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Synthesis and Characterization of Piperazine-Modified Linseed Oil Fatty Amide Coatings

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Abstract: Piperazine-modified fatty amide (PMF) was prepared from N,N-bis(2-hydroxy ethyl) linseed oil fatty amide and piperazine through condensation polymerization. It was further cured with butylated melamine formaldehyde in different phr (parts per hundred part of resin) (PMF-BMF). PMF and PMF-BMF systems were subjected to spectroscopic analysis to ascertain their structure and curing scheme. Thermal studies and curing behavior of these resins were carried out by thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC). The physico-mechanical performance and chemical resistance of PMF-BMF coatings were evaluated by standard methods. The effect of BMF content and curing temperature (ambient and elevated) on aforementioned coating properties was also investigated. It was found that PMF resin with 80 phr BMF cured at 120°C showed the best performance among all compositions.

Keywords: Linseed oil; Piperazine; Butylated melamine formaldehyde; Coatings; FT-IR, ¹H-NMR, and ¹³C-NMR characterization; TGA analysis; Mechanical tests

INTRODUCTION

Synthesis of polymeric coating materials has long been carried out from petrochemical-based monomers. To meet the challenges of high prices of petroleum-based precursors as well as petroleum's fast depletion,^[1,2] efforts

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have been made to develop coatings through some alternative resource such as oil-based polymeric coating materials. Low molecular weight polymers like alkyds,^[3] polyepoxies,^[4] polyurethanes,^[5] polyesteramides,^[6] and polyetheramides^[7] have been synthesized from various seed oils such as pongamia glabra, linseed, soya bean, argemone, and castor^[5,8,9], and have found wide application in the field of paints and coatings.

Oil-based polymeric coatings have shown good corrosion resistance performance and higher values of physico-mechanical properties, while petrochemical-based polymeric coatings exhibit low UV resistance, brittleness, and low shrinkage energy.^[10,11] One of the major drawbacks of oil-based polymeric coating materials is that they lack room temperature curing; they normally cure at high temperatures (175–220°C),^[12] involving higher energy in their curing process. In order to overcome the problem of high-temperature curing and also to improve the physico-mechanical properties, a number of modifications in such polymers have been introduced through the incorporation of metals/metalloids and other functional groups in the backbone of the polymeric chain.^[6,13]

An important oil-based monomer, N,N bis 2-hydroxy ethyl oil fatty amide (HELA), has been used in the synthesis of oil-based polyetheramide and polyesteramide.^[14,2] The presence of ester and ether along with amide groups in this monomer enhances the physico-mechanical, thermal, and film-forming properties over the conventional alkyds. These polymeric moieties, however, fail to give good alkali resistance performance and also do not cure at room temperature. To overcome the above shortcomings, these polymers have been further modified by some other moieties such as urethane,^[15] butylated melamine formaldehyde,^[14] styrene co polymer, and styrene.^[16,17] Oil fatty amide diol can be modified in a similar way by an amine. We have attempted to use piperazine, a secondary amine, to modify oil fatty amide for obtaining an amine-modified fatty amide. Piperazine and its derivatives such as methyl piperazine, benzyl piperazine, and diphenyl methyl piperazine have been used as an effective corrosion inhibitor for steel in acidic medium.^[18]

The present communication deals with the synthesis of oil fatty amide diol and its modification by piperazine to obtain piperazine-modified fatty amide (PMF). Although melamine resins, commonly called baked enamels, were used as a high-temperature curing agent,^[12] we have used butylated melamine formaldehyde (BMF) as a room temperature curing agent for PMF, since butylated melamine formaldehyde possesses higher values of hardness, and water, alkali, and solvent resistance, along with adequate thermal stability, provided by s-triazine ring.^[19] The structural elucidation of PMF resin and PMF-BMF adduct systems were carried out by FT-IR, ¹H-NMR, and ¹³C-NMR spectroscopic analyses. Physico-mechanical characterization and chemical resistance properties were studied by standard methods. Thermal analysis and curing behavior

were studied by thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC).

EXPERIMENTAL METHODS

Materials

Linseed oil was procured from the local market. Fatty acid composition of the oil was determined by gas chromatography (GC: 111/8ss column, FID detector). Xylene, sodium methoxide, diethanolamine (Merck, India), piperazine (diazacyclohexane) (SD Fine-Chem, Delhi, India), and butylated melamine formaldehyde (Synthetic and Polymer Industries, Gujrat, India) were used as curing agents and phosphoric acid (Merck, India) as catalyst.

