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Studies on Melamine Modified Polyesteramide as Anticorrosive Coatings from Linseed Oil: A Sustainable Resource

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Melamine modified polyester amide (MPEA) was synthesized by the reaction of linseed oil fatty amide. The resin was further cured at room temperature by polystyrene co-maleic anhydride (SMA) in different phr (30–80) to obtain MPEA coatings. The probable structure of MPEA was confirmed by FT-IR, ¹H-NMR and ¹³C-NMR spectroscopic techniques. The physico-chemical characterization of these resins viz. iodine value, saponification value, refractive index, inherent viscosity were carried out by standard methods. MPEA (40 wt%) solution in ethylene glycol monomethyl ether (EGME) was applied on a mild steel strip of standard sizes to study their physico-mechanical and chemical resistance properties. It was found that coatings of MPEA with 60 parts per hundred of the resin (phr) of SMA showed the best performance in physico-mechanical and alkali resistance properties. Thermal stability and curing behavior were studied by Thermo Gravimetric Analyses (TGA) and Differential Scanning Calorimetry (DSC), respectively.

Keywords linseed oil, melamine, polyesteramide, coatings

Introduction

The development of high performance coatings material with good mechanical and anticorrosive properties from a sustainable resource are a timely need. Vegetable seed oils such as linseed, pongamia glabra, annona squamosa, castor, soybean, and argemone were used to prepare the polymeric resins as a sustainable resource (1–6). They are considered important, due to their functional attributes (7). These oils have been utilized to develop low molecular weight polymers viz. alkyds (8), polyesters (9), polyepoxies (10), polyurethane (1), polyesteramides (2) and polyetheramides resins (5). Linseed oil based polymers have poor stiffness and hardness. In order to overcome these shortcomings, several chemical modifications have been carried out in the backbone of the polymeric chains through the incorporation of aluminium (11), boron (12), styrene (13–16) and urethane or through the reaction of bulky compounds at the unsaturation in the fatty acid chain (17).

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N, N-bis 2 hydroxyethyl linseed oil fatty amide has been used as a monomer for the synthesis of polyesteramide (11) and polyetheramide (5). The linseed oil polyesteramide cures at 220°C to yield coatings of poor alkali resistance (11) and physico-mechanical characteristics. In order to improve the alkali resistance and physico-mechanical properties of polyesteramides suitable modification of this polymer through such moieties were carried out, which can bring about a marked enhancement in these properties.

Melamine resins are characterized by good hardness, resistance to alkali and solvents, along with adequate thermal stability (18). Melamine resin has been used as melamine formaldehyde (19), sulphonated melamine formaldehyde (20), butylated melamine formaldehyde (4) and hexamethoxy melamine (21) for the development of thermosetting coating materials. We have reported the use of butylated melamine formaldehyde (BMF) as a curing agent in polyesteramide (4) and polyetheramide (7), which has resulted in the enhancement of thermal, physico-mechanical and anticorrosive properties of coatings. The presence of styrene has also been reported to enhance the physico-mechanical and chemical resistance properties of coatings (13). We have therefore, considered taking advantage of the presence of both melamine and styrene in the coating of linseed oil polyesteramide to obtain room temperature cured coating of high performance, superior in terms of physico-mechanical properties to the coatings of two materials individually.

A literature survey has revealed that the modification of linseed oil fatty amide diol using melamine and polystyrene co-maleic anhydride has not been undertaken. In the present work, melamine modified linseed oil fatty amide diol has been cured with styrene co-maleic anhydride, resulting into the formation of melamine-modified polyesteramide (MPEA) (Scheme 1). The proposed reaction scheme for the synthesis and curing of the resin was confirmed by FT-IR, ¹H-NMR and ¹³C-NMR spectroscopic techniques. Thermal studies were carried out by TGA and DSC techniques. The physico-mechanical and chemical resistance properties of coatings of MPEA were studied by standard methods.

