Synthesis and Characterization of Poly(esteramideurethane) from Linseed Oil as Anticorrosive Coatings

Manawwer Alam,¹ Alok R. Ray,^{1,2} Sharif Ahmad³

¹Centre for Biomedical Engineering, Indian Institute of Technology Delhi, Hauz Khas, New Delhi 110 016, India ²Biomedical Engineering Unit, All India Institute of Medical Science, New Delhi 110 029, India ³Department of Chemistry, Materials Research Laboratory, Jamia Millia Islamia, New Delhi 110 025, India

Received 17 September 2008; accepted 25 March 2009 DOI 10.1002/app.30936 Published online 7 August 2009 in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: Ethylene diamine polyesteramide (Ed-PEA) was synthesized from *N*, *N*-bis (2-hydroxy ethyl) linseed oil fattyamide and ethylene diamine tetra acetic acid through condensation polymerization. It was further treated with toluylene 2,4-diisocyanate (TDI) in different weight percentage to obtain urethane-modified polyesteramide (Ed-UPEA). The structural elucidation of Ed-PEA and Ed-UPEA were carried out by FTIR, ¹H-NMR, and ¹³C-NMR spectroscopic techniques. Thermal studies of these resins were carried by thermogravimetric analysis

(TGA) and differential scanning calorimetry (DSC). The coatings of urethane-modified polyesteramide were prepared on mild steel strips and their anticorrosive behavior of in acid, alkali, water, and xylene were investigated. Thermal stability performance suggests that the system could be safely used upto 200°C. © 2009 Wiley Periodicals, Inc. J Appl Polym Sci 114: 3268–3273, 2009

Key words: linseed oil; ethylene diamine tetra acetic acid; polyesteramide; coatings

INTRODUCTION

The global scenario in the field of surface coatings has now been shifted to sustainable resource-based coatings. Petroleum-based products, which were earlier main source of the coating material, are being replaced by vegetable oil due to escalating prices and depleting petroleum stocks.^{1–4} Vegetable seed oils, as a sustainable resource, are considered important due to their functional attributes. They have been actively utilized to develop low-molecularweight polymers, eg., alkyds, polyesters, polyepoxies, polyurethanes, and monomers such as fatty amide diols.^{5–12}

Fatty amide diols are obtained by the base catalyzed aminolysis of seed oils viz. linseed, soybean, pongamia glabra, castor oil, annona squamosa oil, and argemone oil with diethanolamine.^{13–16} Polyester modifications of fatty amide diols have been exhaustively reported through their reaction with dicarboxylic acids such as maleic acid, phthalic acid, isophthalic acid, fumaric acid, sebacic acid, terphthalic acid, adipic acid, succinic acid, and their anhydrides^{17,18} by using suitable curing agents such as isocyanates and melamine formaldehyde that are capable of reacting with hydroxyl moieties.^{9,14,17} The modification of fatty amide diols has been reported with styrene and acrylic monomers.¹⁷

Ethylene diamine tetra acetic acid (EDTA) is a tetra functional compound. EDTA has been widely used as ligand in coordination chemistry; its sodium salts are widely used in water softening. EDTA is also used in the preparation of chelating polymers.^{19–21}

An exhaustive scanning of the literature reveals that voluminous research work has been carried out and good numbers of publications have appeared on the introduction of ester moieties in fatty amide diol to yield polyesteramide resins. However, the modification of oil fatty amide diol using EDTA has not been reported yet.²²⁻²⁷ In this work, we have attempted to explore the film and chemical resistance properties of the resin obtained by the modification of HELA with EDTA, which looks to an attractive proposition to the above end. We have found that coatings of Ed-UPEA are superior to this genera in some respect. The approach holds several advantages such as cost effectiveness, eco-friendliness, and simple curing route operative at ambient temperature involving shorter curing route over several other reported petro-based system.

HELA was reacted with ethylene diamine tetra acetic acid (EDTA) to obtain ethylene diamine polyesteramide (Ed-PEA), which was further treated

Correspondence to: M. Alam (malamiitd@gmail.com).

