹³C-NMR spectra of Zn/Cd-LPEAUr (Fig. 2) shows the signals at δ = 154.15–153.48 ppm, which is due to the carbonyl carbon of urethane group. The signals of aromatic carbons are observed between δ = 142.5–115 ppm, while in Zn/Cd-LPEA⁵⁶ these signals are observed between δ = 137–124 ppm. The additional signals observed in aromatic region of the spectra of Zn/Cd-LPEAUr are due to the aromatic ring carbons of TDI, the CH₃ of the latter is observed at δ = 17.23 ppm. FTIR, ¹H-NMR, and ¹³C-NMR spectral studies confirm the structure of the synthesized Zn/Cd-LPEAUr. These spectral studies also confirm the presence of hydrogen bonding in the system.

Physico-chemical characterizations

Physical and chemical characteristics of Zn/Cd-LPEAUr were determined by using several tests. The results of these tests are summarized in Table I.

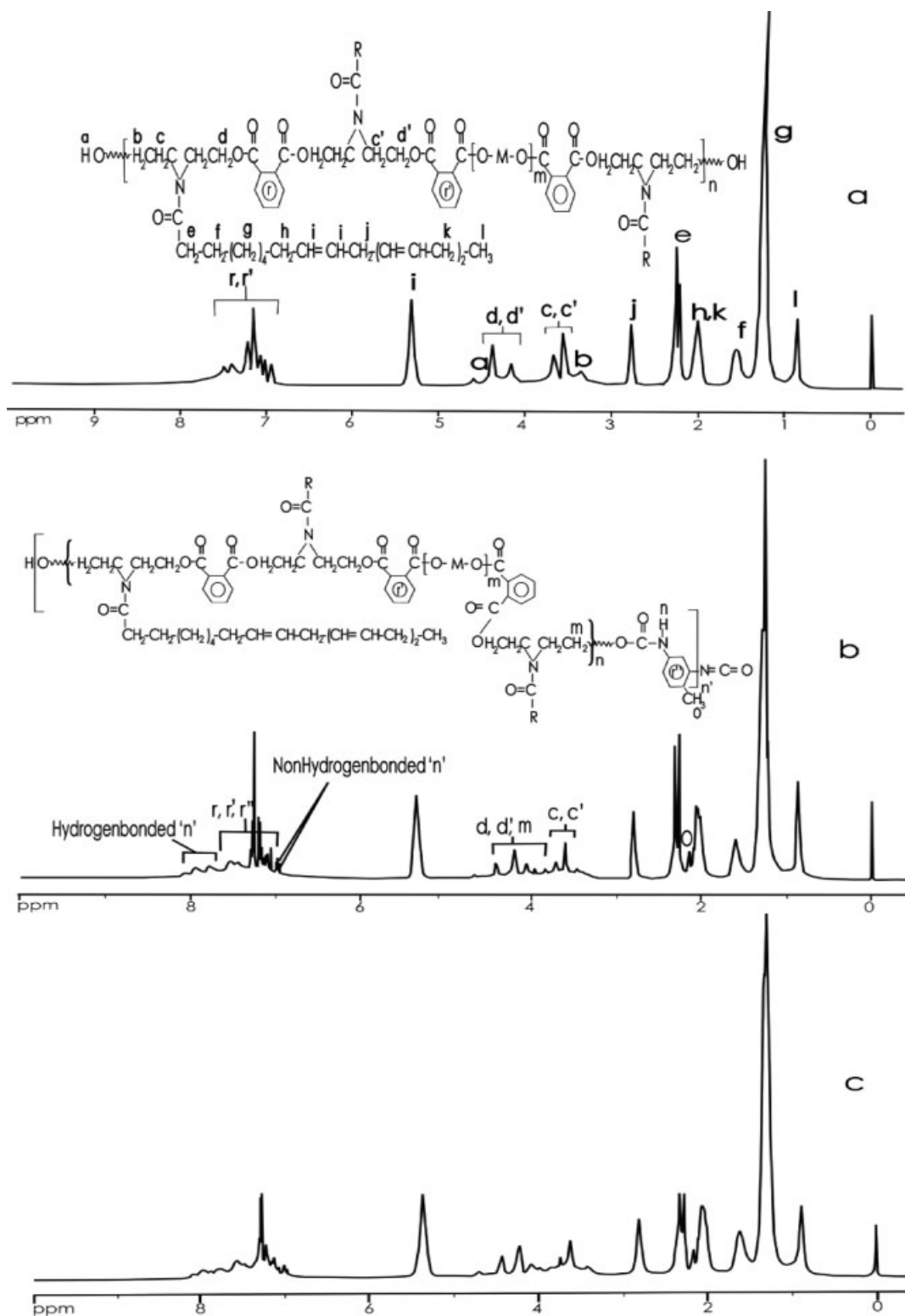


Figure 1 $^1\text{H-NMR}$ spectra of (a) Zn/Cd-LPEA, (b) Zn-LPEAUr-10 and (c) Cd-LPEAUr-10.

It is observed that the hydroxyl, saponification and iodine values decrease from Zn/Cd-LPEA to Zn/Cd-LPEAUr. In the same system these values further decrease with the increase in loading of TDI. This effect can be correlated to the increase in molar

mass of the resins with the higher loading of TDI. The increase in molar mass of the resins would enhance the values of specific gravity, refractive index, and inherent viscosity from Zn/Cd-LPEA to Zn/Cd-LPEAUr. These characteristics were found to

