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ORIGINAL PAPER

Synthesis, Characterization and Performance of Amine Modified Linseed Oil Fatty Amide Coatings

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Abstract A novel attempt has been made to develop ambient cured polyamine amide (PAA) resins by the condensation polymerization reaction of oil fatty amide diol (*N*,*N*-bis 2-hydroxy ethyl linseed oil fatty amide) (HELA) and *o*-phenylene diamine, which was further modified by poly(styrene-*co*-maleic anhydride) (SMA) at different phr (parts per hundred part of resin) to get a series of PAA–SMA resins. The structural elucidation of HELA, PAA and PAA–SMA were carried out by FT-IR, ^{1}H-NMR and ^{13}C-NMR spectroscopic techniques. The physico-chemical and physico-mechanical analyses were carried out by standard laboratory methods. Thermal analyses of these resins were accomplished by thermogravimetric analyses (TGA) and differential scanning calorimetry (DSC) techniques. Coatings of PAA–SMA were prepared on mild steel strips to evaluate their physico-mechanical and chemical/corrosion resistance performance under various corrosive environments. It was found that among the PAA–SMA systems, PAA-35 showed the best physico-mechanical and corrosion resistance performance. Thermal studies reveal that the coatings can be safely used up to 305 °C.

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Introduction

The current interest in the development of useful biodegradable polymeric materials has encouraged scientists and industrialists to use readily available renewable, inexpensive raw materials such as carbohydrate, lignin, starch, gums, chitosan and vegetable oils. Out of these vegetable oils linseed, soybean, castor, safflower, coconut, and argemone are major sustainable raw materials [1–3].

Vegetable oil is being increasingly used as a source of monomers for sustainable resource based polymers [2]. *N*,*N*-bis (2-hydroxy ethyl) vegetable oil fatty amides are excellent example to this end. They are obtained by base-catalyzed aminolysis of various oils viz. linseed, soybean, castor and others. They have been modified by different moieties viz. phthalic acid, tartaric acid, maleic acid and bisphenol-A. Consequently, a number of polymers have been obtained from vegetable oils such as alkyds, polyepoxies, polyethers, polyesters, polyurethanes, polyesteramides, polyetheramides, and others [4–6]. Depending upon the nature of their use, these polymers can be further modified. Organic coatings derived from vegetable oils possess good physico-mechanical and corrosion protection properties, foremost among them being gloss, flexibility, impact and resistance against several corrosive chemicals. In comparison, petrochemical based polymeric coatings possess low shrinkage energy and are usually brittle [7, 8]. The major drawback of the vegetable oil based polymeric coatings is their need to be cured at high temperatures and, in some cases, their low resistance to alkalis [9]. To overcome these shortcomings, suitable chemical modifications of oil derived polymers and the appropriate curing agents are utilized to obtain ambient cured oil derived polymeric coatings.

N,*N*-bis 2-hydroxy ethyl oil fatty amide diol obtained from vegetable oil has been widely used to obtain polyetheramides, polyesteramides and polyurethanes [2, 5, 6, 10], which have been investigated for their coating properties. The unsaturation in its fatty amide chain can further be exploited to obtain new polymers for coating applications. In all these cases curing of coatings occurs at around 200 °C. This step is energy consuming, so attempts been made to obtain ambient cured coatings possessing high performance [2].

Aromatic amines have shown good corrosion inhibition on mild steel. Aromatic amine such as *p*-phenylene diamine, 3,4-diaminophenyl ether, *o*-phenylene diamine, aniline and their polymers are widely used in conducting polymer synthesis and also as curing agents for epoxies, natural rubber, unsaturated polyester and others [11–13]. Amine groups have a strong affinity for surface iron and can protect the latter against corrosion. This can be attributed to the abundance of pi electrons and unshared electrons on the nitrogen atom that can interact with iron's *d*-orbital to form coordinate bonds. It suggests that amino polymers are adsorbed on metal surface through the imine moiety of polymer chains.