Contract grant sponsor: Council of Scientific and Industrial Research (CSIR) (New Delhi, India); contract grant number: 9/86/0859/08 EMR-I.

Journal of Applied Polymer Science, Vol. 114, 3268–3273 (2009) © 2009 Wiley Periodicals, Inc.

	rhysico-Chemical Characterization of Ed-FEA and Ed-OFEA								
Resin code ^a	Acid value	Iodine value	Hydroxyl value	Saponification value	Ref. index	In. viscosity	Sp. gravity		
HELA	_	68							
Ed-PEA	25	50	15	125	1.4501	0.6465	0.9209		
Ed-UPEA14	15	36	12	90	1.5058	0.6480	0.9271		
Ed-UPEA16	10	32	10	85	1.5085	0.6489	0.9293		
Ed-UPEA18	8	30	8	83	1.5113	0.6552	0.9300		
Ed-UPEA20	7	30	7	80	1.5138	0.6592	0.9305		

TABLE I nysico-Chemical Characterization of Ed-PEA and Ed-UPEA

Ref, refractive index; In viscosity, inherent viscosity; Sp. gravity, specific gravity.

^a Last digit of resin code indicate the amount of TDI loading in percentage.

with TDI to obtain urethane polyesteramide (Ed-UPEA). The stipulated reaction schemes for synthesis and curing of the resins were confirmed by FTIR,¹H-NMR, and ¹³C-NMR spectroscopic techniques. Thermal analyses were carried out by TGA and DSC techniques.

EXPERIMENTAL

Materials

Linseed oil, (procured from local market), the fatty acid composition of the oil was determined by gas chromatography (GC; 111/85.5 column, FID detector), Diethanolamine, sodium methoxide, xylene, ethylene glycol monomethyl ether, ethylene diamine tetra acetic acid (Merck, India), toluylene-2,4-diisocyanate (TDI) (Merck, Germany), and xylene were of analytical grade.

Synthesis of *N*,*N*-bis(2-hydroxy ethyl) linseed oil fatty amide (HELA)

HELA was prepared according to a previously reported method.²⁶

Synthesis of ethylenediamine polyesteramide (Ed-PEA)

HELA (0.04 mol) and ethylene diamine tetraacetic acid (EDTA) (0.014 mol) were dissolved in 50 mL xylene and were placed in a four-necked round bottom flask fitted with Dean Stark trap, nitrogen inlet tube, thermometer, and mechanical stirrer. The reaction mixture was heated at 180°C and refluxed until the calculated amount of water was collected in Dean Stark trap. The progress of the reaction was monitored by acid value as well as TLC at regular intervals, excess solvent was removed from the product under reduced pressure in rotary vaccum evaporator.

Synthesis of urethane-modified ethylenediamine polyesteramide (Ed-UPEA)

Ed-PEA and TDI (14–20 wt %) in xylene were placed in a four-necked round bottom flask fitted with cold water condenser, nitrogen inlet tube, thermometer, and magnetic stirrer. The reaction was carried out under stirring at 120°C. The reaction was monitored by TLC at regular intervals. The solvent was evaporated to obtain Ed-UPEA.

Characterization

FTIR spectra of Ed-PEA and Ed-UPEA resins were taken by Perkin Elmer 1750 FTIR spectrophotometer (Perkin Elmer Cetus Instrument, Norwalk, CT) using NaCl cell. ¹H-NMR and ¹³C-NMR spectra were recorded on Bruker Spectrospin DPX300 MHz using deuterated chloroform (CDCl₃) as solvent and TMS as an internal standard. Thermal analysis was carried out by TGA 51 (TA Instrument, New Castle, DE) in nitrogen atmosphere at the heating rate of 20°C/min. The curing behavior of Ed-UPEA was studied by DSC10 (TA Instrument) in nitrogen atmosphere. The physico-chemical properties, e.g., iodine value, hydroxyl value, acid value, saponification value, specific gravity, and refractive index were determined by standard laboratory methods (Table I). Inherent viscosity of Ed-PEA and Ed-UPEA were determined in ethylene glycol mono methyl ether, (0.5 g/100 mL solvent) at 25°C with the help of Ubbelhode viscometer and solubility of the resin was tested in various organic solvents.