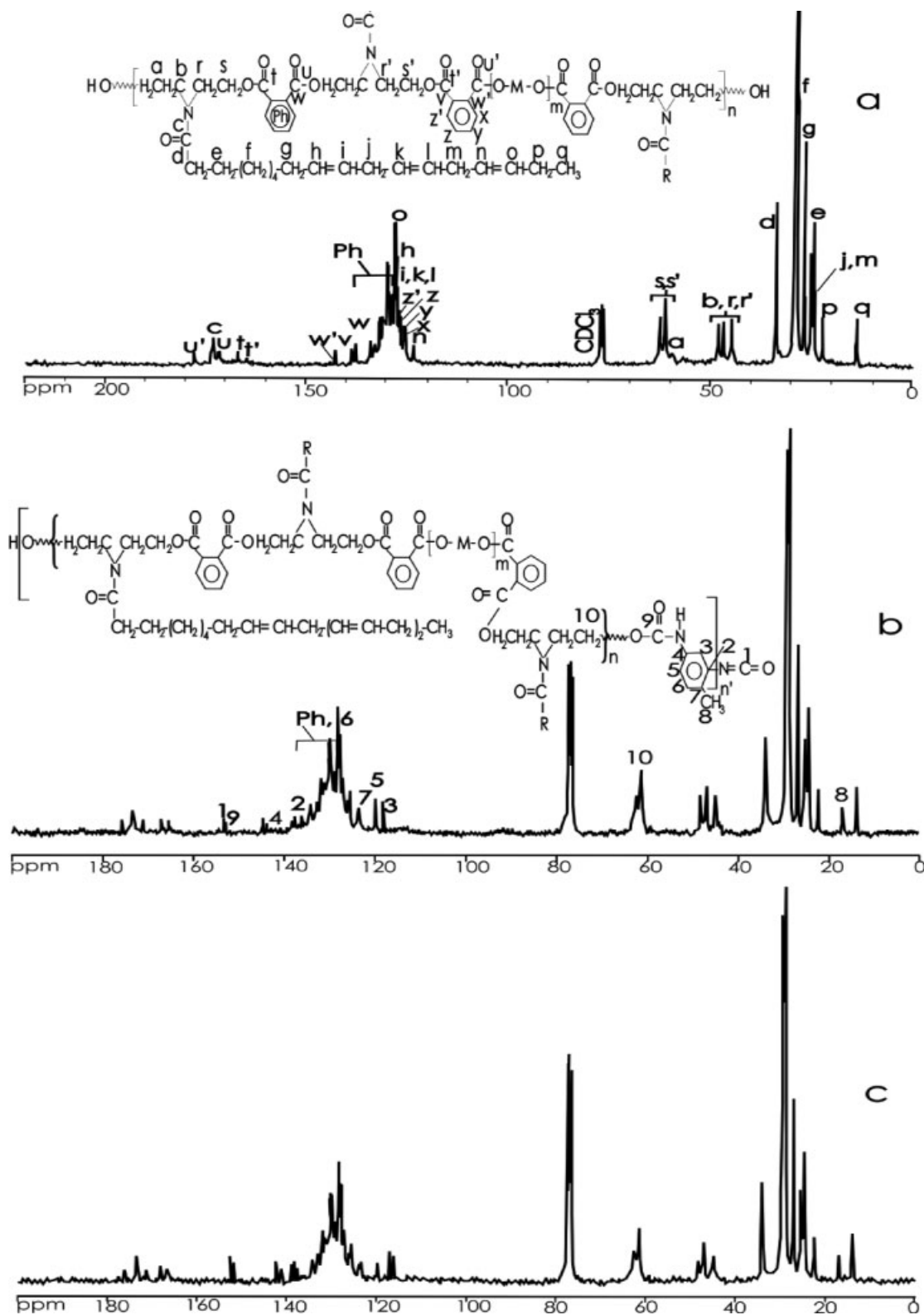


Figure 2 ^{13}C -NMR spectra of (a) Zn/Cd-LPEA, (b) Zn-LPEAU_r-10 and (c) Cd-LPEAU_r-10.

further increase with the increase loading of TDI in the same system (Table I).

Zn/Cd-LPEAU_r resins showed good solubility (100 wt %) in xylene, toluene, chloroform, carbon

tetrachloride, ether, acetone, dimethylsulfoxide (DMSO), and dimethylformamide (DMF) while it has lower solubility (20 wt %) in ethanol and methanol and are insoluble in water. The solubility