Synthesis of N, N Bis(2-Hydroxy Ethyl) Linseed Oil Fatty Amide (HELA)

HELA was prepared according to our previously reported method.^[6]

Synthesis and Characterization of Piperazine-Modified Oil Fatty Amide (PMF)

HELA (0.08 mol) and piperazine (0.05 mol) were dissolved in 50 ml xylene. The solution was then transferred to a four-necked round-bottom flask equipped with a Dean-Stark trap, nitrogen inlet tube, thermometer, and magnetic stirrer. The reaction mixture was heated at 150°C until the calculated amount of water was collected in the Dean-Stark trap. The reaction conversion was monitored by thin layer chromatography (TLC) at regular intervals up to the completion of the reaction, followed by cooling of the reaction product at room temperature. The solvent was evaporated in a rotary vacuum evaporator under reduced pressure to obtain PMF resin. The PMF was treated with butylated melamine formaldehyde (60–90 phr) in the presence of phosphoric acid as a catalyst. The PMF-BMF systems were further cured at ambient (30°C) and elevated temperature (120°C).

PMF and PMF-BMF resins were 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, Conn.) using a 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

Table I. Physicochemical characterization of PMF and PMF-BMF systems

Resin code ^a	Iodine value	Hydroxyl value	Refractive index	Inherent viscosity	Specific gravity
PMF	149	2.0	1.4650	0.6005	0.8665
PMF-60	63	1.57	1.5048	0.6165	0.8670
PMF-70	58	1.40	1.5188	0.6269	0.8679
PMF-80	54	1.50	1.5192	0.6455	0.8688
PMF-90	45	1.30	1.5229	0.6658	0.8702

^aLast digit indicates the loading of BMF.

(TMS) as an internal standard. Thermal analysis of the PMF-BMF systems was carried out by thermogravimetric analysis (TGA51, TA Instruments, USA) and differential scanning calorimetry (DSC10, TA Instruments, USA) at the heating rate of 20°C/minute in nitrogen atmosphere. Solubility of PMF and PMF-BMF resins was tested in various organic solvents. The inherent viscosity of PMF and PMF-BMF system in xylene (0.5 g/100 mL) at 25°C was determined by a Ubbelohde viscometer. The physicochemical properties like iodine value (ASTM D555-6), hydroxyl value (ASTMD-42748), specific gravity (g/cc at 25°C), and refractive index (η_D 45°) were determined by standard laboratory methods (Table I).

Preparation and Testing of Coatings

Brush technique was used to apply 40 wt% solutions of PMF-BMF resins in xylene systems on commercially available mild steel strips of 30 × 10 × 1 mm size for chemical resistance and 70 × 25 × 1 mm size to determine the specular gloss at 45° by a glossmeter (Model RSPT 20; Digital Instrument, Santa Barbara, Calif.), as well as bending (ASTM D3281-84), scratch hardness (BS3900), and impact resistance (IS:101 part 5/sec, 3 1988) tests. The coated panels of PMF-BMF resins were cured at two different temperatures; one set of PMF-BMF was cured at 120°C for 10 minutes and another set of the same system was cured at ambient temperature (30°C). Coating thickness was measured by an Elcometer (Model 345; Elcometer Instruments, UK). The thickness of these coatings was found to be 80 ± 5 μm. Corrosion tests were performed in water, acid (5 wt% HCl), alkali (2 wt% NaOH), saline water (3.5 wt% NaCl) (ASTM D1308-57), and xylene environment by pouring them in three-inch diameter porcelain dishes and dipping the coated samples, in the aforementioned media. Periodical examination was conducted until the coatings showed evidence of softening or deterioration.

RESULTS AND DISCUSSION

The stipulated reaction schemes for the synthesis of PMF and curing reaction of PMF with BMF (Schemes 1 and 2) were confirmed by the presence of characteristic FT-IR bands. The $^1\text{H-NMR}$ and $^{13}\text{C-NMR}$ peaks in their respective spectra are given in Figures 1 to 4.