Preparation of coatings

Coatings of Ed-UPEA were prepared on commercial available mild steel strips of $30 \times 10 \times 1$ mm for chemical resistance and $70 \times 25 \times 1$ mm for gloss, scratch hardness (BS 3900), impact resistance (IS: 101 part 5/section 3,1988) and bend test (ASTM D3281-84). The coatings were applied by brush technique using a solution containing 40 wt % of the resin in xylene. The specular gloss was determined at 45° by

Journal of Applied Polymer Science DOI 10.1002/app

Physico-Mechanical and Anticorrosive Properties Ed-UPEA Resins												
Resin code ^a	Gloss (45°)	S. hardness (Kg)	I. resistance (lb/in)	B. test (inch)	Chemical resistance							
					H ₂ O (7 days)	5 wt % HCl (7 days)	5 wt % NaOH (3 h)	Xylene (7 days)				
Ed-UPEA14 Ed-UPEA16 Ed-UPEA18	48 48 49	- 3.5 4.5	150 150 150	1/8 1/8 1/8	c c d	a b e	a a e	d d e				
Ed-UPEA20	52	3.1	150	1/8	d	e	e	e				

TABLE II hysico-Mechanical and Anticorrosive Properties Ed-UPEA Resins

a, film completely dissolves; b, film partially dissolves; c, film swells loss in gloss; d, loss in gloss film unaffected; e, unaffected; S. hardness, scracth hardness; I. resistance, impact resistance; B. test, bend test.

^a Last digit of resin code indicate the amount of TDI loading in percentage.

Glossmeter, Model, RSPT 20 (Digital Instrument, Santa Barbara). Coating thickness was measured by Elcometer Model 345 (Elcometer Instrument, Manchester, UK). Thickness of these coatings was found between 110 μ m and 90 μ m. Corrosion tests were performed in water, acid (5 wt % HCl), alkali (5 wt % NaOH), and xylene by placing them in 3 inch diameter porcelain dishes, in aforementioned media. Periodic visual examination was conducted until the films showed evidence of softening or deterioration (Table II).

RESULTS AND DISCUSSION

Reaction Schemes 1 and 2 provide the synthesis of Ed-PEA by condensation polymerization reaction between HELA and EDTA and the curing reaction of Ed-PEA with TDI to form Ed-UPEA, respectively. These reactions were confirmed by the presence of characteristic absorption bands and peaks in FTIR, ¹H-NMR, and ¹³C-NMR spectra.

Spectral analysis of Ed-PEA and Ed-UPEA

In FTIR spectra of Ed-PEA, broad band of hydroxyl group occurs at 3447 cm⁻¹. –CH₂ symmetric and



In FTIR spectra of Ed-UPEA, the aforementioned absorption bands are also observed along with some additional bands. The band appearing at 2273 cm⁻¹ can be attributed to that of free —NCO group and another at 1728 cm⁻¹ is correlated to the carbonyl of urethane linkages. The bands of residual hydroxyl groups occur at 3346 cm⁻¹.

¹H-NMR spectra of Ed-PEA (Fig. 1) reveals peaks at $\delta = 4.20$ ppm for –CH₂ attached to –O–(CO)– confirming the reaction of HELA with ethylene diamine tetra acetic acid through the formation of ester linkages. The peaks at $\delta = 0.99$ –0.86 ppm occur for terminal –CH₃ of fatty amide chain, at $\delta = 1.30$ –1.25 ppm for internal –CH₂ of fatty amide chain and at $\delta = 2.08$ –2.02 ppm for –CH₂ attached to olefinic double bonds. Peak at $\delta = 3.56$ –3.48 ppm is attributed to –CH₂ attached to amide nitrogen while at $\delta = 2.07$ –2.02 ppm occurs for –CH₂ attached to



Scheme 1 Synthesis of ethylene diamine polyesteramide (Ed-PEA).