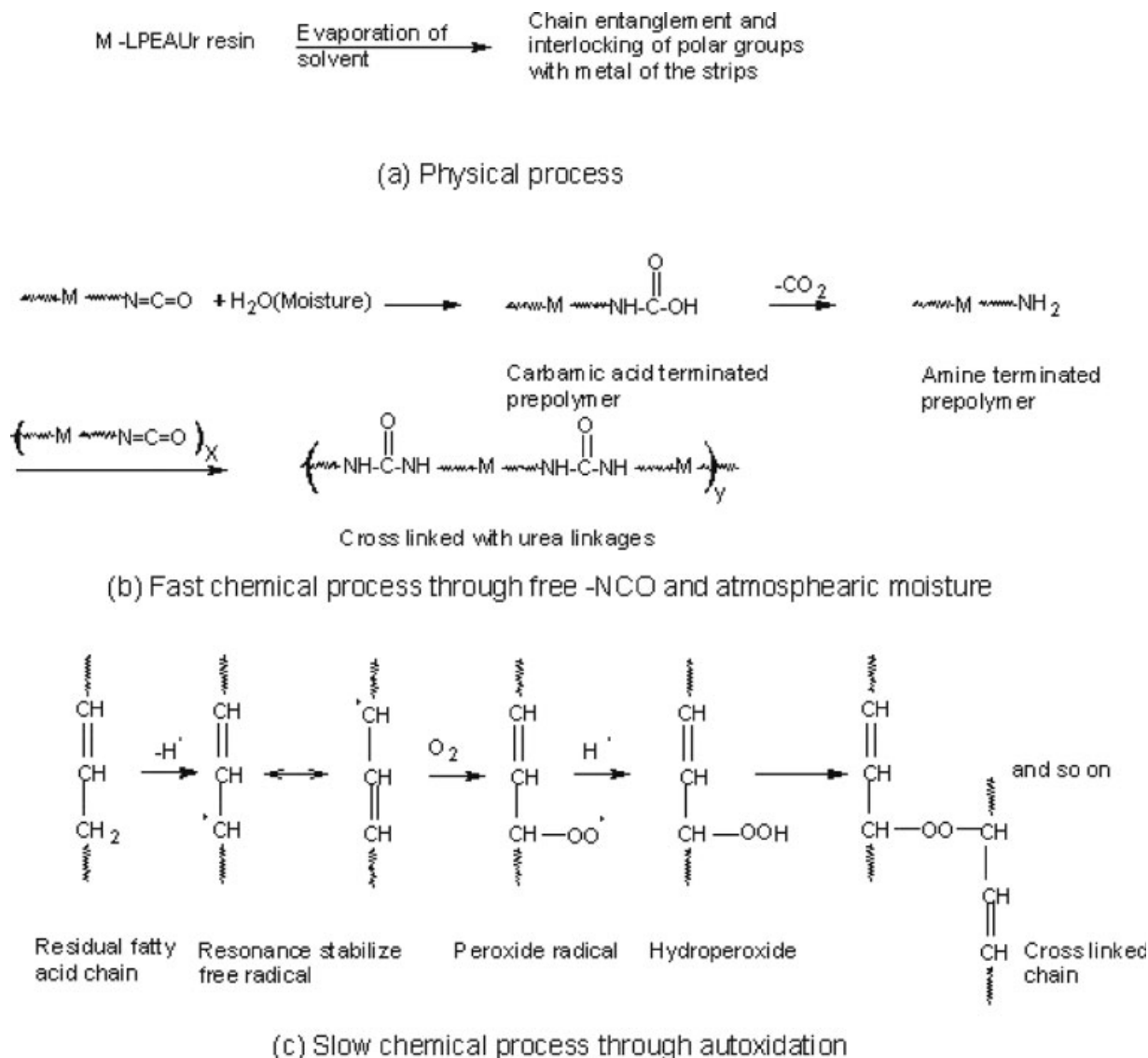


Figure 3 The reactions involved in an ambient cure film of Zn/Cd-LPEAUr resin.

behavior of these resins can be attributed to the presence of long fatty acid hydrocarbon chain as well as polar groups.

Coatings properties

Coatings of the Zn-LPEA and Cd-LPEA were obtained by baking, respectively, at 150 and 170°C,⁵⁶ that of LPEAUr at ambient temperature for 20 min (dry to touch)⁴¹ whereas coatings of Zn-LPEAUr/Cd-LPEAUr with loading of TDI, 4–10 wt % of resin, were obtained at ambient temperature (28–30°C) within 15–20 min (dry to touch). It is reported that the reaction of the isocyanate groups of TDI with the diols or triols produce curing of the polyurethane films at room temperature.^{38,39,41} The reactions involved in the curing of Zn/Cd-LPEAUr coatings