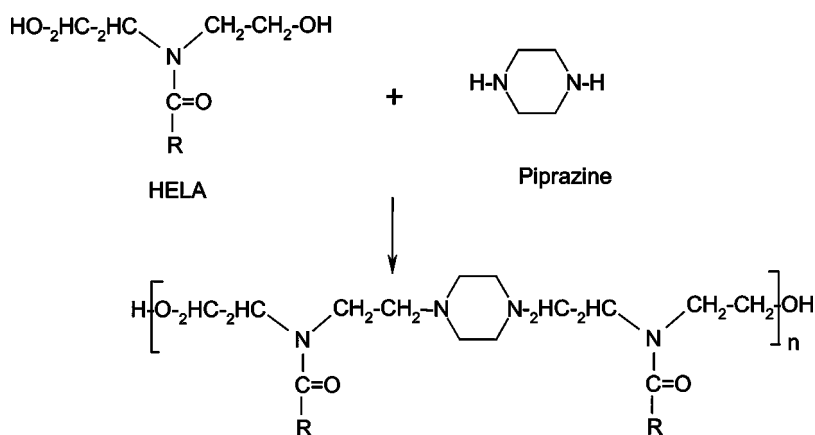
N,N-Bis(2-Hydroxy Ethyl) Linseed Oil Fatty Amide (HELA)

The structure of HELA was confirmed by FT-IR and $^1\text{H-NMR}$ spectral analysis according to our earlier work.^[6]

Piperazine-Modified Fatty Amide (PMF)

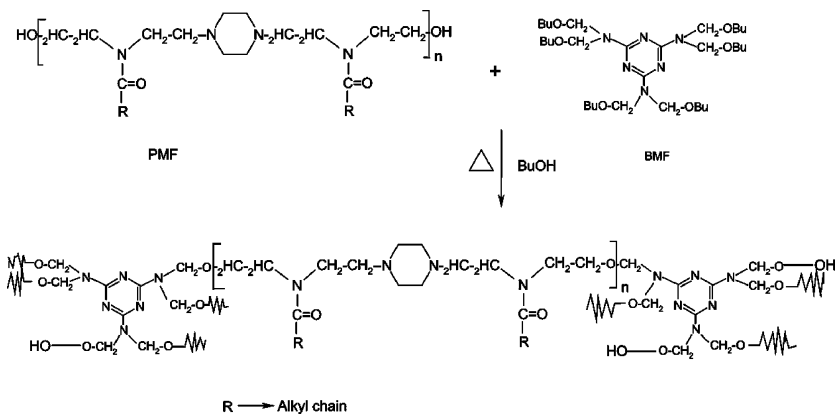
In FT-IR spectra of PMF, the characteristic band of hydroxyl groups was present at 3369 cm^{-1} , and $-\text{CH}_2$ symmetrical and asymmetrical stretching vibration occurred at 2527 cm^{-1} and 1854 cm^{-1} . The amide carbonyl band was found at 1629 cm^{-1} . The absorption band for C-N of amide and the band for $-\text{CH}-$ of unsaturation occurred at 1400 cm^{-1} and 3011 cm^{-1} , respectively. The band at 1354 cm^{-1} is attributed to C-N of piperazine.^[20]

The above-mentioned bands were also observed in the spectra of PMF-BMF along with some additional bands found at 1634 cm^{-1} for $-\text{CN}-$ stretching of melamine and at $1560\text{--}1557\text{ cm}^{-1}$ for inplane stretching



R-Alkyl chain

Scheme 1. Synthesis of piperazine modified fatty amide (PMF).



Scheme 2. Curing reaction of PMF with BMF.

of *s*-triazine ring.^[21] Additional bands were distinctly observed at 1045 cm^{-1} for ether linkages formed by the curing reaction of PMF with BMF.

In $^1\text{H-NMR}$ spectra, the presence of peaks at $\delta = 3.41\text{ ppm}$ and at $\delta = 2.15\text{ ppm}$ for CH_2 of piperazine ring and $-\text{CH}_2$ attached to $-\text{N}$ of piperazine, respectively, confirm the incorporation of piperazine in HELA.

