

Studies on Poly(Styrene-*co*-Maleic Anhydride)-Modified Polyesteramide-Based Anticorrosive Coatings Synthesized from a Sustainable Resource

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ABSTRACT: Polyesteramide (PEA) coating resin, synthesized from linseed oil, a sustainable resource, was found to show improved physicomechanical and acid-resistance properties. To further improve these properties in terms of alkali resistance, scratch hardness, and thermal stability and to reduce the baking temperature, we have attempted to incorporate styrene into the polymer backbone through its copolymer with maleic anhydride. The structural elucidation of modified PEA resin (SCPEA) was carried out by FTIR, $^1\text{H-NMR}$, and $^{13}\text{C-NMR}$ spectrometers. The physicomechanical and chemical-resistance properties were investigated by standard methods and thermal stability was investigated by thermogravimetric analysis method. A comparative study of these properties of PEA and SCPEA was carried out. It was observed that the SCPEA showed better properties than the reported one. © 2004 Wiley Periodicals, Inc. *J Appl Polym Sci* 92: 2538–2544, 2004

Key words: coatings; curing of polymers; adhesion; gloss

INTRODUCTION

Alkyds comprise an important class of polymeric binders in the field of coatings and paints. However, under stringent environment, their applicability is limited owing to their relatively inferior water, alkali, and chemical resistance. This is attributed to the ester linkages present in the resin backbone, which is prone to hydrolysis.¹ Vegetable oil based polyesteramide (PEA) resins containing sufficient amide linkages are known to impart satisfactory water, chemical, and thermal resistance to their films.² Several PEA resins have shown their superiority to alkyd resins.³

PEA resins were developed from linseed oil, dehydrated castor oil, pilu fat, annona squamosa, argemone seed oil, pongamia glabra, and other oils.^{3–7} The high melting point, low solubility, lower intractability, high drying time, and temperature cause difficulties in their application as coating materials.⁸ To overcome these drawbacks, in our earlier publications, we reported the development of alumina-filled PEA and urethane-modified alumina-filled PEA anticorrosive coating materials.^{2,3} Other modifications include the incorporation of isocyanates, amino resins, acrylic monomer, vinyl, and chlorinated rubber in PEA and alkyds, which have also been reported.^{2,9–12}

Literature survey reveals that polystyrene has been a subject of popular interest for coating technologists.¹³ It gives fairly hard, colorless, and water alkali as well as thermal-resistant coatings.^{14,15} Over the years, several attempts were made for the incorporation of styrene in the backbone of polymeric resins by various methods. Usually, such an incorporation of polystyrene is carried out through double bonds where homopolymerization cannot be ruled out. Contrary to the above, polystyrene can expectedly be incorporated in the backbone of polymer through suitable functional groups.^{16–19} Because this approach does not involve fatty acid unsaturation, it would provide a wider perspective for selection of oils. It was also observed that other factors being the same, the higher the styrene content in the resin backbone, the lower the resistance to aromatic solvents with a lower gloss.²⁰ Poly(styrene-*co*-maleic anhydride), a bifunctional acrylic copolymer, is capable of reacting with alcohols, amines, and other groups to produce many derivatives because of the anhydride groups in its backbone.²¹ It possesses a combination of chemical and mechanical properties that may help in the development of high-performance anticorrosive coatings. It was reportedly used as a modifier of latex paints to increase adhesion and gloss in the resin of low-baking temperature and time.²² It is reported that replacement of phthalic anhydride by maleic anhydride in the case of alkyds has led to shorter stoving time and alkyds of better color and drying properties.²³ Surprisingly, in the case of fatty acid PEA formed from vegetable oil where high baking temperature is often a

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problem, no advantage has yet been taken of the favorable properties of poly(styrene-co-maleic anhydride).

In the present work, we report the synthesis, spectroscopic, thermal, physicomechanical, and physicochemical characterization of poly(styrene-*co*-maleic anhydride)-modified linseed oil PEA (SCPEA) resin and its use as an anticorrosive coatings material. On the basis of the above observations, the modified coatings are expected to have improved physicochemical, physicomechanical, and anticorrosive properties as compared to those of plain fatty acid PEA.