Linseed oil is an important vegetable oil. Its major producers are Argentina, Canada, China, US and India. The annual production of this oil was reported as 2.6 million tons worldwide and 0.20 million tons in India in the year 2002–2003 [14, 15]. The paint and allied industries are major consumers of linseed oil in India accounting for 70% of the total consumption. A literature survey has revealed that the modification of linseed oil fatty amide diol by *o*-phenylene diamine and further with poly(styrene-*co*-maleic anhydride) has not been undertaken. We now report the synthesis of amine modified fatty amide diol. The proposed reaction schemes for the synthesis and curing of the resins were confirmed by FT-IR, ^{1}H-NMR and ^{13}C-NMR spectroscopic techniques. Thermal studies were carried out by TGA and DSC techniques. The physico-mechanical and chemical resistance properties of coatings were studied by standard methods.

Experimental Procedures

Materials

Linseed (*Linum usitatissimum L.*, Iodine value = 181, drying index = 102) was finely powdered in a seed grinder. Oil was extracted from it in a Soxhlet apparatus by refluxing in petroleum ether. Oil was separated from the solvent in a rotary evaporator and was suitably purified. The fatty acid composition of the oil was determined using its methyl ester on a Hewlett-Packard 5890 Series II gas liquid chromatography with FID detector. The injection temperature was 250 °C; nitrogen was used as the carrier gas at a flow rate of 20 mL/min. The fatty acid composition was observed as oleic acid 22%, linoleic acid 14%, linolenic acid 44% palmitic acid 5% stearic acid 4%. Xylene, sodium methoxide, diethanolamine (Merck, India), *o*-phenylene diamine (Loba Chemie, India), poly(styrene-*co*-maleic anhydride), average molecular wt. 1,600 Da (Aldrich Chemical Company, USA), ethylene glycol mono methyl ether (Qualigens, India) were used as received.

Characterization

The physico-chemical properties such as iodine value, hydroxyl value, acid value, saponification value, specific gravity and refractive index were determined by standard laboratory methods (Table 1). The inherent viscosity of PAA and PAA–SMA in ethylene glycol mono methyl ether (EGME), 0.5 g/100 ml, was determined by an Ubblehode viscometer at 25 °C. The solubility of the resin was also tested in various organic solvents namely, dimethyl sulfoxide, ethylene glycol monomethyl ether, tetrahydrofuran, ethanol, methanol, ethyl methyl ketone, xylene, toluene, benzene, chloroform, 1-4 dioxane, acetone, carbon tetra chloride, *N*,*N*-dimethyl formamide, heptane, diethyl ether.

Table 1 Physico-chemical characterization of PAA and PAA–SMA resins

Resin code*	Iodine value	Acid value	Hyd. value	Ref. index	Inh. viscosity	Sap. value	Specific gravity	DTT (min)
PAA	85	–	18.07	1.5150	0.6005	–	0.9702	–
PAA-20	54	1.77	14.84	1.4590	0.6165	75	0.9820	30
PAA-25	50	2.50	13.88	1.4653	0.6269	78	0.9853	25
PAA-30	48	3.00	12.00	1.5082	0.6455	79	0.9871	15
PAA-35	47	4.50	11.07	1.4980	0.6658	85	0.9888	10
PAA-40	47	4.70	10.01	1.4943	0.6700	89	0.9891	10

* Last two digits indicate the phr of SMA

Hyd hydroxyl, *Inh* inherent, *Sap* saponification, *DTT* dry to touch time

FT-IR spectra of these resins were taken on Perkin Elmer 1750 FT-IR spectrophotometer (Perkin Elmer Cetus Instrument, Norwalk, CT, USA) using NaCl cell. ^{1}H-NMR and ^{13}C-NMR spectra were recorded on a Bruker Spectrospin DPX300 MHz using deuterated chloroform ($CDCl_3$) as solvent and TMS as an internal standard. Thermal analysis of PAA–SMA was carried out by TGA 51(TA Instrument, USA) and the curing behavior was studied by DSC (DSC10, TA Instrument, USA) in a nitrogen atmosphere at the heating rate of 20 °C/min.

Synthesis of *N*,*N*-Bis (2-hydroxy ethyl) Linseed Fatty Amide (HELA) (Scheme 1)

HELA was prepared according to previously reported method [4].