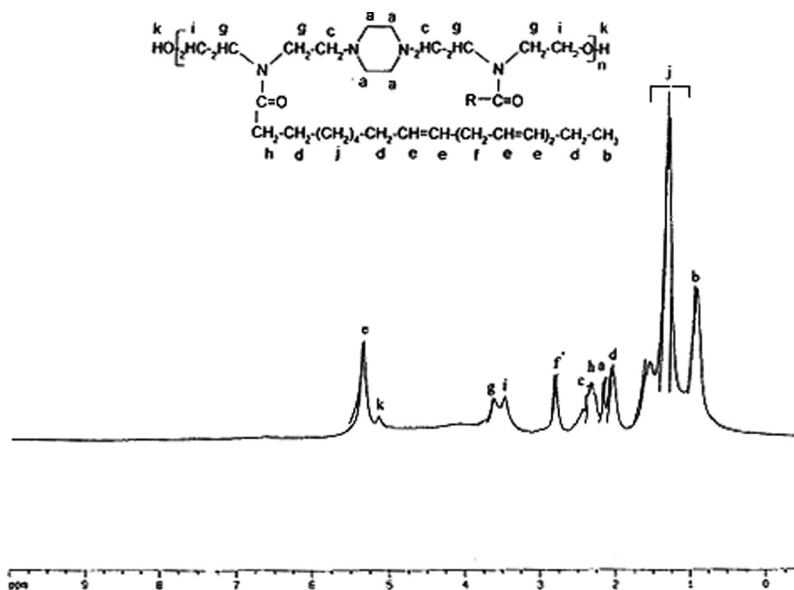


Figure 1. $^1\text{H-NMR}$ spectra of PMF.

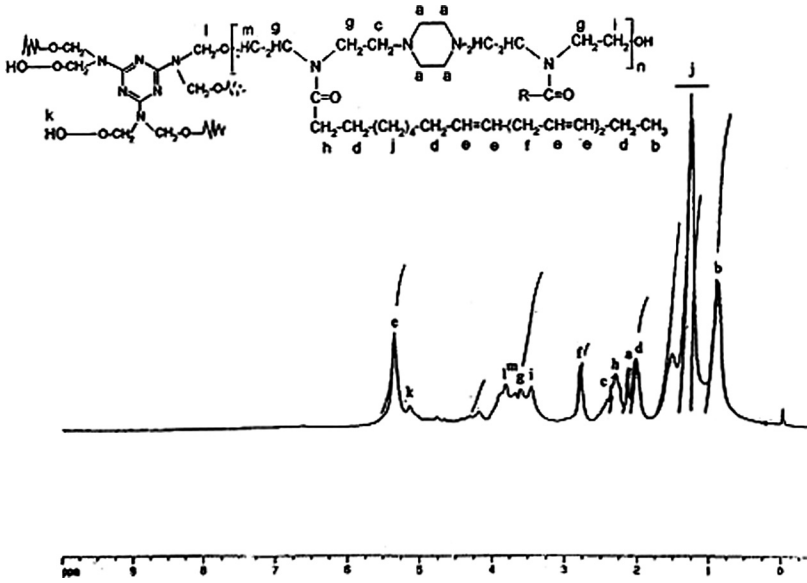


Figure 2. ¹H-NMR spectra of PMF-BMF.

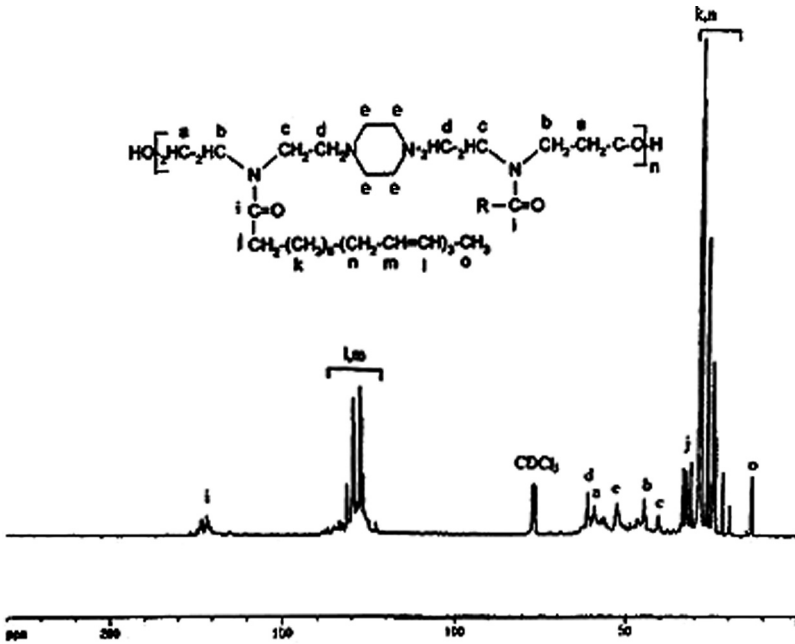


Figure 3. ¹³C-NMR spectra of PMF.

