

# Development of Linseed Oil Based Polyesteramide without Organic Solvent at Lower Temperature

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Received 22 June 2005; accepted 22 October 2006

DOI 10.1002/app.25774

Published online in Wiley InterScience (www.interscience.wiley.com).

**ABSTRACT:** Linseed oil based polyesteramide was synthesized at lower temperature in the absence of organic solvent through condensation polymerization reaction [Sf-LPEA]. In this reaction *N,N*-bis(2-hydroxyethyl) linseed oil fatty amide and phthalic anhydride were heated at temperature lower than their onset of melting points and the by-product, such as water was removed by application of vacuum technique. This approach was employed to overcome the use of volatile organic solvents used during processing and application of resin, which are ecologically harmful. The solubility of Sf-LPEA was checked in different polar and nonpolar solvents. The FTIR,  $^1\text{H}$  NMR, and  $^{13}\text{C}$  NMR spectral techniques were used to confirm the structure of Sf-LPEA. The physicochemical, physicochemical, and chemi-

cal resistance properties of the resin were investigated by standard methods. DSC and TGA were used to determine, respectively, the curing behavior and thermal stability of the resin. The comparative study of these properties of Sf-LPEA with reported polyesteramide [LPEA], which are normally synthesized at higher temperature in organic solvent, was done. It was found that Sf-LPEA exhibited improved physicochemical, chemical resistance properties, and higher thermal stability compared with LPEA, and hence can find application as corrosion protective coating. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 104: 1143–1148, 2007

**Key words:** linseed oil; solvent free method; condensation polymerization; polyesteramide; properties

## INTRODUCTION

Vegetable oil has a number of excellent properties that could be utilized in producing a number of valuable polymeric materials.<sup>1–8</sup> The synthesis of different polymers from oil is economically, scientifically, and environmentally significant because of their environment friendly nature, low cost, abundance, and possible biodegradability.<sup>9–11</sup>

Linseed oil is one of the widely occurring vegetable oil and is sustainable in its nature. It may be employed as a sustainable resource to replace chemicals and their products obtained from petroleum feed stock and also to expand the existing range of chemicals and raw materials, which can lead to the development of novel products like polymers.<sup>7,10,12–14</sup> Number of low molecular weight polymers such as alkyd, polyurethane, epoxies, polyetheramide, and polyesteramide have been developed from linseed oil.<sup>7,12,14–20</sup> They have found applications in the field of paints and anticorrosive coatings.<sup>7,15–16,19</sup>

Seed oil based polyesteramide is an amide-modified alkyd that has superior characteristics over normal alkyds in terms of hardness, ease of drying, and

water vapor resistance.<sup>19</sup> The resin shows satisfactory chemical resistivity and durability but it lacks alkali resistance and possesses high melting point, high curing temperature, which causes difficulties in its application as a coating material.<sup>8,16</sup> The high temperature processibility impairs the structural integrity of the end product by the side reactions and involves higher energy and volatile organic solvents. These solvents are used in surface coatings during the synthesis and application of the resin but are ecologically harmful. For its easy application as eco-friendly coating material the foregoing undesirable characteristics of this type of resin need to be overcome.

In the present work we have attempted for the first time the synthesis of linseed oil based polyesteramide resin in the absence of organic solvent at low temperature [Sf-LPEA]. Literature survey reveals that as yet no work have been reported on this method for the synthesis of oil based polyesteramides.<sup>6,21,22</sup>

The structure of the Sf-LPEA resin was characterized by FTIR,  $^1\text{H}$  NMR, and  $^{13}\text{C}$  NMR spectral techniques. The thermal stability and curing behavior was investigated by TGA and DSC techniques. The physicochemical, physicochemical, and anticorrosive properties of Sf-LPEA resin have also been compared with those of reported linseed oil based polyesteramide; synthesized by solution method at higher temperature [LPEA]. The coating Sf-LPEA has shown improved physicochemical, chemical resistance, and thermal behavior than LPEA.

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**TABLE I**  
**Characterizations of Linseed Oil, LPEA, and Sf-LPEA**

Property	Linseed oil	HELA	LPEA	Sf-LPEA
Hydroxyl value (%)	0.3	–	7.87	5.5
Saponification value (mg KOH/g)	160	–	128	120
Iodine value (gm I <sub>2</sub> /100 g)	181	86	48	40
Specific gravity (g/mL)	0.896	0.926	0.938	0.942
Refractive index	1.478	1.497	1.507	1.509
Inherent viscosity (dL/dg)	–	–	0.652	0.669
Fatty acid composition (%)				
Linolenic acid (C 18 : 3)	54			
Linoleic acid (C 18 : 2)	14			
Oleic acid (C 18 : 1)	22			
Stearic acid (C 18 : 0)	4			
Palmitic acid (C 16 : 0)	5			
Palmitoleic acid (C 16 : 1)	Trace (<0.5)			
Arachidic acid (C 20 : 0)	Trace (<0.5)			