are shown in Figure 3. Coatings with loading of TDI, 2 wt % of resin, did not harden at room temperature even after a week. It seems that TDI, 2 wt % of resin, fail to provide required crosslinking for hardening of the films. Therefore, physicomechanical properties of Zn/Cd-LPEAUr coatings above 2 wt % of resin loading, i.e., TDI, 4–10 wt % of resin, are given in Table II. These properties are compared with those of Zn/Cd-LPEA and petrobased polyurethane [PPU].²⁹ It was found that scratch hardness increases from PPU and Zn/Cd-LPEA to Zn/Cd-LPEAUr. The values of these characteristics further increase in Zn/Cd-LPEAUr with the loadings of TDI. Coatings of Zn/Cd-LPEAUr of all compositions pass 1/8 in. conical mandrel and 150 lb/in. impact resistance tests. The good toughness and flexibility of films result from the higher molar mass and

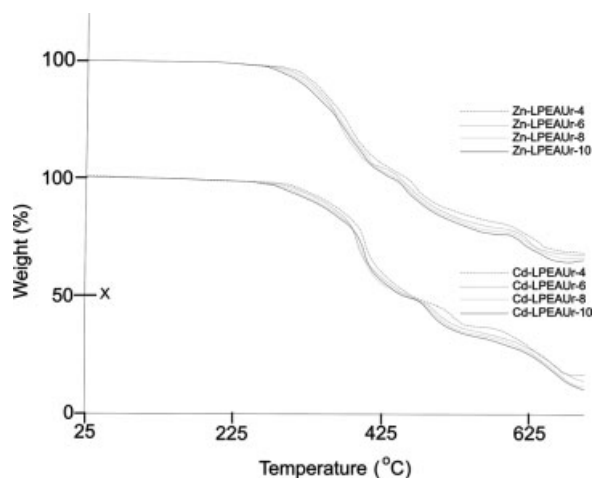


Figure 4 TGA thermogram of ambient cured Zn-LPEAUr and Cd-LPEAUr films.