Spectral Analysis

FT-IR, cm^{-1}: 3370 (OH attached to CH_2); 2853 (CH_2 symmetrical); 2928 (CH_2 asymmetrical); 3010 (–CH=CH unsaturation); 1620 (C=O amide). *^{1}H-NMR, $CDCl_3$, δ, ppm*: 1.30–1.25 (m,–**CH$_2$**–8H); 5.30 (q,–**CH**=**CH**,–6H); 3.52 (t,–**CH$_2$**OH, 4H); 5.18 (s, CH_2 **OH,** 2H); 0.87–0.99 (t,–**CH$_3$**, 3H) (Fig. 1a). *^{13}C-NMR, $CDCl_3$, δ, ppm*: 175 (**C**=O, amide); 32–22 (**CH$_2$** fatty amide chain); 14 (**CH$_3$** fatty amide chain); 60 (–**C**H$_2$OH); 130–127 (–**C**H=**C**H–) Fig. 2a).

Synthesis of Poly(Amine–Amide) (PAA) (Scheme 2)

HELA (0.02 mol) and *o*-phenylene diamine (0.02 mol) were dissolved in xylene (50 ml) and were placed in a four-necked round-bottom flask fitted with a Dean Stark Trap, a nitrogen inlet tube, a thermometer and a mechanical stirrer. The reaction mixture was heated at 150 ± 5 °C and refluxed until the calculated amount of water was collected in the Dean Stark Trap. The progress of the reaction was monitored by thin layer chromatography (TLC) and by the determination of the hydroxyl value at regular intervals. After the completion of the reaction, xylene was removed from the product under reduced pressure to obtain PAA. The latter was purified by repeatedly washing with distilled water till the unreacted compounds were completely removed. It was further washed with methyl alcohol and dried in vacuum oven at 60 °C.

Spectral Analysis

FT-IR, cm^{-1}: 3390 (OH attached to CH_2, NH attached amine); 2854 (CH_2 symmetrical); 2927 (CH_2, asymmetrical); 3011 (–CH=CH, unsaturation); 1654 (C=O, amide); 1508,762 (aromatic). *^{1}H-NMR, $CDCl_3$, δ, ppm*: 3.53–3.50 (N**H$_2$**); 3.56–3.55 (N**H**); 2.3–2.6 (–**CH$_2$** amide); 7.5–6.71 (aromatic); 3.50–3.48 (C**H$_2$**–NH); 0.83 (–C**H$_3$** fatty amide chain) (Fig. 1b). *^{13}C-NMR, $CDCl_3$, δ, ppm*: 175 (**C**=O, amide); 22.1–29.1 (**C**H$_2$ fatty amide chain); 13.8 (**C**H$_3$); 38 (–**C**H$_2$–N); 144.6 (aromatic carbon attached to NH_2) (Fig. 2b).

Synthesis of PAA–SMA (Scheme 3)

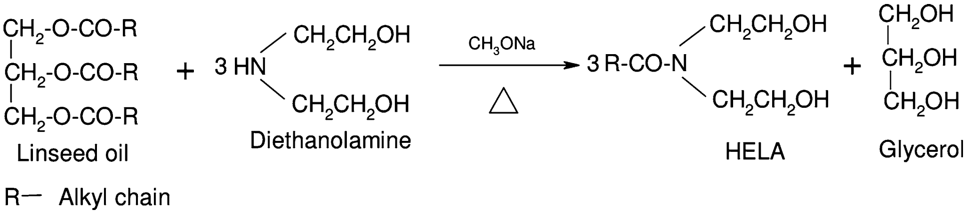
10.00 g PAA was dissolved in 20 ml xylene; 10 ml of 2.0, 2.5, 3.0, 3.5 and 4.0% w/v solution of SMA in ethylene glycol mono methyl ether was mixed separately with previous solution to obtain 20–40 phr loading of SMA in a four-necked round-bottom flask fitted with a condenser, a nitrogen inlet tube, a thermometer and a magnetic stirrer. The reaction was carried out under stirring at 150 °C. The progress of the reaction was monitored by the acid value and TLC. In each case we found that SMA had fully reacted. The solvent was removed from the resin in a rotary vacuum evaporator.