Scheme 2 Synthesis of urethane-modified ethylene diamine polyesteramide (Ed-UPEA).



Figure 1 ¹H-NMR spectra of Ed-PEA.

amide carbonyl. –CH₂ attached to hydroxyl groups is characterized by peak at $\delta = 3.56$ –3.39 ppm, and the peak at $\delta = 5.37$ ppm for protons of olefinic unsaturation.

¹H-NMR spectra of Ed-UPEA (Fig. 2) along with aforementioned peaks show some other characteristic peaks. $-CH_2$ attached to urethane linkage appears at $\delta = 2.34$ ppm, that for $-CH_3$ of TDI appears at $\delta = 2.29$ ppm. The peak for aromatic ring protons of TDI occur at $\delta = 7.28-7.02$ ppm and the peak for -NH of urethane occur at $\delta = 7.80$ ppm. These peaks support the formation of Ed-UPEA through reaction of free -OH group of Ed-PEA with -NCO groups of TDI. The peak for residual -OH groups shows at $\delta = 5.38$ ppm.

¹³C-NMR spectra of Ed-PEA (Fig. 3) gives out peaks of $-CH_3$ (fatty amide chain and TDI), at $\delta =$ 13 ppm and 22 ppm, respectively. The peak of internal $-CH_2$ of fatty amide chain occurs at $\delta = 29-25$ ppm, for $-CH_2$ attached to double bond at $\delta = 24.5$ and for $-CH_2$ attached to amide carbonyl at $\delta = 33-$ 31 ppm. The peak at $\delta = 131-126$ ppm is assigned to unsaturation of fatty amide chain of fatty acid. The peak at $\delta = 61-60$ ppm for $-CH_2$ of HELA attached to ester linkages confirms the incorporation of EDTA into fatty amide chain.

¹³C-NMR spectra of Ed-UPEA (Fig. 4) shows the aforementioned peaks as well as some other characteristics peaks. The small peak at $\delta = 131-126$ ppm appears for the aromatic ring carbons of TDI and unsaturation. The peak at $\delta = 176$ ppm is attributed to the carbonyl of fatty amide chain. Spectral analyses thus confirm the structure of Ed-UPEA.



Figure 2 ¹H-NMR spectra of Ed-UPEA.

Physico-chemical analysis

Table I for physico-chemical characterization data indicates a decrease in hydroxyl and iodine values from HELA to Ed-PEA and subsequently to Ed-UPEA-14, Ed-UPEA-16, Ed-UPEA-18, and Ed-UPEA-20. The following trend is correlated to the reaction of HELA with ethylene diamine tetra acetic acid (EDTA) to form Ed-PEA resulting in an increase in molar mass of the polymer; the molar mass of fatty ester amide polymer further increases with gradual increase in the loading of TDI.

In due course of reaction involving the incorporation of ester and urethane moieties in Ed-PEA and





Figure 4 ¹³C-NMR spectra of Ed-UPEA.

Ed-UPEA, the polymeric resins attain large chain length, which is also confirmed by the increase in inherent viscosity, specific gravity, and refractive index from Ed-UPEA-14 to Ed-UPEA-20 with increased loading of TDI. This further ascertains the higher molar mass of these resins when compared with virgin Ed-PEA and also explains the gradual decrease in hydroxyl, iodine, and saponification values.

Ed-UPEA resin is soluble in chloroform, butanone, benzene, xylene, dimethyl formamide, dimethyl sulphoxide, tetrahydrofuron, acetone, 1–4 dioxane, carbon tetra choloride, ethylene glycol monomethylether, and insoluble in water. The solubility trends of Ed-UPEA resin can thus be attributed to the dense and polar nature of the resin. The water insoluble behavior of resins can be attributed to the water repellent nature of oils due to hydrophobicity of their constituent triglycerides.⁹

Coating properties

The urethane-modified Ed-UPEA resins were applied on mild steel strips of standard sizes to evaluate their coating properties. It was found that Ed-UPEA-14, Ed-UPEA-16, Ed-UPEA-18, and Ed-UPEA-20 take 35–50 min to become dry-to-touch. It was observed that the optimum crosslinking required to attain the drying stage was achieved at 18 wt % loading of TDI in Ed-UPEA resin.