EXPERIMENTAL

Materials

Oil was extracted from linseed (procured from a local market) by using a Soxhlet apparatus. Petroleum ether (boiling range, 60–80°C) was used as a solvent. The fatty acid composition of the oil was determined by gas chromatography³ (GC; 111/8s.s column, FID detector). Phthalic anhydride, sodium methoxide, xylene (Merck, India), diethanolamine, and sulfuric acid (S. D. Fine Chemicals, Delhi, India) were of analytical grade and poly(styrene-*co*-maleic anhydride) was an Aldrich product with an average molecular weight of 1600 Da.

Synthesis

Synthesis of *N,N'*-bis (2 hydroxyethyl) linseed amide (HELA) and PEA

HELA and PEA were prepared as per our previously reported method.³

Synthesis of SCPEA

HELA and xylene : acetone mixture (3 : 1) were placed in a four-neck conical flask fitted with a Dean-Stark trap, nitrogen inlet tube, thermometer, and mechanical stirrer. The contents were heated under continuous stirring up to 100°C. Copolymer (5 to 25 wt %) in xylene : acetone (3 : 1) was added dropwise in the presence of acid catalyst over a period of 30 min. After the complete addition of copolymer, the temperature was raised to 145 ± 5°C; progress of the reaction was monitored by acid value and thin layer chromatography (TLC) test until a theoretical amount of water was collected in a Dean-Stark trap. On obtaining a desired acid value, phthalic anhydride was added and the progress of the reaction was again monitored by acid value and TLC test.³ On completion of the reaction, xylene was removed from the resin in a rotary vacuum evaporator under reduced pressure to obtain SCPEA resin.

TABLE I
FTIR peaks of PEA & SCPEA

Functional groups	PEA	SCPEA	IR (cm^{-1})
OH	3460	3429.4	
>C=O (ester)	1725	1731.8	
>C=O (amide)	1636	1645.6	
C—O	1145	1150	
C—N	1130	1135	
C—O—C	1280	1273.3	
C=C	1560	1562	
$\text{CH}_2 \nu_{\text{sym}}$	2840	2853	
$\text{CH}_2 \nu_{\text{asym}}$	2935	2926.6	
CH_3	2980	2978.8	
C=CH	1460	1458	
Ar—H (stretching)	3008.8	3009.98	
Benzene ring	1615, 1585 1070, 750	1600, 1584 1070, 750, 704	

CHARACTERIZATION

HELA, PEA, and SCPEA were characterized by FTIR, ¹H-NMR, ¹³C-NMR, and TGA. FTIR spectra of these resins were taken on a Perkin-Elmer 1750 FTIR spectrophotometer (Perkin-Elmer Instruments, Norwalk, CT) by using an NaCl cell. ¹H-NMR and ¹³C-NMR spectra were recorded on a JEOL GSX 300 MHz FX-1000 spectrometer by using deuterated chloroform and dimethyl sulfoxide (DMSO) as a solvent, respectively, and tetramethylsilane (TMS) as an internal standard. TGA (TA2000, TA Instruments USA) was done in a N₂ atmosphere to study the thermal behavior. The inherent viscosity of PEA and SCPEA in *N*-methyl pyrrolidone (0.5 g/100 mL) at 25°C was determined by a Ubbelhode viscometer. Iodine value, hydroxyl value, and saponification values were determined as per ASTM method D555-6. Specific gravity and refractive index were determined by standard laboratory methods (Tables I and II).