Experimental

Materials

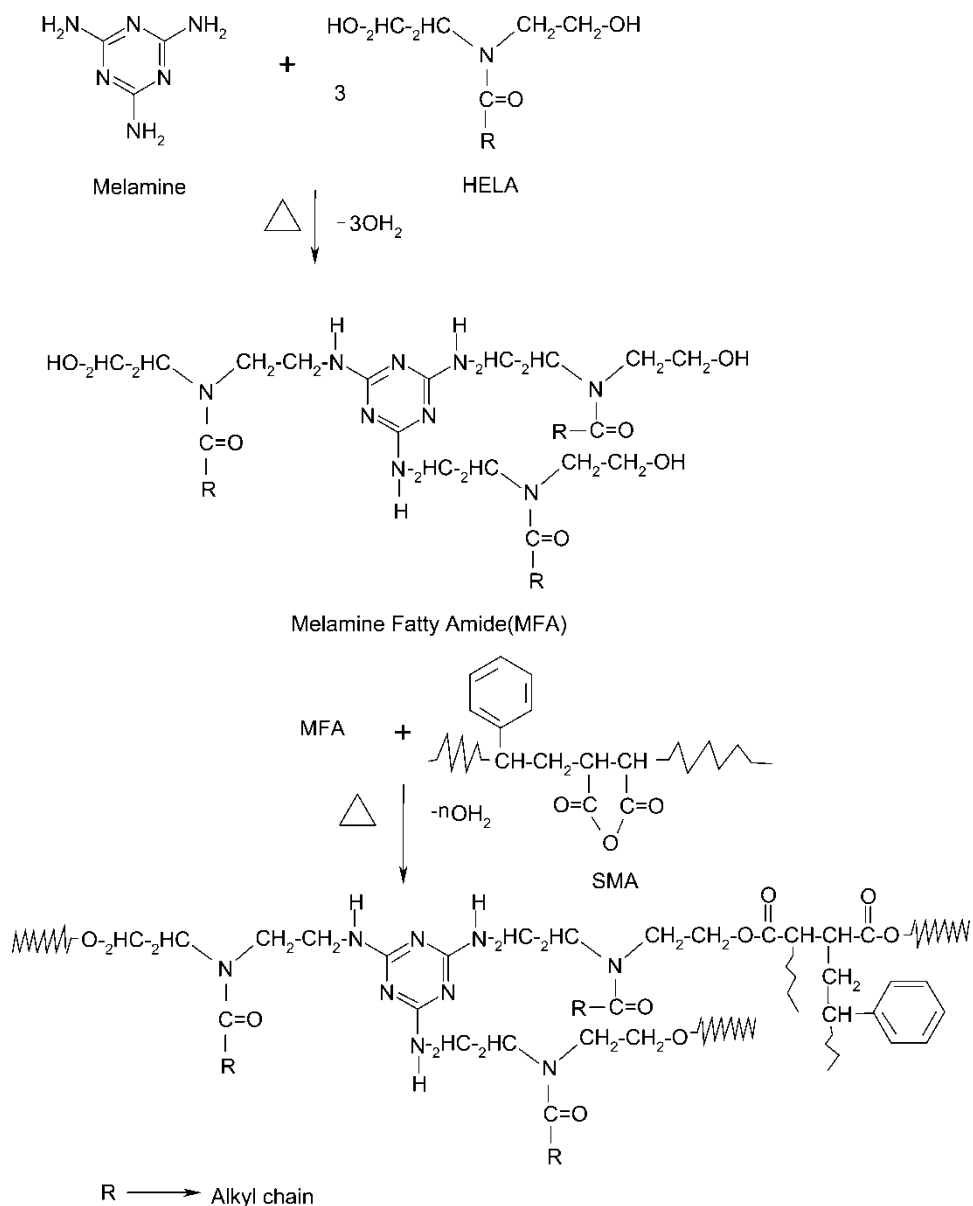
Linseed oil was procured from a local market. Fatty acid composition of the oil was determined by gas chromatography (GC; 111/855 column, FID detector). Diethanolamine, xylene (Merck, India), sodium methoxide (Merck, India), melamine (Loba Chemie, India), poly(styrene-co-maleic anhydride), average molecular wt.1600 Da (Aldrich Chemical Company, USA), ethylene glycol mono methyl ether (Qualigens, India) were used as received.

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

HELA was prepared according to a previously reported method (11).

Synthesis of melamine modified Polyesteramide (MPEA)

HELA (0.03 mol) and melamine (0.01 mol) were dissolved in 50 ml ethylene glycol mono-methyl ether (EGME), and used as a solvent in a four-necked round bottom flask equipped with Dean Stark trap, nitrogen inlet tube, thermometer and magnetic stirrer. The reaction



Scheme 1. Synthesis of Melamine modified polyesteramide (MPEA).

mixture was heated at 140°C and refluxed until the theoretical amount of water was collected in a Dean Stark trap. Progress of the reaction was monitored by thin layer chromatography (TLC). SMA (in different phr) was then added in the same reaction mixture and temperature was raised to 160°C. It was refluxed for 6 h, resulting in the formation of melamine-modified polyesteramide as the end product. TLC, as well as acid value, monitored the progress of the reaction. On completion of the reaction, the reaction product was cooled to room temperature. The solvent was removed in a rotary vacuum evaporator under reduced pressure to obtain MPEA.