## EXPERIMENTAL

### Materials

Oil was extracted from linseed (obtained from local market) through soxhlet apparatus for 24 h. Petroleum ether (60–80%) was used as a solvent. The oil was dewaxed and stored in sealed clean glass bottle for experimental use. The fatty acid composition of oil was determined by gas liquid chromatography (GLC; 111/8 s.s. column, FID detector) (Table I). Sodium methoxide, xylene (Merck, New Delhi, India), diethanolamine, phthalic anhydride [PA] (s.d. Fine Chemicals, New Delhi, India) were of analytical grade.

### Synthesis of *N,N*-bis(2-hydroxyethyl) linseed oil fatty amide and their polyesteramide

*N,N*-bis(2-hydroxyethyl) linseed oil fatty amide (HELA) and their polyesteramide (LPEA) were prepared as per reported method.<sup>8</sup>

### Synthesis of Sf-LPEA

HELA (0.05 mol) was placed in a four-necked flat bottom flask equipped with condenser, nitrogen gas inlet and thermometer. The reaction content was heated up to  $80 \pm 5^\circ\text{C}$  with continuous stirring. At this temperature the fine powdered PA (0.05 mol) was added slowly over a period of 30 min along with continuous stirring and supplied N<sub>2</sub> for 15–20 min. After complete addition of PA, temperature was raised up to  $100 \pm 5^\circ\text{C}$ . TLC and acid value was used to monitor the progress of the reaction. The reaction was conducted under constant vacuum. The reaction was allowed to continue under the above conditions till the desired acid value was obtained. The reaction product was transferred and Sf-LPEA was obtained. In TLC test, finally, we have got a single spot of the product. It reveals that the HELA is completely converted into Sf-LPEA by the reaction with PA and no

unreacted reagents are left. So, further purification of the resin is not required. Further, the purity of the final product has also been confirmed by spectral analysis (FTIR, <sup>1</sup>H NMR, and <sup>13</sup>C NMR).

### Test methods

The chemical structure of Sf-LPEA was characterized by FTIR, <sup>1</sup>H NMR, <sup>13</sup>C NMR spectroscopic techniques whereas thermal stability and curing behavior was studied by TGA and DSC techniques. FTIR spectrum of the resin was taken on Perkin-Elmer 1750 FTIR spectrophotometer (Perkin-Elmer Instruments, Norwalk, CT), by using a NaCl cell. <sup>1</sup>H NMR and <sup>13</sup>C NMR spectra were recorded on JEOL GSX 300 MHz FX-1000 spectrometer, by using deuterated chloroform as solvents and tetramethylsilane as an internal standard. TGA (TA 2000, T A Instruments) was done at 20°C/min in Nitrogen atmosphere, while DSC (Dupont 910) was done at 10°C in N<sub>2</sub> atmosphere. The inherent viscosity of Sf-LPEA in toluene (0.5 g/100 mL) was determined by Ubbelohde viscometer at 25°C. The Iodine, hydroxyl, and saponification value, specific gravity and refractive index of Sf-LPEA was determined according to standard methods (Table I).

### Coatings preparations

Sf-LPEA coatings were cured in an oven at different temperature (150–250°C) and time (5–30 min) to get optimum curing temperature and time. The curing temperature and time are given in Table II. The coatings were prepared by brush technique, using solution containing 60% Sf-LPEA in xylene, applied on mild steel strips. The strips were polished on various grades of silicon carbide papers and then washed with water and degreased with alcohol and carbon-tetrachloride. They were dried under vacuum for several hours. The standard sized strips of 30 × 10

**TABLE II**  
Film Properties of LPEA and Sf-LPEA

Property	LPEA	Sf-LPEA
Physico-mechanical		
Curing temp (°C)	220	190
Curing time (min)	10	10
Scratch hardness (kg)	2.0	2.5
Impact resistance (lbs/inch) pass	100	150
Gloss at 45°	50	55
Bend test (1/8")	Passes	Passes
Chemical resistance		
H <sub>2</sub> O (7 days)	– <sup>a</sup>	– <sup>a</sup>
5% NaOH(1 h)	– <sup>b</sup>	– <sup>c</sup>
2% HCl (7 days)	– <sup>d</sup>	– <sup>a</sup>
3.5% NaCl (7 days)	– <sup>d</sup>	– <sup>a</sup>
Xylene (7 days)	– <sup>e</sup>	– <sup>a</sup>

The coating passes adhesion test with no visible damage.

<sup>a</sup> Unaffected.

