Studies on a Newly Developed Linseed Oil-Based Alumina-Filled Polyesteramide Anticorrosive Coating

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Received 8 June 1998; accepted 30 September 1998

ABSTRACT: Polyesteramide (PEA) and alumina-filled polyesteramide (APEA) resins were synthesized from N,N'-bis(2 hydroxyethyl) linseed amide. The FTIR, ¹H-NMR, DSC, TGA, thermal curing, and physico-chemical characterization of these polymers were carried out. The coatings of PEA and APEA were made on mild steel strips. The mechanical behavior and protective efficiency of these coatings in acid, alkali, and organic solvents were investigated. APEA coatings have been found to show superior performance in comparison to other coatings. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 72: 1679–1687, 1999

Key words: coating; anticorrosive; polyesteramide; alumina; curing

INTRODUCTION

Fatty acids and alkyds from linseed and other vegetable oils have been long used as a renewable resource in the formation of industrially important protective coatings for exterior use.^{1–3} However, synthetic resins obtained from interactions of vegetable oils and amino alcohols with amide and imide linkages have previously not been extensively studied. Amide- and imide-modified alkyds made from glycerylamine, phthalic anhydride, and glycerol have improved film characteristics over conventional alkyds in terms of drying, hardness, and water vapor resistance.⁴ Among these products, polyesteramide resin has shown good chemical resistivity and durability at ambient temperature besides other interesting physico-chemical properties. They are also important from high temperature application point of view.5-9

A number of polyesteramides were synthesized from equimolar quantities of N,N'-bis(2 hydroxyethyl) linseed amide and either dibasic acids or anhydrides.^{1,2} The high melting point, low solubility, lower intractability, and high drying time cause difficulties in their application as coating material.^{10–11} The addition of metallic salts such as Co, Mn, and Pb napthenates or octoates to polyesteramide has reduced the drying time and curing temperature.¹²

The properties developed as a result of metals/ metalloids incorporation in the polymers are the enhancement of thermal stability, conductivity, protective efficiency, and reduction in curing temperature.¹³ Literature survey reveals that no work has been reported on the alumina-filled polyesteramide coatings.^{7,13,14,16}

With a view to improve thermal stability, physico-chemical properties, and protective efficiency of polyesteramide coatings, the synthesis of an alumina-filled polyesteramide was attempted. The present communication reports the synthesis, physico-chemical characterization, and preparation of polyesteramide and alumina-filled polyesteramide coatings on mild steel. It is observed that the presence of alumina in the polyesteramide enhances its solubility, thermal stability, and protective efficiency and reduces the curing temperature.

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Contract grant sponsor: UGC, India; contract grant number: F.12-45/94 (SR-I).

Journal of Applied Polymer Science, Vol. 72, 1679-1687 (1999)

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Characteristics	Linseed Oil	HELA	PEA	APEA
Acid value (mg of KOH)	8.3	_	_	_
Saponification value	160	136	128	118
Iodine value	181	86	48	20
Specific gravity	0.896	0.926	0.938	0.976
Refractive index	1.478	1.497	1.507	1.543
Inherent viscocity (dl/g)	—	—	0.652	0.680
Lenolenic acid	44%			
Linoleic acid	14%		—	
Oleic acid	20%	—	—	

Table ICharacterization of Oil, HELA, PEA,and APEA

EXPERIMENTAL

Materials

Oil was extracted from linseed (obtained from local market) through soxhlet apparatus. Petroleum ether was used as solvent. The fatty acid composition of oil is given in Table I. Phthalic acid, sodium methoxide, and aluminium hydroxide were of analytical grade (Merck, India). The diethanol amine used was also of analytical grade (S.D. Fine Chemicals, India), which was further distilled under reduced pressure before use.

Synthesis

N,N'-bis(2 hydroxyethyl) Linseed Amide (HELA)

Diethanol amine (25 g, 0.32 mol) and sodium methoxide (0.13 g, 0.007 mol) were mixed in a fourneck, round-bottom flask fitted with an electrical stirrer, thermometer, dropping funnel, and condenser. The contents were heated up to 115°C. Linseed oil (30 g, 0.1 mol) was added dropwise over a period of 30 min. The progress of the reaction was monitored by TLC.¹ The reaction mixture was further heated for 1.5 h to ensure the conversion of oil into HELA. After cooling, the product was dissolved in ether, washed with 15% aqueous Na Cl solution, and dried over anhydrous sodium sulphate. The etherial solution of polymer was filtered and evaporated in rotary vacuum evaporator to obtain yellow oil of N, N'-bis(2 hydroxyethyl) linseed amide (HELA).