Characterization

The physico-chemical properties, like iodine value (ASTM D5556) hydroxyl value, acid value, saponification value, specific gravity and refractive index were determined by standard laboratory methods (Table 1). The inherent viscosity of MPEA in ethylene glycol mono methyl ether (EGME), 5 g/100 ml, at 25°C was determined by a Ubbelohde viscometer. The solubility of the resin was also tested in various organic solvents. MPEA was characterized by FT-IR, ¹H-NMR and ¹³C-NMR spectroscopy. FT-IR spectra of these polymers were taken on Perkin-Elmer 1750 FT-IR spectrophotometer (Perkin-Elmer Cetus Instruments, Norwalk, CT) using NaCl Cell. ¹H-NMR and ¹³C-NMR spectra were recorded on a Bruker Spectrospin DPX 300 MHz using deuterated chloroform as a solvent and tetra methyl silane (TMS) as an internal standard. Thermal analysis of polymers was carried out by Thermogravimetric Analysis (TGA) TA2000, TA Instrument, USA and Differential Scanning Calorimetry (DSC) (TA Instrument, USA) in nitrogen atmosphere.

Preparation and Testing of Coatings

The MPEA resin solution (40 wt%) 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 a Gloss meter RSPT 20, Digital Instruments, Santa Bara). Physico-mechanical properties, viz. scratch hardness (BS 3900), impact resistance (IS: 101part 5/sec 3, 1988) and bend test (ASTMD 3281–84) of the coating 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 coating were determined by elcometer model 345 (Elcometer Instruments, Manchester, UK) and were found to be 80–50 μm. Corrosion tests were performed in acid (5 wt% HCl), alkali (5 wt% NaOH), water and xylene by placing them in 3 inch diameter porcelain dishes in the aforementioned media. The corrosion test was also carried out by salt spray test in salt mist chamber containing 3.5% NaCl. Periodic visual examination was conducted until the film showed evidence of softening or deterioration (Table 2).

Results and Discussion

Scheme 1 shows the proposed reaction for the synthesis of MPEA. MPEA was synthesized by the chemical reaction of HELA and Melamine in 3:1 molar ratio. The free hydroxyl groups of HELA were further treated with anhydride of SMA in different phr to obtain a series of MPEA resins. The structure of MPEA was ascertained with the help of FT-IR, ¹H-NMR and ¹³C-NMR spectral analysis.

Spectral Analysis

FT-IR (cm^{-1}). 3391 (NH attached melamine); 1738 (C=O ester); 1625 (C=O amide); 1634 (CN melamine); 2854 (CH₂, CH₃ symmetrical); 2926 (CH₂ asymmetrical); 3010 (-CH=CH unsaturation); 1560-1557 (s-triazine ring); 3050, 1585, 721 (styrene).

¹H-NMR ($CDCl_3$) δ (ppm). 6.01 (NH melamine); 7.7–6.9 (m, styrene); 2.3–2.6 (d, -CH₂ amide); 4.2–4.3 (-CH₂, ester); 0.83 (-CH₃ fatty amide chain).

Table 1
Physico-chemical characterization of MPEA system

Resin code ^a	Acid value	Iodine value	Saponification value	Refractive index	Inherent viscosity	Specific gravity	Dry to touch
MPEA-30	5.78	149	80.76	1.4860	0.2305	0.9514	3 h
MPEA-40	8.32	130	95.01	1.4912	0.2465	0.9581	2 h
MPEA-50	9.68	120	99.10	1.5038	0.2569	0.9599	1 h
MPEA-60	10.26	78	105.10	1.5019	0.2655	0.9788	25 mins
MPEA-70	10.21	71	108.00	1.5129	0.2758	0.9790	25 mins
MPEA-80	10.20	70	110.00	1.5132	0.3047	0.9795	25 mins

^aLast digit indicate the loading of SMA in phr.