An examination of Table II reveals that scratch hardness values increase upto Ed-UPEA-18, beyond which deterioration is observed. All the systems pass 150 lb/inch impact resistance and 1/8 inch conical mandral bend test. The good impact resistance shows higher adhesion of the coatings with the sub-

Journal of Applied Polymer Science DOI 10.1002/app

strate through coordinate linkage with nitrogen and oxygen atoms. The increased loading of TDI enhances the urethane linkages, which also increase the crosslinking between the chain and improves its toughness and scratch hardness. Beyond 18 wt % loading of TDI, the scratch hardness was found to deteriorate. Infact beyond optimum loading of TDI, urethane linkages will enhance the cross-link density, which will impart stiffness and strain, the coating leading to lower scratch hardness. We find excellent flexibility in the coatings due to the presence of long aliphatic chain and tetra functional EDTA moieties. The gloss at 45° was found to be between 48 and 52. It seems that the gloss of the resins is independent of the amount of TDI.

The chemical resistance tests (Table II) exhibit that the coatings of all the resins show no change in xylene; (7 days) in water (7 days) only the coatings of Ed-UPEA-18 and 20 remain intact. Likewise, in NaOH (5 wt %, 3 h) and HCl (5 wt %, 7 days) the above two resins remain unaffected. It was observed Ed-UPEA systems comprise an excellent combination of amine, ester, urethane groups, and pendant alkyl chain. It reveals a highly cross-linked structure with polar groups, which facilitate good adhesion to the substrate. We understand that the completely cured Ed-UPEA coatings serve the function of anticorrosive primarily by acting as an efficient barrier that prevents the diffusion of chief corrodent, e.g., oxygen and water along with the corrosive ions of various media such as alkali, acid, and salt.²⁹ The chain enhances the flexibility of coatings. Consequently, the coatings show good resistance against

Figure 5 DSC thermogram of Ed-UPEA-18.







Figure 6 TGA thermogram of Ed-UPEA-18.

attack of alkali, acid, and other chemicals. It can thus be concluded that Ed-UPEA-18 shows the best physico-mechanical and chemical resistance properties followed by Ed-UPEA-20.

Thermal analysis

The TGA thermogram (Fig. 5) of Ed-UPEA-18 shows the onset of degradation at 140°C. 10% weight loss is observed at 210°C and 50% weight loss occurs at 401°C. It is also observed that the degradation occurs in two steps. It has been reported that the decomposition of urethane linkage starts between 150 and 200°C depending upon the nature of substituents on its sides. The first degradation events conlinus upto 450°C, since Ed-UPEA contains both ester and amide linkages, this events encompasses their degradation, respectively, at 400 and 450°C. The next decomposition event ensues at 550°C, which corresponds to breaking of hydrocarbon chain.

DSC themogram (Fig. 6) of Ed-UPEA-18 shows an endothermic peak at 137.5°C. The TGA thermogram shows the onset of degradation beyond this temperature. This endothermic peak may be correlated to the melting; this is followed by another sharp and narrow endotherm which represents some molecular reorganization before onset of decomposition of the resin.

CONCLUSIONS

The ethylene diamine tetra acetic acid modified fatty amide diol is excellent example of a novel polyesteramide resin. Its physico-mechanical and anticorrosive performance evaluation present satisfactory results. A novel combination of properties of amide, urethane, EDTA could be achieved by this approach. It offers a simple curing route at ambient temperature and also highlights the significant role played by the aforementioned acid and TDI in improving the coating properties of the systems. The studies reveal that these systems may be safely used upto 200° C.