Spectral Analysis

FT-IR, cm^{-1}: 3368 (OH, NH); 1654 (C=O amide); 2854 (CH_2 symmetrical); 2927 (CH_2 asymmetrical); 3011 (–CH=CH unsaturation); 1508, 762 (aromatic); 702 (styrene). *^{1}H-NMR, $CDCl_3$, δ, ppm*: 3.53–3.50 (N**H$_2$**); 3.56–3.55 (N**H**); 2.3–2.6 (–**CH$_2$** amide); 7.5–6.71 (aromatic), 3.50–3.48 (**CH$_2$–NH**) 0.83 (–C**H$_3$** fatty amide chain); 2.1 (C**H**-styrene); C**H$_2$**-Styrene) (Fig. 1c).*^{13}C-NMR, $CDCl_3$, δ, ppm*:175 (**C**=O, amide); 22.1–29.1 (**C**H$_2$ fatty amide chain); 13.8 (**C**H$_3$ fatty amide chain); 38 (–**C**H$_2$–N); 144.6 (aromatic carbon attached to NH_2); 40–58 (**C**H$_2$, **C**H of Styrene) (Fig. 2c).

The presence of above mentioned characteristic peaks in FT-IR, ^{1}H-NMR and ^{13}C-NMR (Figs. 1, 2) confirms the formation of HELA, PAA resin and curing reaction between PAA and SMA.