Table 2
Physico-mechanical and chemical resistance performance of MPEA systems

Resin code ^a	Scratch hardness (Kgs)	Impact resistance (lb/in)	Bend test (1/8 in)	Gloss (45°)	Corrosion resistance test HCl 5% (4 h)				
					NaOH 5% (4 h)	HCl 5% (5 d)	NaCl 3.5% (8 d)	H ₂ O (7 d)	Xylene (7 d)
MPEA-30	2.0	100	Fails	42	d	d	b	b	e
MPEA-40	5.0	150	Fails	46	a	b	d	b	e
MPEA-50	5.5	150	Passes	68	d	b	e	d	b
MPEA-60	4.0	250	Passes	79	b	c	c	c	e
MPEA-70	3.5	200	Fails	82	b	c	d	c	d
MPEA-80	3.2	200	Fails	82	b	c	b	d	d

^aLast digit indicate the loading of SMA in phr.

a-Loss in gloss.

b-Slight loss in gloss and film swell.

c-Unaffected.

d-Slightly film swell.

e-Film completely removed.

$^{13}\text{C-NMR(DMSO)}$ $\delta(\text{ppm})$. 172.4 (C=O, ester); 160.3 (C=O, amide) 22.1–29.1 (CH_2 fatty amide chain); 13.0 (CH_3 fatty amide chain).

The presence of the above mentioned characteristic peaks in FT-IR, $^1\text{H-NMR}$ and $^{13}\text{C-NMR}$ (Figures 1 and 2) confirmed the formation of MPEA resin.

Physico-Chemical Characterization

Table 1 reveals information about the change in iodine value, saponification value, refractive index, inherent viscosity and specific gravity of MPEA resins. The decrease in iodine value followed by an increase in acid, saponification, refractive index, inherent viscosity and specific gravity values were observed. The decrease in iodine value can be attributed to the increase of polymeric chain size and increase in molar mass. The dense and high molar mass structure can be ascribed to the increase in the values of specific gravity, refractive index and inherent viscosity.

MPEA resin was also subjected to solubility test in various organic solvents at room temperature. MPEA was completely soluble in polar solvents viz. dimethyl sulfoxide, ethylene glycol monomethyl ether, tetrahydrofuran, ethanol, methanol and N, N dimethyl formamide, and insoluble in nonpolar solvent viz. ethyl methyl ketone, xylene, toluene, benzene, chloroform, heptane, 1–4 dioxane, di ethyl ether, acetone and carbon

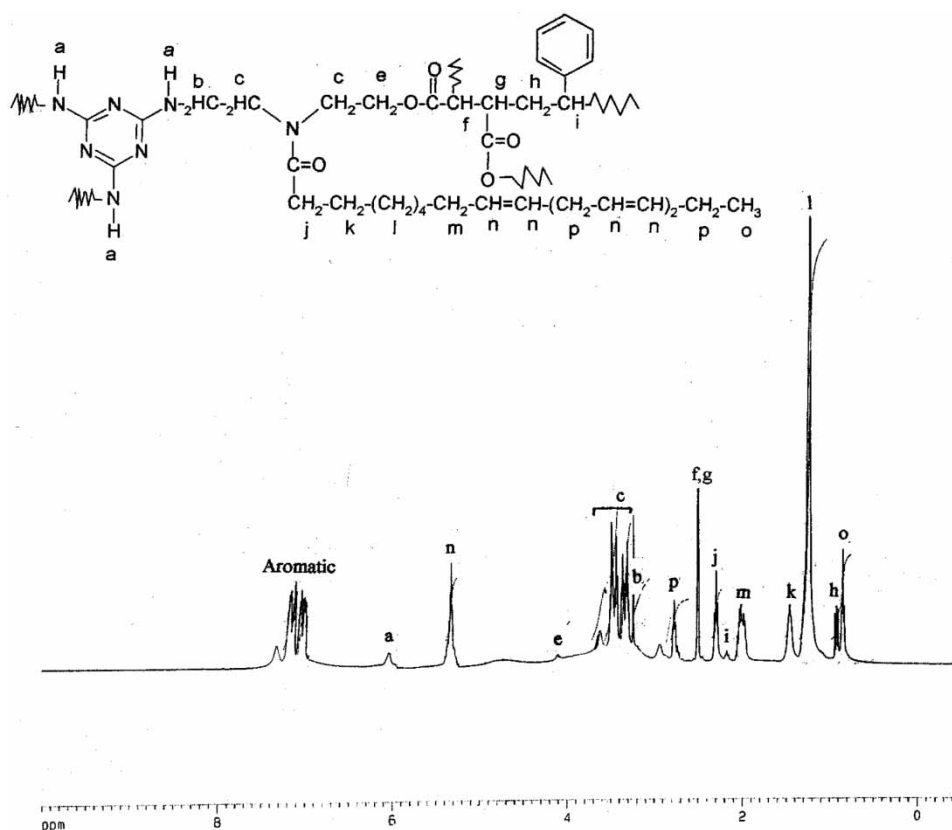


Figure 1. $^1\text{H-NMR}$ spectra of MPEA.