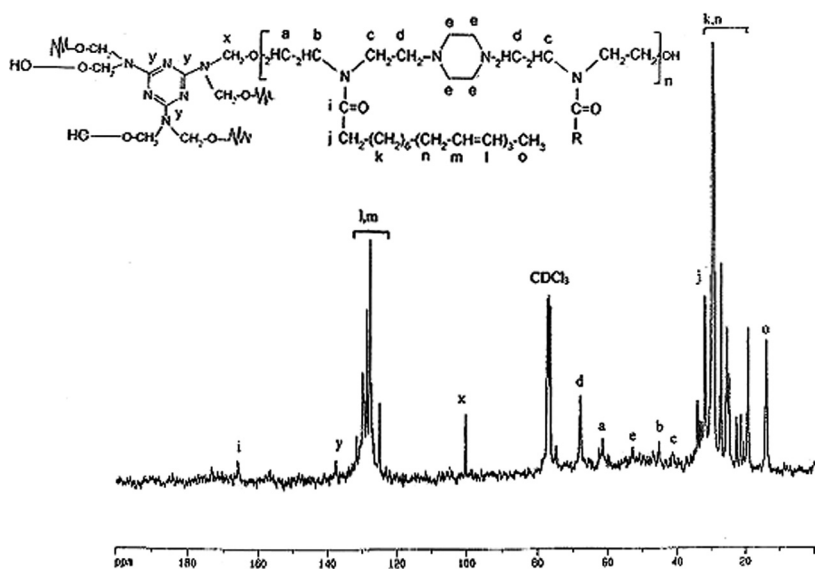


Figure 4. ^{13}C -NMR spectra of PMF-BMF.

In ^{13}C -NMR spectra, peaks for $-\text{CH}_2$ of piperazine ring and CH_2 -attached to N- of piperazine occur at $\delta = 52$ ppm and $\delta = 61.6$ ppm, respectively. ^1H NMR spectra of PMF-BMF peaks at $\delta = 3.8$ ppm and $\delta = 3.30$ ppm correspond to $-\text{CH}_2$ of BMF and $-\text{CH}_2$ of piperazine, respectively. ^{13}C -NMR spectra represent peaks at $\delta = 137$ ppm and $\delta = 100.53$ ppm for ring carbons of BMF as well as for $-\text{CH}_2$ of BMF, thus confirming the curing reaction of piperazine with BMF.

The presence of the above characteristic peaks in FT-IR, ^1H -NMR, and ^{13}C -NMR spectra confirm the formation of PMF resin and its curing reaction with BMF.

Physicochemical Characterization

The data on physicochemical properties of PMF and PMF-BMF systems are given in Table I. The hydroxyl value and iodine value decrease while refractive index, specific gravity, and inherent viscosity increase from PMF to PMF-BMF systems. This can be attributed to the increases in molar mass of PMF system by subsequent addition of BMF. The solubility behavior of PMF and PMF-BMF resins was also studied in different organic solvents at room temperature. PMF and PMF-BMF resins were found to be completely soluble in various polar and nonpolar solvents, i.e., ethyl methyl ketone (butanone), ethylene-glycol-monomethylether

(2-methoxy ethanol), xylene, toluene, benzene, N,N-dimethyl formamide, diethyl ether (ethoxy ethane), tetrahydrofuran, carbon tetra chloride (tetra chloromethane), chloroform (tri chloromethane), n-hexane, ethanol, and 1-4 dioxane. The solubility behavior of the resin can be attributed to the presence of polar groups and the long aliphatic chain of the polymer.