Polyesteramide (PEA)

HELA (0.05 mol), phthalic acid (0.08 mol), and xylene (50 ml) as solvent were placed in four-

neck, round-bottom flask fitted with Dean-Stark trap, nitrogen inlet tube, thermometer, and mechanical stirrer. The reaction mixture was heated up to 145°C and refluxed until the theoretical amount of water was collected in Dean-Stark trap. The progress of the reation was monitored by TLC. The reaction mixture was refluxed for 6 h to complete the reaction. After the completion of the reaction, the product was taken out from the reaction flask, and xylene was removed from it in a rotary vacuum evaporator under reduced pressure to obtain the polyesteramide resin.

Alumina-Filled Polyesteramide (APEA)

 $Al(OH)_3$ (0.006 mol) and PEA (0.05 mol) was taken along with 50 ml of xylene in the four-neck, round bottom flask of the same set-up used for the synthesis of polyesteramide resin. The reaction mixture was heated at a rate of 10°C/min up to 60°C. It was heated for 1 h at this temperature. The water formed as a byproduct was collected in Dean-Stark trap. The formation of the end product was confirmed by TLC. After cooling, the product was dissolved in ether and washed with 15% aqueous NaCl. It was dried over anhydrous sodium sulphate. The solvent was removed from APEA in a rotary vacuum evaporator under reduced pressure.

Characterization

The HELA, PEA, and APEA were characterized by FTIR, ¹H-NMR, TGA, and DSC. FTIR spectra of the film of these polymers on NaCl cell was recorded on Perkin Elmer 1750 FTIR spectrophotometer. ¹H-NMR spectra were recorded on JEOL 200 MHz FX100 model spectrometer using deuterated chloroform and TMS as standard. TGA (TA 2000) was done in N₂ atmosphere to study the thermal behavior. The curing behavior of PEA and APEA was studied by DSC 910 (Dupont) in nitrogen atmosphere. Solubility of polymers in various organic solvent was checked at room temperature. The inherent viscosity of PEA and APEA in N-methyl pyrrolidone (0.5 g/100 ml) at 25°C was determined with the help of Ubblehode viscometer. Iodine and saponification values, specific gravity, and refractive index of polymers were also determined (Table I).

Preparation and Testing of Coatings

Coatings of PEA and APEA were prepared on commercially available mild steel strips ($30 \times 10 \times 1 \text{ mm}$ for chemical resistance and $70 \times 25 \times 1 \text{ mm}$

Scratch Hardness Resin (2 kg)		Chemical Resistance ^b				
	Scratch Hardness (2 kg)	Impact Resistance [lbs/in (passes)]	H ₂ O (7 days)	20% HCl (7 days)	5% NaOH (1 h)	Xylene (7 days)
PEA APEA	Passes the test Passes the test	100 150	e e	c e	a b	d e

Table II Properties of Baked Coatings of PEA and APEA Resins^a

^a Baked for 10 min: PEA at 220°C and APEA at 200°C. The coatings passing adhesion test show no visible damage.

b a = Film completely removed, b = film cracked and partially removed, c = loss in gloss, d = slight loss in gloss, e = unaffected.

mm for gloss, scratch, and Impact resistance) by spray technique using a solution containing 5% of polymer in toluene. Coated strips were baked for 10 min in an oven at temperature 200 and 220°C, respectively, for former and latter. Coating thickness of a few samples were measured by Elcometer (345 digital coating thickness gauge, Elcometer Instruments Ltd., Manchester, UK). The thickness of the coatings were found between 120 and 150 μ m. Air drying and baking time test were performed; impact and hardness were also determined. Corrosion tests were performed in water, acid (5% HCl), alkali (5% NaOH), and xylene by tacking them in a 3-inch diameter porcelain dish and by placing coated samples in these dishes. Periodic examination was conducted until the coatings showed evidence of softening or deterioration (Table II).

RESULTS AND DISCUSSION

Scheme of chemical reaction and polymerization in the synthesis of HELA, PEA, and APEA are given in Figure 1(a), (b, i, ii), and (c, i, ii). The reaction of oil in the form of triglyceride with diethanolamine was carried out to make the HELA [Fig. 1(a)]. Sythesis of polyesteramide from the reaction of HELA and phthalic acid may result in the formation of polyesteramide polymeric chain by direct reaction [Fig. 1(b, i)] or in its formation through acyl migration from nitrogen to oxygen [Fig. 1(b, ii)], containing both ester and amide linkages in the back bone of the polymer.¹ The probable structure for APEA [Fig. 1(c, i and ii)] suggests the presence of alumina in the back bone of the polymer chain through formation of sigma bond with oxygen resulting in to C—O—Al linkage.¹⁵

FTIR and ¹H-NMR spectra of the polymers were analyzed to ascertain the structures. Although most of the previous workers¹⁻³ have reported the formation of HELA and PEA, they have not confirmed them by spectroscopic studies. We attempt the analysis of the above polymers by FTIR, ¹H-NMR, DSC, and TGA studies in these sections.