Preparation and testing of coatings

Coating of PEA and SCPEA resins were prepared by brush technique by using 40 wt % SCPEA resin in xylene on commercially available mild steel strips 30 × 10 × 1 mm size for chemical resistance and 70 × 25 × 1 mm size strips to determine the specular gloss at 45° by glossmeter (model RSPT 20; Digital Instruments, Santa Barbara, CA), scratch hardness(BS3900), bending (ASTM D328184), and impact resistance (IS: 101part5/Sec. 3, 1988). Coated strips were stoved at 160°C for 15 min (Table III). Coating thickness was measured by Elcometer (model 345; Elcometer Instrument, Manchester, UK). The thickness of these coatings was found to be 70 ± 5 μm. Corrosion tests were performed in water, acids (5 wt % HCl, 5 wt % HNO₃), alkali (5 wt % NaOH), xylene, and other organic sol-

TABLE II
Characterization of PEA and SCPEA

Resin code ^a	Hydroxyl value (%)	Saponification value	Iodine value	Specific gravity	Refractive index	Inherent viscosity (dl/g)
PEA	7.87	128	48	0.938	1.507	0.652
SCPEA-5	4.12	98	35	0.970	1.529	0.731
SCPEA-10	3.86	92	30	0.973	1.533	0.735
SCPEA-15	3.66	90	27	0.977	1.536	0.737
SCPEA-20	3.20	82	24	0.983	1.540	0.744
SCPEA-25	2.98	79	22	0.985	1.542	0.747

^a Last digit of resin code indicate the wt % of copolymer.

vents by placing them in 3-in.-diameter porcelain dishes and dipping the coated samples in the aforementioned media. Periodic examination was conducted until the coatings showed evidence of softening or deterioration (Table III). Salt-spray test (ASTM B177-94) was also carried out for a period of 10 days in a salt-mist chamber.

RESULTS AND DISCUSSION

Reaction schemes for the synthesis of HELA and PEA were reported elsewhere.² Synthesis of SCPEA is given in Figure 1. The proposed structure for SCPEA [Fig. 1(d)] incorporating styrene in the polymer backbone through maleic anhydride was confirmed by FTIR, ¹H-NMR, and ¹³C-NMR spectroscopies. Thermal analysis of SCPEA film was done by TGA. The above analysis is discussed in a later section.

HELA and PEA

The FTIR and ¹H-NMR spectra of HELA and PEA have been presented earlier.³

SCPEA

Relevant FTIR peaks of SCPEA resin are shown in Table I. The peaks at 2853 and 2926.6 cm⁻¹ are ob-

served for asymmetric and symmetric CH₂ vibrations; peaks at 1731.8 and 1645.6 cm⁻¹ are due to C=O (ester), C=O (amide), and peaks at 3429 cm⁻¹ are for OH stretching. The shifts observed in the values of the above peaks from those in the case of PEA may presumably be due to the increase in polar groups in SCPEA. A sharp band at 704 cm⁻¹ in SCPEA due to styrene confirms the incorporation of styrene in PEA.

The ¹H-NMR peak values of characteristic protons in SCPEA are shown in Figure 2. The peaks for methylene attached to free-hydroxyl, amide nitrogen, and amide carbonyl are observed at δ = 3.491 ppm, δ = 3.745 ppm, and δ = 2.35–2.25 ppm, respectively. The characteristic peaks at δ = 7.8–6.9 ppm for aromatic ring protons of styrene and phthalic anhydride further confirm the structure of PEA. It could be noted that the ¹H-NMR peaks of plain PEA of oils found by earlier workers² were observed in this case also.

A closer examination of ¹H-NMR spectra also reveals the peaks at δ = 2.24–2.17 ppm and δ = 1.11 ppm for —CH— and —CH₂ of styrene and at δ = 2.6–2.5 ppm characteristic of —CH— of maleic anhydride, thus confirming the incorporation of poly(styrene-co-maleic anhydride) in polyesteramide.