Coating Properties

As mentioned, 40 wt% solution of PMF-BMF resins in xylene systems were applied on mild steel strips of standard sizes and were cured at ambient temperature (30°C) as well as at elevated temperature (120°C). The effect of BMF loading and the influence of curing temperatures on coating properties (physico-mechanical and chemical resistance) of resins were also investigated (Tables II and III). It was observed that with increased content of BMF (from 60 to 90 phr) in the case of coating systems cured at 120°C, the scratch hardness, impact resistance, bend test, and gloss values increase up to PMF-80. However, beyond 80 phr of BMF loading, these properties showed gradual deterioration in their values. The best physico-mechanical properties for 80 phr BMF loading can be attributed to pendant fatty amide chains, ether linkages due to etherification reaction of PMF and BMF, and additional cross-links due to thermal polymerization of unsaturation of fatty amide chain along with the s-triazine ring of melamine resin. These parameters collectively impart good flexibility, adhesion, and toughness to the resin, which lead to a gradual improvement in their physico-mechanical properties. However, beyond PMF-80, the additional introduction of melamine causes brittleness in the polymer chains,^[14] thus leading to the deterioration of these properties. These results highlight the fact that 80 phr is the optimum content of melamine required to achieve improved coating properties.

Chemical resistance tests indicate that PMF-60 coated panels underwent loss in gloss when immersed in 2 wt% NaOH for 4 h, while they were unaffected in 5 wt% HCl solution (three days). Loss in gloss and adhesion as well as complete removal of their films were observed when the panels were tested for water (four days) and xylene (seven days) resistance, respectively. However at PMF-90, the coated panels exhibit loss in adhesion in NaOH (2 wt%, 4 h), HCl (5 wt%, three days), NaCl (3.5 wt%, ten days), and H₂O (four days), while complete removal of their films occurred in xylene within seven days.

In the case of PMF-BMF systems cured at room temperature, it is noticeable that unlike their counterparts cured at 120°C, these resins do not show any deterioration of values of scratch hardness, impact resistance, bend test, and gloss even up to 90 phr loading of BMF. This is because when curing occurs at ambient temperature, excessive cross-linking was

Table II. Physico-mechanical and chemical resistance performance of PMF-BMF systems

Resin code ^a	Scratch hardness (gms)	Impact resistance (lb./inch)	Bend test (1/4 inch)	Gloss (45°)	Corrosion resistance test				
					NaOH 2% (4h)	HCl 5% (3 days)	NaCl 3.5% (8 days)	H ₂ O (3 days)	Xylene (5 days)
PMF-60	900	100	passes	55	e	d	c	e	e
PMF-70	1000	100	passes	62	d	b	d	e	e
PMF-80	1200	150	passes	65	c	b	b	b	b
PMF-90	1500	150	passes	70	c	b	b	b	b

^aLast digit indicates the loading of BMF.

Table III. Physico-mechanical and chemical resistance performance of PMF-BMF systems baked at 120°C

Resin code [*]	Scratch hardness (Kgs)	Impact resistance (lb./inch)	Bend test (1/8 inch)	Gloss (45°)	Corrosion resistance test				
					NaOH 2% (4h)	HCl 5% (3 days)	NaCl 3.5% (10 days)	H ₂ O (4 days)	Xylene (7 days)
PMF-60	1.5	150	passes	60	d	c	b	b	e
PMF-70	2.1	150	passes	62	a	c	d	b	e
PMF-80	2.5	200	passes	75	d	d	d	d	b
PMF-90	2.0	150	passes	70	b	d	c	d	e

^{*}Last digit indicates the loading of BMF.

a Loss in gloss.

b Slight loss in gloss and film swell.

c Unaffected.

d Slight film swell.

e Film completely removed.

not involved, even up to 90 phr BMF loading. Anticorrosive performance tests also reveal an improvement in chemical resistance with increased content of BMF (90 phr) in alkali, saline water, xylene, and tap water.

These results distinctly highlight that irrespective of the curing temperature, factors that affect physico-mechanical performance also influence the chemical resistance of the resins in a similar manner.

Mechanical properties of the systems cured at elevated temperature generally show improvement over the systems cured at ambient temperature in oil-based polymeric resins.^[2] Curing at higher temperature involves thermal polymerization of unsaturation of alkyl chains while curing at room temperature occurs through auto-oxidation, the latter reportedly a slow process. We assume that the former plays a more influential role in improving the coating properties of the resins than the latter. Our studies reveal that PMF-80 cured at 120°C exhibits better physico-mechanical and chemical resistance performance. The physico-mechanical and anticorrosive tests results indicate that these coatings may find application under moderately corrosive environments.

Thermal Analysis

PMF-70 and PMF-80 were subjected to thermal analysis. The TGA thermogram (Figure 5) shows the onset of degradation beyond 225°C for both cases. A 10 wt% loss was observed at 210°C and 215°C in PMF-70 and PMF-80 respectively. A 50 wt% loss for PMF-70 and PMF-80, occurs at 345°C and 350°C. It is distinctly noticeable that at the initial stage of degradation (10 wt% loss), thermal stability of PMF increases with increased content of BMF.