crosslinked structure of these resins. Besides these factors, the increase in polar groups such as urethane, presence of metal in the backbone, and long fatty amide chains contribute to the excellent flexibility and adhesion of the coatings. Along with these the -NH group of urethane linkage forms hydrogen bonds with the substrate as well as with the carbonyl oxygen atom of the polymer itself which also results in well adhered coatings.^{2,29} Zn/Cd-LPEAUr coatings show excellent gloss in comparison to Zn/Cd-LPEA, LPEAUr, and PPU^{29,58} because of the metal and urethane groups in the resins.

The results of chemical resistance tests of the coatings of Zn/Cd-LPEAUr are given in Table II. The results reveal that the chemical resistance performance remains same for all compositions of the urethane modified systems but each give better results than Zn/Cd-LPEA under water, acid (5%), salt (3.5%), and xylene. The alkali (5% NaOH) resistance of the Zn/Cd-LPEAUr coatings improved in comparison to Cd-LPEA/Zn-LPEA and LPEAUr coatings (Table II). These performances can be correlated to the urethane linkage, which is less hydrolysable in nature than ester groups of the system.²⁹ Besides this, well adhered coating formed through the polar groups as well as crosslinked structure of the coatings do not allow the corrosive ions to penetrate easily through the coating structure on interaction with various solvents and chemicals.^{2,41} The chemical resistance properties of Zn/Cd-LPEAUr coatings compared with those of PPU coatings and found comparable.^{29,58}

It is observed that coatings of Zn/Cd-LPEAUr with loading of TDI, 10-wt % of resin show best physicochemical and chemical resistance performance in comparison to all compositions. The coatings of compositions beyond the loading of TDI, 10-wt % of resin was not obtained due to the high viscosity

of the resins that make them unbrushable. The coating of Cd-LPEAUr-10 system show better physicochemical and chemical resistance performance than the coatings of Zn-LPEAUr-10 system which may have been caused by the highest molar mass of Cd-LPEA.⁵⁶

Thermal analysis

TGA analysis (Fig. 4) of all compositions of Zn/Cd-LPEAUr with different TDI loadings, wt % of resin, is given in Table III. It is revealed that the thermal stability of Zn/Cd-LPEAUr coatings decreases in comparison to Zn/Cd-LPEA while it increases in respect to PPU²⁹ and LPEAUr. Thermal stability of former resins slightly decreases with the increase loading of TDI; the urethane linkages cause the decrease in thermal stability of Zn/Cd-LPEAUr.⁴² It is also observed that the thermal stability of Zn/Cd-LPEAUr is higher than that of Zn/Cd-incorporated petrobased polyurethane.^{5,30} This can be due to the long fatty acid hydrocarbon chains and amide linkages in the former resin. DSC thermograms of Zn/Cd-LPEAUr-10 (Fig. 5) show the glass transition temperatures (T_g) respectively, at above 115 and 120°C. Although the decomposition observed to start, respectively, at 325 and 335°C, which matches with onset of decomposition observed in TGA