The peaks of the ¹³C-NMR spectra of SCPEA have been shown in Figure 3. The peaks at δ = 59.376 ppm, δ = 47.0–40.0 ppm, and δ = 33.69 ppm are attributed to —CH₂ attached to free-hydroxyl, amide nitrogen,

TABLE III
Coating Properties of PEA and Modified PEA

Resins Code*	Stoving		Scratch hardness (Kg)	Impact Resistance (lbs/in.)/ passes	Gloss at 45°	Bending 1/8 in.	Corrosion resistance				
	Temp. (°C)	Time (min)					H ₂ O (10 days)	NaOH (5%) (3 h)	HCl (5%) (10 days)	NaCl (3.5%) (10 days)	Xylene (10 days)
PEA	200	10	2.0	100	50	Passes	e	a**	c	c	d
SCPEA5	190	15	1.5	200	60	Passes	e	e	c	c	d
SCPEA10	180	15	2.9	200	65	Passes	e	c	d	d	e
SCPEA15	160	15	3.3	200	70	Passes	e	d	e	e	e
SCPEA20	155	15	2.5	200	70	Passes	e	b	b	e	e
SCPEA25	150	15	1.9	200	72	Fails	e	a	b	e	e

* Last digit of resin indicates wt % of copolymer; a, film completely removed; b, film cracked and partially removed; c, loss in gloss and wt; d, slight loss in gloss; e, unaffected.

** After 1 h.

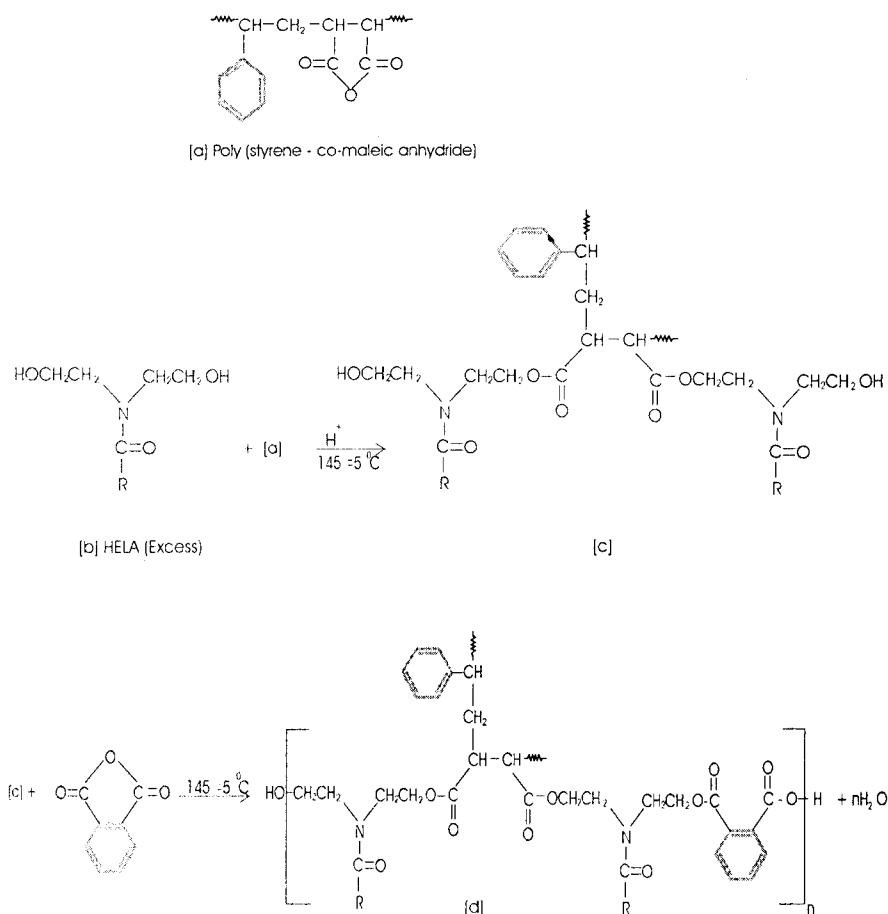


Figure 1 Synthesis of poly(styrene-*co*-maleic anhydride)-modified polyesteramide (SCPEA). *R* = alkyl chain of fatty acid of oil.