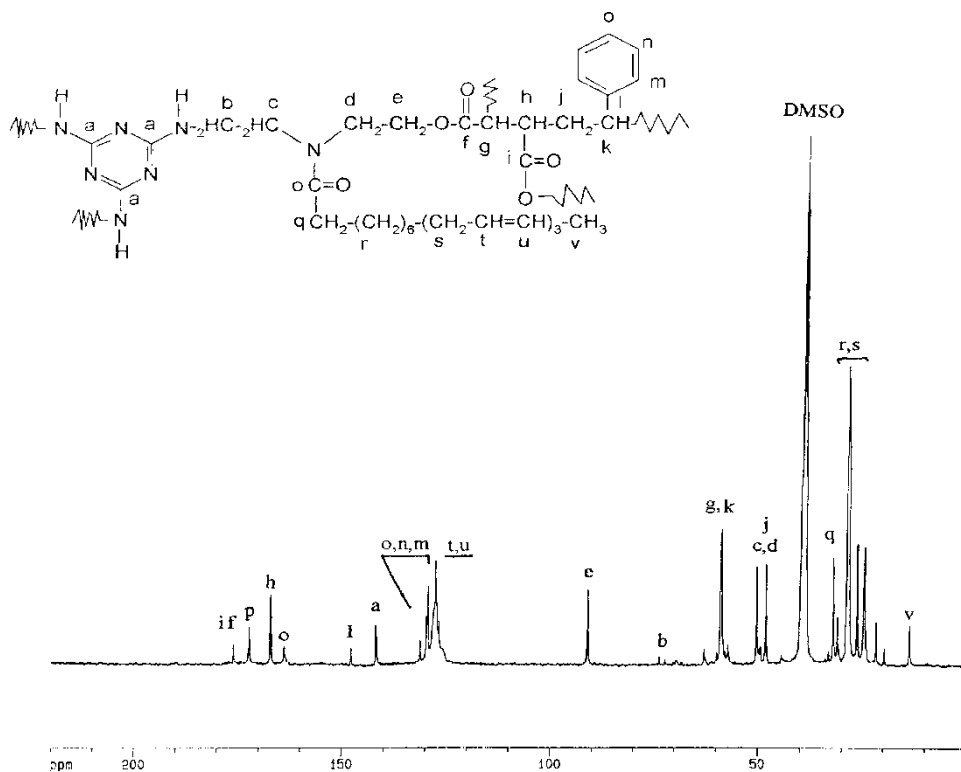


Figure 2. ^{13}C -NMR spectra of MPEA.

tetra chloride. The solubility behavior of the resin suggests that the resin is having excessive polar groups that cause increase in adhesion and mutual interaction between chains.

Coating Properties

The data in Table 1 deals with the physico-mechanical and chemical resistance properties of MPEA (30–80) systems. The dry to touch (DTT) time was found to decrease up to MPEA-50 (1 h) Beyond this composition, DTT of resins was found to be constant (25 min) while the value for dry to hard (DTH) time which is correlated to the complete curing of these resins was found to be 10–12 days. It shows that the optimum extent of crosslinking of coatings is achieved at MPEA-60. Scratch hardness values were found to increase upto MPEA-50 followed by the decrease in scratch hardness. This can be attributed to presence of larger number of aromatic moieties and higher cross-linking between OH groups of HELA and anhydride group of SMA. The higher cross-link density of the resin can produce strain in the coatings causing brittleness that support the lowering of scratch hardness. The increased number of polar groups in MPEA coatings impart good adhesion in between the coatings and metal surface, this will cause an increase in impact resistance as has been observed.

It is further observed that the gloss values increased with an increase of SMA content. Presumably, the increase in SMA content helped in the formation of more dense structure

of the resin responsible for the increase in the gloss values. It is interesting to note that MPEA coatings have lower bend test values (1/8 inch) because of the strain produced in the coatings due to enhanced crosslink density.