N,N-Bis(2 hydroxyethyl) Linseed Amide [HELA]

The FTIR spectrum (Fig. 2) of HELA showed the peak of alcoholic OH group at $3500-3315 \text{ cm}^{-1}$. CH₂ asymmetric and symmetric stretching peaks are at 2915 cm⁻¹ and 2850 cm⁻¹, respectively. The amide carbonyl peak is observed at 1615 cm⁻¹. The C—N stretching peak (C—N—H group) is observed at 1515 cm⁻¹, the CH₂ bending is found at 1460 cm⁻¹, and the C—H bending mode at 728 cm⁻¹.

The ¹H-NMR spectrum (Fig. 3) of HELA showed proton of terminal CH₃ at $\delta = 0.87-0.9$, chain CH₂ at $\delta = 1.28$, —CH—CH₃ attached to olefinic carbon atom, CH—CH₂ adjacent to terminal olefinic apparent group in R at $\delta = 2.02-2.18$, CH₂ to C group is at $\delta = 2.37$, CH₂ attached to amide nitrogen at $\delta = 3.46-3.75$,)CH₂—O region at $\delta = 4.02$, and alcoholic OH at $\delta = 5.3$. These spectral characteristics establish the formation of HELA as in [Fig. 1(a)].

Polyesteramide (PEA)

The formation of polyesteramide is confirmed by the presence of peaks of CH_2 asymmetric stretching at 2935 cm⁻¹ and CH_2 symmetric stretching at 2840 cm⁻¹. The amide carbonyl and carbonyl group of ester are observed at 1636 and 1725 cm⁻¹, respectively, and the C—O—C asymmetric and symmetric peaks are at 1280 cm⁻¹ and 1305 cm⁻¹, while the peak of C—O stretching vibration is observed at 1145 cm⁻¹. The aromatic ring of phthalic acid is found at 1615, 1585, and 750 cm⁻¹ (Fig. 4).



Fig. : 1 - C (i) & (ii) Synthesis of APEA

Figure 1 (a) Synthesis of HELA; (b) synthesis of polyesteramide (PEA); (c) synthesis of APEA.



Figure 2 FTIR of HELA.

The ¹H-NMR spectrum (Fig. 5) of PEA shows proton of terminal CH₃ at $\delta = 0.9$, chain CH₂ at $\delta = 1.29$, CH₃=CH attached to olefinic carbon atom, and =CH-CH₂ adjacent to terminal olefinic group at $\delta = 2.02$. The sharp peak of methylene adjacent to ester group is observed at $\delta = 2.3$, CH₂ attached to amide nitrogen at $\delta = 3.43$, and alcoholic OH at $\delta = 5.33$. Ring protons are observed at $\delta = 6.92-7.33$, and carboxylic OH at $\delta = 7.92$, supporting the structure of polyesteramide as shown in Figure 1(b, i and ii).

Alumina-Filled Polyesteramide (APEA)

Figure 4 shows the FTIR spectrum of APEA. The broad peak of OH stretching is observed at 3460

cm⁻¹, CH₃ asymmetric at 2980 cm⁻¹, CH₂ asymmetric at 2920 cm⁻¹, CH₂ symmetric stretching at 2850 cm⁻¹. The peak of C=O (ester) is observed at 1760 cm⁻¹, C=O (amide) at 1660 cm⁻¹, CH₂ bending at 1560 cm⁻¹, C—N at 1480 cm⁻¹, OH bending at 1320 cm⁻¹, C=O stretching at 1170 cm⁻¹. Bending and stretching of benzene ring are observed at 1050, 780, and 750 cm⁻¹.

The IR spectra of HELA and PEA show the presence of —C—OH, C—OR, and C—N groups. The IR spectrum of APEA shows no separate peak for Al-0, but shifting of peaks due to C—O ester and formation of doublet in the region 1420-1460 cm⁻¹, along with pronouncement of these peaks, is observed in the case of APEA. This shows that $Al(OH)_3$ has interacted with PEA and withdraws electrons toward it, causing decrease in the bond strength of C—O and R—C—O, leading to the aforementioned shifts in their peaks.