and amide carbonyl groups, whereas those between $\delta = 136\text{--}129$ ppm are attributed to aromatic ring carbons as in the case of plain PEA of oil.¹³ ¹³C-NMR peaks for quaternary carbon of styrene is observed at $\delta = 144.5$ ppm. Peaks for $-\text{CH}_2$ and $-\text{CH}$ of styrene and maleic anhydride copolymer ($\delta = 47\text{--}40$ ppm) overlapped with peaks of CH_2 attached to amide carbonyl.^{24,25} The peak at $\delta = 96.0$ ppm was assigned to the $-\text{CH}_2\text{O}-$ group of the ester obtained through the reaction of $-\text{CH}_2\text{OH}$ group of HELA with $-\text{COOH}$ group of poly(styrene-*co*-maleic anhydride). The reaction was also confirmed by the monitoring of $-\text{OH}$ and $-\text{COOH}$ groups, which were found to progressively decrease during the course of polymerization.

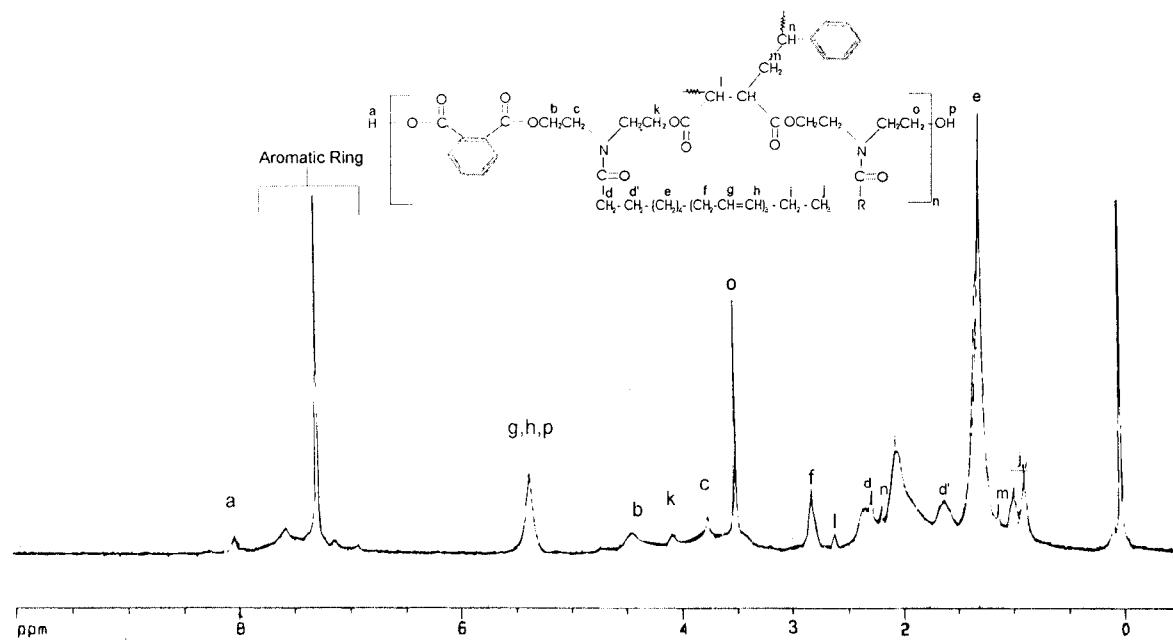
Physicochemical characterization

Table II provides information about the physicochemical characterization of PEA and SCPEA. It is observed that the hydroxyl value, saponification value, and iodine value decrease with an increase in the wt % loading of copolymer in PEA chain. The specific gravity, refractive index, and inherent viscosity increase at

the same time because of the increase in the molar mass of the resin with the increased loading of copolymer in it. A closer examination of Table II indicates a marked increase in the aforementioned characteristics, particularly beyond 15 wt % addition of copolymer, which may be due to a pronounced increase in the molar mass of the resin.