References

- 1. Guo, A.; Javni, I.; Petrrovic, Z. J Appl Polym Sci 2000, 77, 467.
- Ahmad, S.; Ashraf, S. M.; Zafar, F. J Appl Polym Sci 2007, 104, 1143.
- Ahmad, S.; Haque, M. M.; Ashraf, S. M.; Ahmad, S. Eur Polym J 2004, 40, 2097.
- Aigbodion, A. I.; Pillai, C. K. S.; Bakare, I. O.; Yahaya, L. E. Ind J Chem Technol 2001, 8, 378.
- 5. Wang, C.; Jones, F. N. J Appl Polym Sci 2000, 78, 1698.
- Motawie, A. M.; Hassan, E. A.; Manieh, A.; Aboul-Fetouch, M. E.; Fakhrel-Uddin, A. J Appl Polym Sci 1995, 55, 1725.
- Ahmad, S.; Ashraf, S. M.; Hasnat, A.; Noor, A. Ind J Chem Technol 2001, 8, 76.
- Chen, J.; Soucek, M. D.; Simonsick, W. J.; Celikay, R. W. Polymer 2002, 43, 5379.
- Alam, M.; Sharmin, E.; Ashraf, S. M.; Ahmad, S. Prog Org Coat 2004, 50, 224.
- 10. Das, S. K.; Lenka, S. J Appl Polym Sci 2000, 75, 1487.
- Motawie, A. M.; Sadek, E. M.; Awad, M. M. B.; Fakhr El-Din, A. J Appl Polym Sci 1998, 67, 577.
- 12. Ahmad, S.; Ashraf, S. M.; Naqvi, F.; Yadav, S.; Hasnat, A. Prog Org Coat 2003, 47, 95.
- Ahmad, S.; Ashraf, S. M.; Naqvi, F.; Yadav, S.; Hasnat, A. J Polym Mater 2001, 18, 53.
- 14. Roy, T. K.; Mannari, V. M.; Raval, D. A. J Sci Ind Res 1997, 159.
- Zafar, F.; Sharmin, E.; Ashraf, S. M.; Ahmad, S. J Appl Polym Sci 2005, 97, 1818.
- Dighe, A. K.; Toliwali, S. D.; Khotpal, R. R. J Sci Ind Res 2000, 59, 808.
- 17. Mannari, V. M.; Raval, D. A. Res Ind 1995, 40, 38.
- Arvanitoyannis, I.; Nakayama, A.; Kawasaki, N.; Yamamoto, N. Polymer 1995, 36, 857.
- 19. Hong, L.; Ruckenstein, E. J Appl Polym Sci 1998, 67, 1891.
- Hsu, W. C.; Kuo, J. F.; Chen, C. Y. J Polym Sci Part A: Polym Chem 1993, 31, 267.
- Arai, T.; Freddi, G.; Colonna, G. M.; Scotti, E.; Boschi, A.; Murakami, R.; Tsujkanda, M. J Appl Polym Sci 2001, 80, 297.
- 22. Mikroyannidis, J. A. J Appl Polym Sci 1992, 46, 1001.
- 23. Arayapranee, W.; Prassassarakich, P.; Rempel, G. L. J Appl Polym Sci 2002, 83, 2993.
- Fragouli, P. G.; Iatrou, H.; Hadjichristidis, N. Polymer 2002, 43, 7141.
- Alla, A.; Rodriguez-Galan, A.; Martinez De Llarduya, A.; Munoz-Guerra, S. Polymer 1997, 38, 4935.
- Ahmad, S.; Naqvi, F.; Verma, K. L.; Yadav, S. J Appl Polym Sci 1999, 72, 1679.
- 27. Gorkum, R. V.; Bauwaman, E. J Inorg Chem 2004, 43, 2456.
- Silverstein, R. M.; Bassler, G. C.; Morill, T. C. Spectrophotometric Identification of Organic Compounds, 5th ed.; Wiley: New York, 1991; p 131.
- 29. Zaarei, D.; Sarabi, A. A.; Sharif, F.; Kassiriha, S. M. J Coat Technol Res 2008, 5, 241.