Scheme 1 Synthesis of HELA



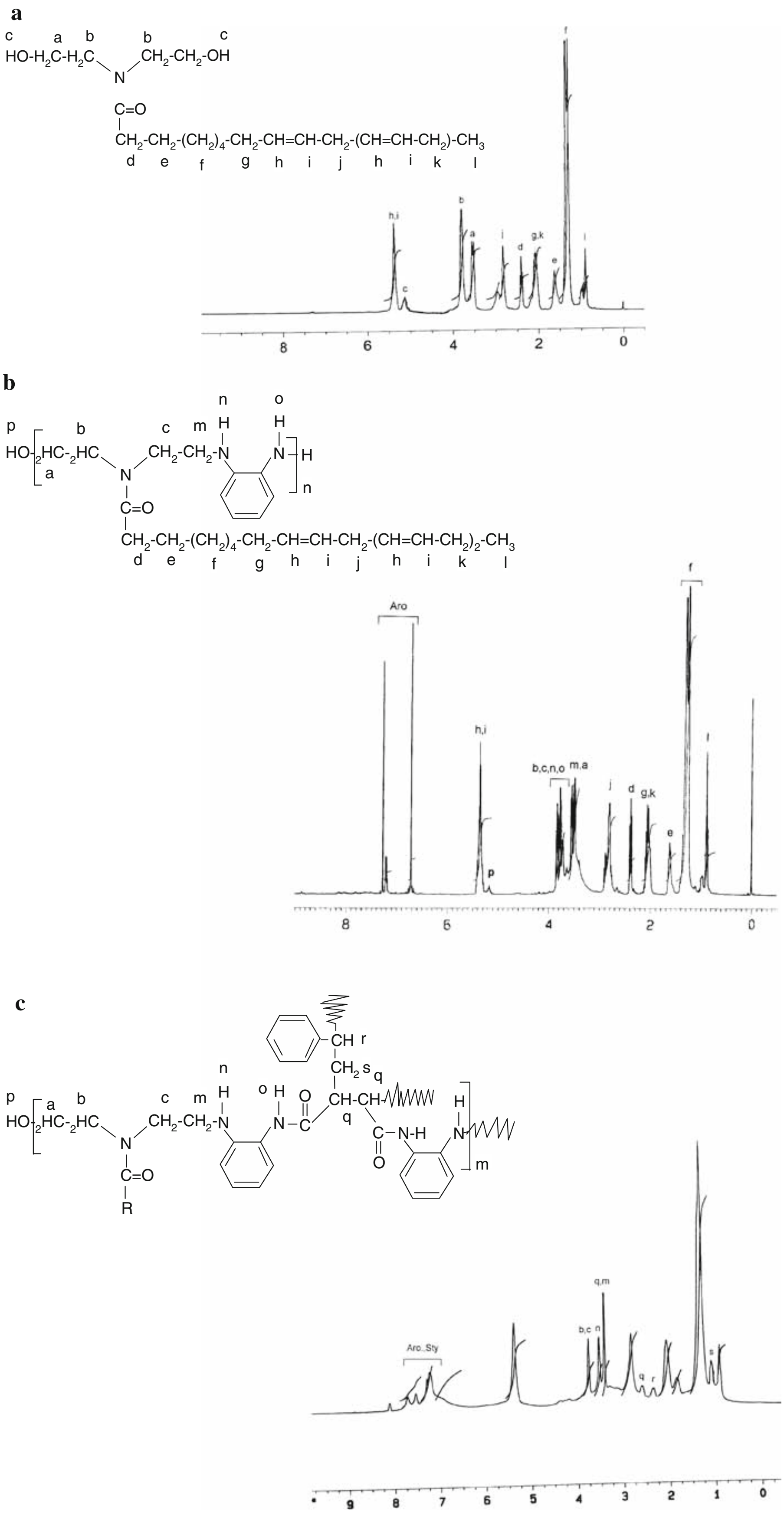
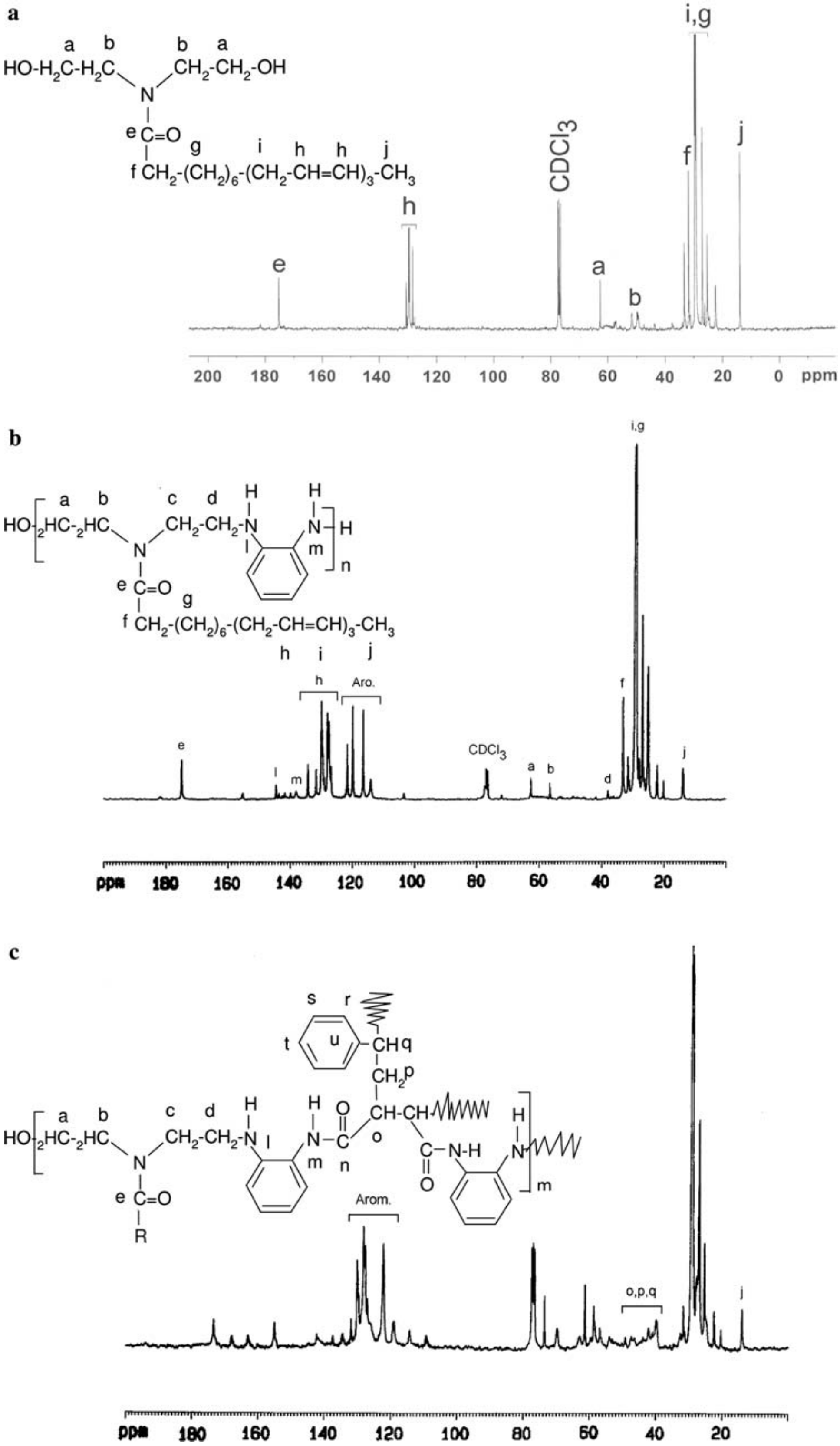
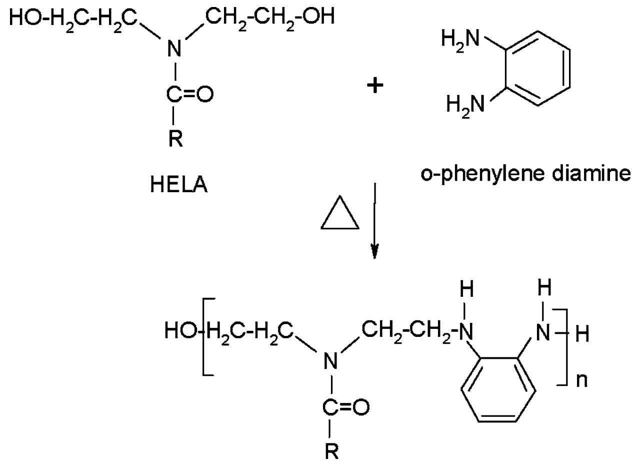