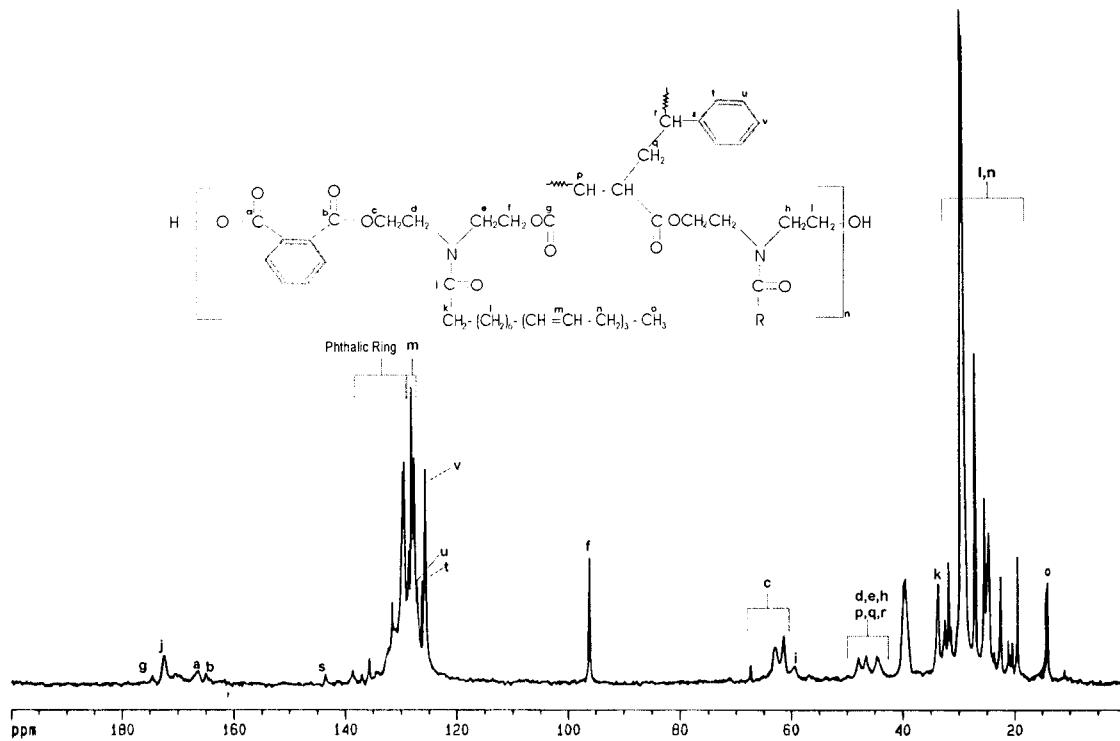
Coating properties

Table III incorporates various physicomechanical and chemical characteristics of SCPEA resin. It is observed that the increase in the loading of copolymer on PEA backbone leads to a decrease in baking temperature of the SCPEA coatings. This is due to the increase in the amount of maleic anhydride of copolymer in PEA. Increased loading of the copolymer in the resin increases the size of the polymer chain and also the number of crosslinks per unit chain, which cause the lowering of the temperature for baking. The coatings exhibit a high degree of gloss with higher copolymer loading; it is a typical characteristic of acrylic-based systems.²⁶ This effect can also be explained consider-

Figure 2 ^1H -NMR spectra of SCPEA.

ing that at higher loading of the copolymer the chain length is larger and there are a larger number of crosslinks resulting in a dense structure which would cause enhancement in gloss. The coatings of all the compositions passed an impact-resistance test, indicating that the coatings material has good adhesion to

the metal substrate due to the presence of anhydride groups. The coatings up to 20 wt % of copolymer loading in SCPEA passed the 1/8 in. conical mandrel bend test, which is a characteristic of oil-based coatings. Beyond this loading, the coatings failed the bend test, showing a disproportionate increase in aromatic

Figure 3 ^{13}C -NMR of SCPEA.