In Figures 5 and 6, ¹H-NMR spectra of PEA and APEA reveal that the combination of Al(OH)₃ with carboxylic group of PEA results in the disappearance of carboxylic OH in the APEA present at $\delta = 7.92$ in PEA. In APEA, terminal CH₃ is at $\delta = 0.92$, chain CH₂ at $\delta = 1.25$, CH₃—CH= attached to olefinic C-atom at $\delta = 1.58$, and =CH · CH₂_ adjacent to treminal olefinic group at $\delta = 2.0$. The alcoholic group present in all polymers is at $\delta = 5.3$. The protons of the ester group in PEA appear at $\delta = 2.3$, while in APEA at $\delta = 2.28$. The reduction in the intensity of the



Figure 3 ¹H-NMR spectra of HELA.



peak and shifting to downfield is due to the effect of metal on the methylene group adjacent to ester linkage. In APEA the chain CH_2 peak is shifted to downfield region from 1.29 to 1.25, which also provides evidence for the incorporation of alumina in polymeric chain. Furthermore, the ring protons get deshielded and appear at $\delta = 7.20$ in APEA, while in PEA the peak is found at $\delta = 6.92$.



Figure 5 ¹H-NMR spectra of PEA.



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These observation strongly support the combination of alumina with PEA through carboxyl group. On the basis of this evidence we have proposed the structure of the APEA as shown in Figure 1(c, i and ii).

Thermogravimetric Analysis

Figure 7 shows the primary thermograms of PEA and APEA. It is observed that the thermal stability of APEA is higher than that of PEA: the former showing a loss of 50% at the decomposition temperature of 450° C, while the latter showing a loss of 50% at a lower decomposition temperature of 400° C. PEA after complete decomposition is left with 3% residue, while APEA is reduced to 20% residue, confirming the presence of alumina ash. It can be concluded that APEA is thermally more stable than PEA.

Differential Scanning Calorimetry (DSC)

The curing temperature range of polymers was investigated by DSC (Fig. 8). The curing of PEA is found to start at 100°C and passes through maximum curing temperature at 225°C, while the starting curing temperature of APEA is much lower, that is, 75°C, and the maximum curing temperature is observed at 235°C. The decrease in the initial curing temperature can be attributed to the presence of metal and enhanced rate of crosslinking in APEA.

Physico-Chemical Characteristics

Table I shows values for various physico-chemical factors. The decrease in the iodine and saponification value from oil to APEA is attributed to the decrease in the degree of unsaturation and progressive increase in polymeric chain.





Figure 8 DSC of PEA (---) and APEA (----).

The higher values of specific gravity, refractive index, and inherent viscosity of APEA indicate the higher crosslinking per unit chain length and molecular size of the APEA.

The solubility of the polymers was tested in solvents like DMSO, DMF, ethanol, methanol, carbon tetrachloride, chloroform, ether, acetone, toluene, and xylene. PEA shows good solubility only in acetone, chloroform, DMF, ether, toluene, and xylene (solubility: 75–100%). With the rest of the above solvents the solubility varies between 20 and 40%. The APEA is also soluble in methanol and ethanol, besides the other solvents used for solubility of PEA. Surprisingly, APEA shows solubility in polar solvents as well as in nonpolar solvents unlike PEA. We presume that due to the presence of hydroxyl group at aluminium, APEA shows such solubility behavior.

Coating Properties of PEA and APEA

The coating of PEA and APEA on mild steel strips passes the adhesion test and shows no visible damage. Air-dried PEA coatings become tack free after 10 days, whereas air drying of APEA coatings takes longer time, about 15 days, to become tack free but they still remain slightly soft. Table II lists properties of baked coatings. These data reveal that APEA coatings have almost same scratch hardness as those of PEA. However, the APEA coating showed improved resistence to impact as compared to PEA coatings.

The chemical resistance data indicate that the acid and xylene resistance of APEA coatings show exactly the same pattern as in water. The PEA coatings exhibit considerable loss in gloss in acid as well as in xylene, while APEA maintains its gloss in these solvents. The APEA coatings also show improvement in alkali resistance as compared to PEA coatings. This is because of nonavailability of hydrolysable ester group in APEA.

CONCLUSION

The presence of alumina in polyesteramide enhances the solubility and curing behavior of polyesteramide. A relative increase in impact resistance and the decrease in the curing temperature is observed in case of APEA as compared to PEA. The chemical resistance and the protective efficiency of APEA is higher in acid, alkali, water, and xylene than that of PEA coatings. These observations confirm that the presence of alumina in polyesteramide improves the physico-chemical properties and protective efficiency.

This work was funded by UGC, India, through Grant F.12-45/94 (SR-I). The authors also thank Prof. S. M. Ashraf (Department of Chemistry, Jamia Milila Islamia, New Delhi-110025) for his valuable suggestions and discussions.

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