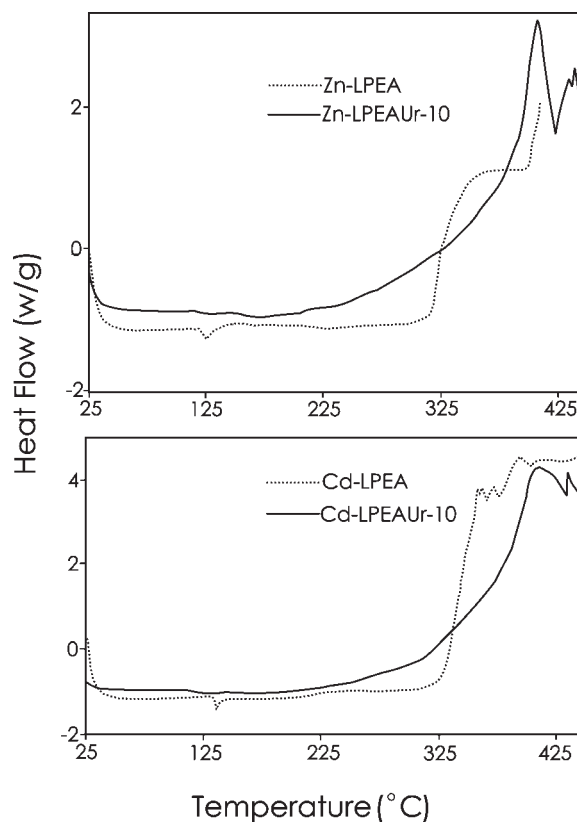


Figure 5 DSC thermogram of the resins.

TABLE IV
Antibacterial Activities of Zn-LPEA, Cd-LPEA, LPEAUr-6, Zn-LPEAUr, and Cd-LPEAUr

Resin code	<i>E. coli</i>	<i>S. aureus</i>
Zn-LPEA	+++	+++
Cd-LPEA	+++	+++
LPEAUr-6	+	+
Zn-LPEAUr-4	+	++
Zn-LPEAUr-6	++	++
Zn-LPEAUr-8	+++	+++
Zn-LPEAUr-10	+++	+++
Cd-LPEAUr-4	+	++
Cd-LPEAUr-6	++	++
Cd-LPEAUr-8	+++	+++
Cd-LPEAUr-10	+++	+++

–, Inactive (0–9 mm); +, mildly active (10–15 mm); ++, moderately active (16–20 mm); +++, highly active (21–30 mm).

(Fig. 4). The appearance of T_g in these resins indicates the increase in the molar mass as well as cross-linking of these resins, which enhances the plasticity in these resins. It is interesting to note that Zn/Cd-LPEA shows melting events in their DSC thermogram (Fig. 5),⁵⁶ which indicates that Zn/Cd-LPEA has lower molar mass than Zn/Cd-LPEAUr resins.

Antibacterial activities

The antibacterial activities of LPEAUr - 6 and Zn/Cd-LPEAUr with loading of 4-wt % to 10-wt % of resin are given in Table IV. It is observed that the antibacterial activity of Zn/Cd-LPEAUr initially decreases but as the loading of TDI increases, the antibacterial activity also increases both in *E. coli* and *S. aureus*. In our earlier work we have found that Zn/Cd-LPEA inhibit the microbial growth.⁵⁶ In Zn/Cd-LPEAUr contain metals and long alkyl chain in the backbone of the resin as well as terminal –OH and –NCO groups that collectively show the inhibitory influence on the cellular metabolic activities by forming bonds or complexes with several organic functional groups (–NH₂, –OH, –COOH, and –SH) of bacterial cell.^{59,60} The antibacterial performance of Zn/Cd-LPEAUr-10 is comparable with the Zn/Cd-incorporated petrobased polyurethane and higher than those of LPEAUr-6.^{5,30}

CONCLUSIONS

In situ conversion of Zn/Cd-LPEA into Zn/Cd-LPEAUr, by the reaction of the former with TDI enhances all the physicochemical and chemical resistance characteristics of the coatings of the latter resins, as well as to avoid the application of excessive amount of volatile organic solvents (VOCs). The thermal stability of these resins is found to slightly decrease while antibacterial activity increases with

the loading of TDI. Zn/Cd-LPEAUr with 10-wt % loading of TDI shows best physicochemical, chemical/corrosion resistance properties, and antibacterial activity among all compositions. While Cd-LPEAUr-10 system shows better performance than Zn-LPEAUr-10 system. Zn-LPEAUr-10 and Cd-LPEAUr-10 resin systems can be safely used respectively, up to 291 and 300°C as protective coatings. These resins show higher thermal stability and comparable antibacterial performance to that of petro-based Zn/Cd-incorporated polyurethane.

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