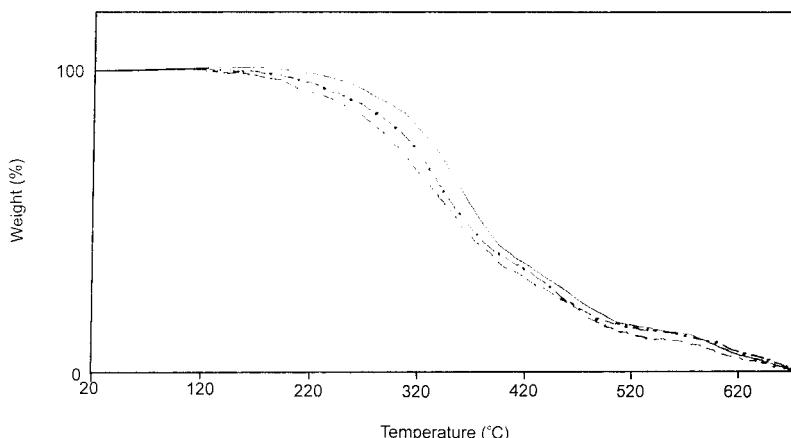


Figure 4 TGA of SCPEA-5 (---), SCPEA-15 (—), and SCPEA-25 (- - -).

moieties and the crosslink density, which hamper the free rotation of polymer chains. The lowering of scratch hardness beyond 15 wt % loading of copolymer can be attributed to high stiffness in the resin at such high loading.

The chemical resistance of SCPEA coatings are better than those of plain PEA (Table III). The coatings of SCPEA are unaffected under water and xylene environment. A considerable resistance to alkali (5 wt % NaOH, 3 h) is observed up to SCPEA-15 due to the optimum amount of styrene in the resin, whereas the plain PEA coatings get completely removed within 1 h.³ Among all compositions, with resin with 15 wt % copolymer loading, SCPEA-15 showed the highest resistance in acidic environment such that only a slight loss in gloss is observed on 10 days immersion in 5 wt % HCl solution. It is attributed to the presence of an optimum amount of ester linkage. Overall, above 15 wt % copolymer loading, a deterioration in coating properties, in particular, the acid and alkali resistance, is noticed. It is correlated to the strain developed in polymeric chain, which adversely affects both the physicomechanical and the anticorrosive behavior of the coatings, making it susceptible to attack by various corrodents. It is important to note that the loading of copolymer in the PEA resin beyond 30 wt % results in the formation of large polymeric chains, causing an excessive increase in viscosity, which makes the resin unbrushable.

Thermogravimetric analysis

The TGA thermograms (Fig. 4) show an initial sluggish degradation in the case of resin samples SCPEA-5 and SCPEA-15, whereas a comparatively faster rate of weight loss is observed in the resin sample SCPEA-25. The onset of degradation in both cases is noted at 181–183°C. This can be correlated to the evaporation of the trapped solvent. In the later stages, after 377°C,

the SCPEA-5 and SCPEA-15 samples show the same degradation pattern, whereas the SCPEA-25 exhibits a still higher decomposition rate. A 10 wt % loss is observed at 258, 285, and 235°C in SCPEA-5, SCPEA-15, and SCPEA-25 resin samples, respectively. The 50 wt % loss is observed at 363, 375, and 356.5°C in the above samples, respectively. The thermal studies thus confirm better thermal resistance of the resin samples SCPEA-15. The SCPEA-25 shows lower thermal stability due to the higher copolymer content in the resin. TGA thermograms (Fig. 4) thus indicate that the sample SCPEA-15, which shows higher physicomechanical and anticorrosive properties, can be safely used, up to 250°C.

CONCLUSION

The presence of bifunctional copolymer moiety in the resin markedly increases the scratch hardness, impact resistance, alkali resistance, and thermal stability of PEA. The fair decrease in stoving temperature is also observed. The above observations justify that modification of PEA through poly(styrene-co-maleic anhydride) leads to better coating properties as compared to those of plain PEA. Among the samples prepared, SCPEA-15 coatings showed the best performance and hence SCPEA-15 resin appears to be a good candidate for commercial application.

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