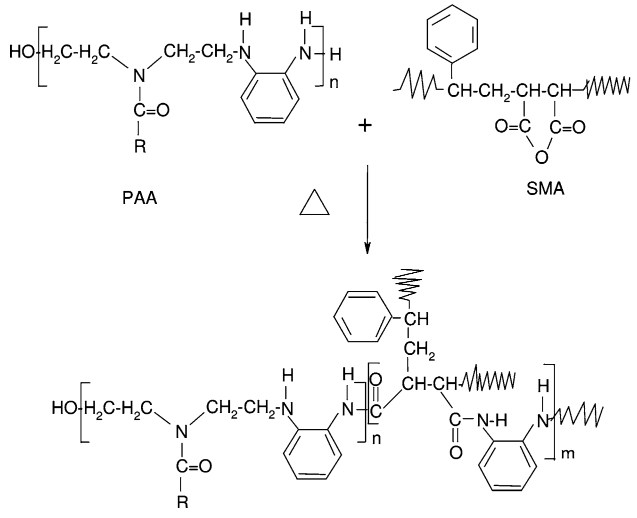
Fig. 1 ^{1}H-NMR, **a** HELA, **b** PAA, **c** PAA–SMA

Fig. 2 ^{13}C-NMR, **a** HELA, **b** PAA, **c** PAA–SMA





Scheme 2 Synthesis of Poly(amine-amide)



Scheme 3 Synthesis of PAA–SMA

Preparation and Testing of Coatings

The PAA–SMA resin (40 wt.%) solution was applied by brush on commercially available mild steel strips of 30 × 10 × 1 mm sizes for chemical resistance and on 70 × 25 × 1 mm sizes to determine the specular gloss at 45° by Gloss meter RSPT 20, (Digital Instruments, Santa Barbara). Physico-mechanical properties, viz. scratch hardness (BS 3900), impact resistance (IS: 101part 5/s 3, 1988) and bend test (ASTM-D3281-84) of the coatings were determined by respective standard methods indicated in the parentheses. The dry to touch (DTT) and dry to hard (DTH) times have also been noted. The thickness of these coatings were determined by Elcometer model 345 (Elcometer Instruments, Manchester, UK) and were found to be 85–90 μm. Corrosion tests were performed in acid (5 wt.% HCl), alkali (2 and 5 wt.% NaOH) water and xylene by placing them in 3-in. diameter porcelain dishes in the aforementioned media. The accelerated corrosion test was also carried out by salt spray test in a salt mist chamber containing 3.5 wt.% NaCl (ASTM D1654). Periodic visual examination was conducted until the film showed evidence of softening or deterioration (Table 2).