Table 2 reveals that MPEA-60, among all MPEA coating systems, exhibits the best chemical resistance properties in mineral acid, saline and aqueous environment and also in an alkaline environment. MPEA-60 coatings were thus found to possess far higher alkali resistance property than other reported polyesteramide coatings (11). Surprisingly, MPEA systems fail to give satisfactory performance in xylene as most of the coatings were completely removed within 7 days presumably because of the presence of styrene moiety.

Thermal Analysis

The TGA thermogram (Figure 3) shows the onset of degradation beyond 175°C, in either case. 10 wt% loss was observed at 200°C, 231°C, 220°C and 215.5°C in MPEA-50, MPEA-60, MPEA-70 and MPEA-80, respectively. 50 wt% loss for MPEA-50, MPEA-60, MPEA-70 and MPEA-80 occurs at 355°C, 370°C, 381.5°C and 380°C. It is distinctly noticeable that at the initial stage of degradation (for 10 wt% loss), the thermal stability increases up to MPEA-60. However, at the medieval stage (for 50 wt% loss) of decomposition of the resin, thermal stability progressively increases up to MPEA-70 beyond which no perceptible change was observed.

DSC thermogram (Figure 4) shows a notch in either case extending from 27°C to 80°C, centered at 37.5°C. The resin systems (MPEA-50, MPEA-60, MPEA-70 and MPEA-80) were actually cured at room temperature; drying involved a purely physical process i.e., by solvent evaporation (13). The notch centered at 37.5°C in either case can be attributed to the evaporation of the trapped solvent resulting into molecular reorganization and physical curing of resins. The endothermic peak, in either case, extends from 80 to 155°C and is centered at 114°C, 117°C, 118°C and 118.5°C for MPEA-50, MPEA-60, MPEA-70 and MPEA-80, respectively. In TGA thermograms, no weight loss is noticeable at the aforementioned temperatures. These endotherms extending from 80°C to 155°C can be imputable to the melting phenomenon of the resins, while the endothermic peaks may be correlated to melting points of these resin system. A slight variation, i.e., an increase is observed in melting points with an increased loading of

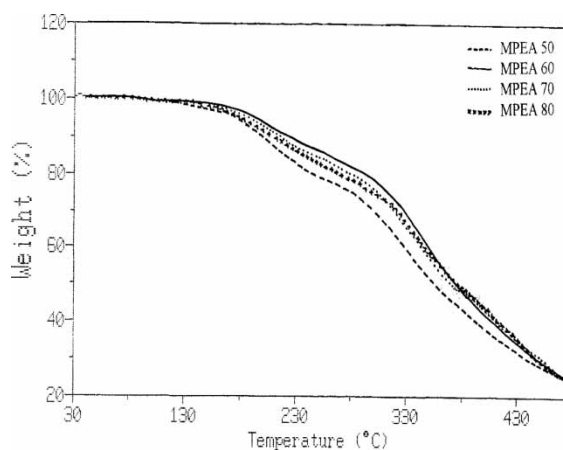


Figure 3. TGA thermograms of MPEA systems.

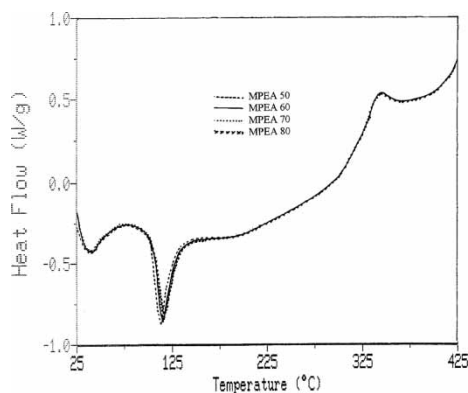


Figure 4. DSC thermograms of MPEA systems.

SMA. It is reported that an increase in flexibility reduces the melting of the resins and vice versa (5, 7, 22). Thus, the higher SMA content (rigid styrene moieties) contributes to higher melting point of these resins with an increase in copolymer content. Beyond 175°C, an exotherm ensues which extends over the rest of the DSC thermograms, in either case, the TGA thermogram shows the onset of degradation beyond this temperature. The exotherm may be correlated to decomposition of the resins.

Conclusions

The synthesis of MPEA resin from linseed oil provides a new way to utilize a sustainable resource. The MPEA coatings show reasonably good performance in alkali (5 wt% NaOH) as compared to those of reported polyesteramide coatings (11). The system has a good combination of properties of amine, ester, melamine and amide linkages in terms of physico-mechanical properties. TGA thermograms reveal that the resin can be safely used up to 200°C.

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