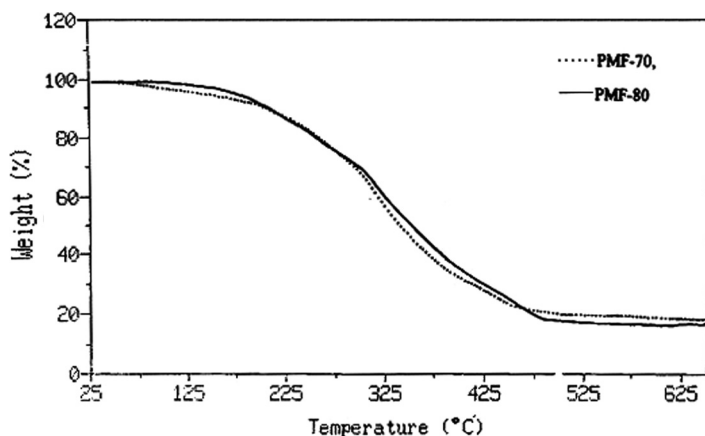


Figure 5. TGA thermograms PMF-70 and PMF-80.

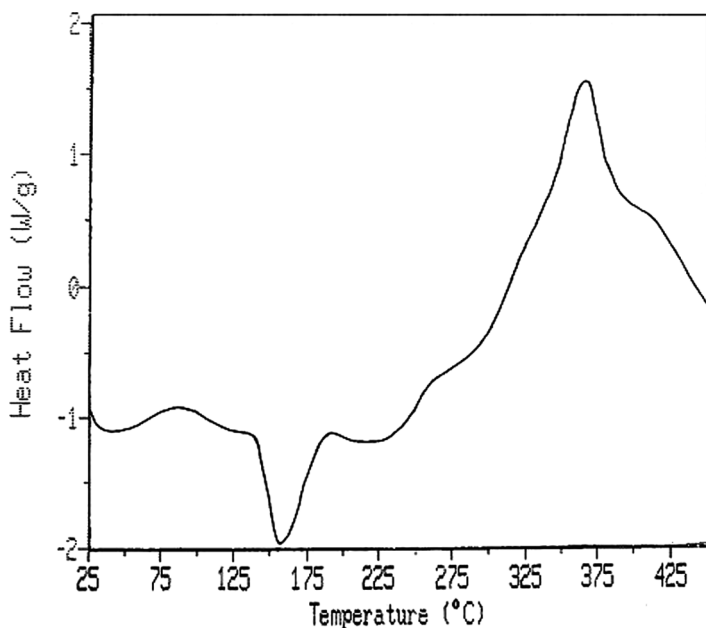


Figure 6. DSC thermogram of PMF-80.

The DSC thermogram (Figure 6) shows a notch for both cases extending from 27 to 50°C, centered at 37°C. The notch centered at 37°C for both cases can be attributed to the evaporation of the trapped solvent resulting in molecular reorganization. The endothermic peak, for both cases, extends from 140 to 185°C and is centered at 155°C for PMF-80. In TGA thermograms, no weight loss is noticeable at the aforementioned temperatures. These endotherms extending from 140 to 185°C can be implacable to the melting phenomenon of the resins while the endothermic peaks may be correlated to melting points of these resin systems.^[2,14] Beyond 225°C, an exotherm occurs that extends over the rest of the DSC thermogram. For both cases, the TGA thermogram shows the onset of degradation beyond this temperature. The exotherm may be correlated to the decomposition of the resins.

CONCLUSION

Piperazine-modified fatty amide systems cured at elevated temperature (120°C) exhibit improved physico-mechanical properties over PMF-BMF systems cured at ambient temperature (30°C). Chemical resistance tests of PMF-BMF systems follow the same trend as physico-mechanical

performance irrespective of curing temperature. This reveals that the factors that govern the physico-mechanical performance also influence the chemical resistance of resins in a similar manner. A novel combination of moieties such as fatty amide, piperazine, ether, and melamine could be obtained by this approach. Among all resin compositions (cured at elevated and ambient temperature), PMF-80 cured at 120°C exhibits the best performance. It can be safely used up to 205°C under moderately corrosive environments.

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