Results and Discussion

Scheme 1 shows linseed oil was converted to HELA by aminolysis. PAA was synthesized by the condensation polymerization reaction between HELA and *o*-phenylene diamine in an equimolar ratio at 150 °C. In this reaction, OH group of HELA reacts with NH_2 of *o*-phenylene diamine (Scheme 2). PAA is further mixed with Poly(styrene-*co*-maleic anhydride) in different (20–40) phr (Scheme 3) to obtain a series of PAA–SMA resins. The structures of HELA, PAA and the curing reaction of PAA with SMA were ascertained with the help of FT-IR, ^{1}H-NMR and ^{13}C-NMR spectral analyses.

Physico-Chemical Characterization

Table 1 reveals information about the change in iodine, saponification, refractive index, inherent viscosity and

Table 2 Physico-mechanical and chemical resistance performance of PAA–SMA systems

Resin code*	Scratch hardness (Kg)	Impact resistance (lb/in.)	Bend test (1/8 in.)	Gloss (45°)	Corrosion resistance test					
					NaOH		HCl	NaCl	H_2O	Xylene
					(2 wt.%) (12 h)	(5 wt.%) (2 h)	(5 wt.%) (5 days)	(3.5wt.%) (8 days)	(7 days)	(5 days)
PAA-25	1.5	250	Passes	70	e	e	d	b	d	e
PAA-30	2.5	250	Passes	80	e	e	d	b	e	e
PAA-35	3.0	250	Passes	90	c	c	c	a	c	d
PAA-40	2.5	250	Passes	93	c	c	c	a	c	d

* The last two digits indicate the phr of SMA

(a) Loss in gloss, (b) slight loss in gloss and film swell, (c) unaffected, (d) film slightly swell, (e) film completely removed specific gravity values of PAA and PAA–SMA of different compositions. PMA–SMA resin was dissolved in xylene to find out the above physico-chemical characteristics. The OH value during the progress of the reaction (Scheme 2) was followed by quantitatively determining its value by the standard method (ASTM D1957-86) in Table 1. It was observed that the OH value decreased as the reaction progressed. This shows that PAA had reacted with SMA. As a result of the reaction the molar mass of the resin, PAA–SMA will increase in proportion to the phr of SMA, which will also contribute to the iodine value, refractive index and specific gravity of the same.

PAA–SMA resin was also subjected to solubility tests in various organic solvents at room temperature. PAA–SMA were completely soluble in dimethyl sulfoxide, ethylene glycol monomethyl ether, tetrahydrofuran, ethanol, methanol, ethyl methyl ketone, xylene, toluene, benzene, chloroform, 1-4 dioxane, acetone, carbon tetra chloride and *N*,*N*-dimethyl formamide; it was insoluble in heptane and partially soluble in diethyl ether. The solubility behavior suggests that the resin contains excessive polar groups.

Coating Properties

The physico-mechanical and chemical resistance performance of PAA–SMA (20–40 phr) are given in Table 2. The dry to touch (DTT) time was found to decrease up to PAA-35. Beyond this composition, DTT of resins was found to be constant (10 min). The value for dry to hard (DTH) time, which is correlated to the complete curing of all these resins, was found to be 10–12 days. Scratch hardness values were found to increase up to PAA-35 after that decrease in scratch hardness values was observed. It shows that the optimum extent of cross-linking of coatings is achieved at PAA-35. All these coatings pass the 250 lb/in. impact test which shows good adhesion of coatings to the substrate due to the increase number of polar groups in the PAA–SMA system. It was observed that these coatings show good bend test values (1/8 in.) indicating good flexibility due to the presence of dangling alkyl chain. The increased numbers of polar groups in PAA–SMA coatings impart good adhesion between the coatings and metal surface; this will cause an increase in impact resistance as has been observed.

It was further observed that the gloss values increased with an increase in SMA content. We consider the gloss is a function of surface smoothness but other factors like the nature of molecule in the film and the molecular structure also contribute to the gloss. In our case, we attribute the enhancement of the gloss to the molecular structure and favorable network formation. As the method of preparation of the film in all cases is the same, hence the surface smoothness would also be the same; the enhancement in the gloss, therefore, is attributed to the dense molecular network formation.

Table 2 reveals that PAA-35 and PAA-40 among all PAA coating systems, exhibited best chemical resistance properties in mineral acid, saline and aqueous environment and also in an alkaline environment. The coatings of the aforementioned resins were found to possess much higher alkali resistance properties than other reported polyesteramide coatings [5]. Surprisingly, PAA–SMA systems fail to give satisfactory performance in xylene; PAA-35 and PAA-40 were found to swell in 5 days while PAA-20 and PAA-25 were completely removed in this period, presumably because of the presence of SMA moieties in the modified SMA.

Thermal Analysis

The TGA thermogram (Fig. 3) of PAA-35 shows a 5 wt.% loss of the resin at 240 °C which can be correlated to the evaporation of the entrapped solvent 10 wt.% loss is observed at 305 °C, but the initial decomposition temperature appears to correspond to 325 °C. The resin shows 50 wt.% loss at 415 °C while it decomposes completely at 525 °C.

The peak at 35 °C is spurious and has no significance in the DSC thermogram. Figure 4 shows an endothermic peak which extends from 90 to 150 °C for PAA-30 and PAA-35, respectively. The peaks for PAA-30 and PAA-35 are, respectively, centered at 120 and 125 °C. In the TGA thermogram, no weight loss is observed at the aforementioned temperatures. The endotherms are, therefore, considered to represent the melting of the resins. A small increase is observed in melting points with the increase in the loading of SMA. The higher SMA content with a larger amount of aromatic moiety appears to contribute to the increase in the melting point of these resins. Beyond 150 °C, an exotherm ensues which extends over the rest of the DSC trace. The thermograms show the onset of

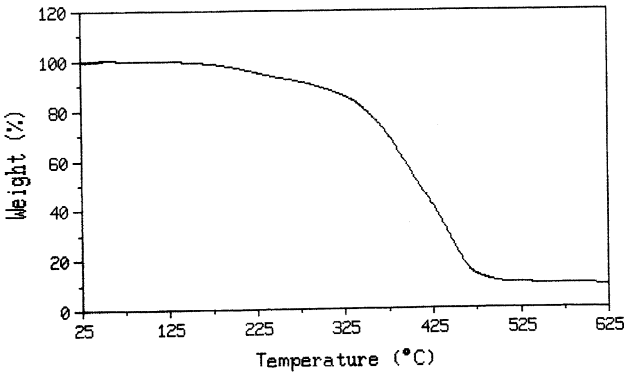


Fig. 3 TGA thermogram of PAA-35

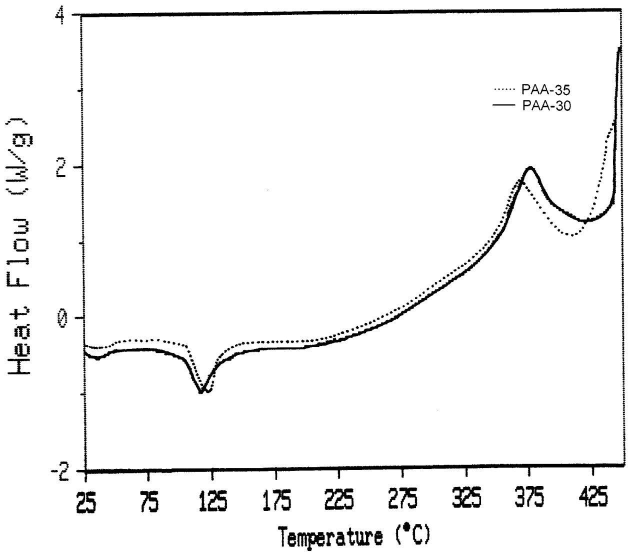


Fig. 4 DSC thermograms of PAA-30, PAA-35

decomposition at 325 °C which is also observed in the case of TGA.

Conclusion

The synthesis of PAA–SMA resin from linseed oil provides a new way to utilize a sustainable resource based raw material. PAA–SMA resin shows good alkali resistance as compared to reported polyesteramide coatings [5]. The system has a good combination of properties of amine, ester, styrene and amide linkages in terms of physico-mechanical properties. TGA thermograms reveal that PAA-35 shows the best performance and can be safely used up to 305 °C.

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