<sup>b</sup> Film completely removed.

<sup>c</sup> Film cracked and partially removed.

<sup>d</sup> Loss in gloss.

<sup>e</sup> Slightly loss in gloss.

× 1 mm<sup>3</sup>, were taken for chemical resistance test in water, acid (5 wt % HCl), alkali (5 wt %), xylene solvents by placing them in 3 in. diameter porcelain dishes, and of 70 × 25 × 1 mm<sup>3</sup> size to evaluate their physicommechanical properties, such as scratch hardness (BS 3900), bending (ASTM D3281–84), impact resistance (IS: 101 part 5/Sec. 3, 1988), and specular gloss at 45° by gloss meter (model RSPT 20; Digital Instrument, Santa Barbara, CA). The thickness of coatings was found to be in between 75 and 100 μm as measured by Elcometer (Model 345; Elcometer Instrument, Manchester, UK). Salt spray test (ASTM B177–94) in 3.5-wt % NaCl solutions was also carried out for a period of 7 days in the salt mist chamber.

## RESULTS AND DISCUSSION

### Synthesis

Linseed oil based polyesteramide was synthesized by different methods shown in Scheme 1. Sf-LPEA was synthesized at lower temperature, 100 ± 5°C, from HELA and PA in the absence of solvent while LPEA synthesized at high temperature in xylene from HELA and phthalic acid. In the solvent free method selfcatalyzed direct esterification of carboxylic end group with hydroxyl end group takes place.<sup>23</sup> It is observed that the reaction occurred at a lower temperature than the melting points of both the monomers and polymers. This may be because of the fairly good fluidity of HELA, in which the finely powdered PA was dissolved. The synthesis condition provides better proximity of the reactants

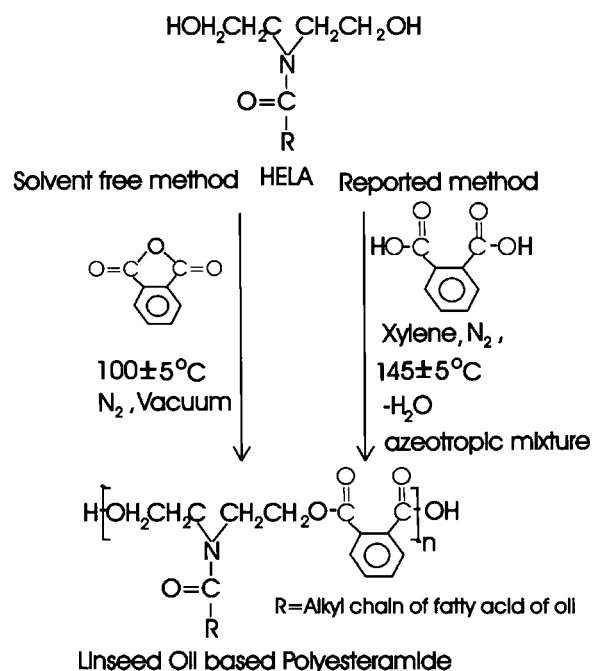
under solvent free environment, causing the reaction to occur at relatively lower temperature.

We have also synthesized Sf-LPEA at temperature above or nearer melting of polyesteramide. However, we found that the properties of these Sf-LPEA were deteriorated as compared with lower temperature synthesized Sf-LPEA. This may be attributed to the formation of oligomers, cyclization, thermal degradation, and gel formation, which reportedly impairs the structural integrity of the end product.<sup>23</sup>

The PA is used for synthesis of Sf-LPEA in solvent free method because of its low cost, lower melting temperature (131°C), and higher reactivity than phthalic acid.<sup>24</sup> It is reported that PA based resins show good solubility and compatibility as well as good film properties.<sup>24,25</sup>

### Spectral analysis

FTIR spectra of Sf-LPEA resin indicated the presence of characteristic bands of oil-based polyesteramide<sup>8</sup> shown in Figure 1. The stretching absorption bands are observed at 1728 cm<sup>-1</sup> for >C=O ester, 1646 cm<sup>-1</sup> for >C=O amide, three bands at 1275, 1167, 1139 cm<sup>-1</sup> for –C–C(=O)–O– whereas bands at 2855 and 2927 cm<sup>-1</sup> are observed for CH<sub>2</sub> asymmetric and symmetric modes. A broad band is observed at 3448 cm<sup>-1</sup> because of the free hydroxyl group, while band observed at 1070 cm<sup>-1</sup> is because of the C–O stretching of primary alcohol. Absorption bands at 3010 and 3080 cm<sup>-1</sup> are weak bands correspond to =C–H stretching of aliphatic and



**Scheme 1** Syntheses of linseed polyesteramide by solvent free (Sf-LPEA) and reported method (LPEA).

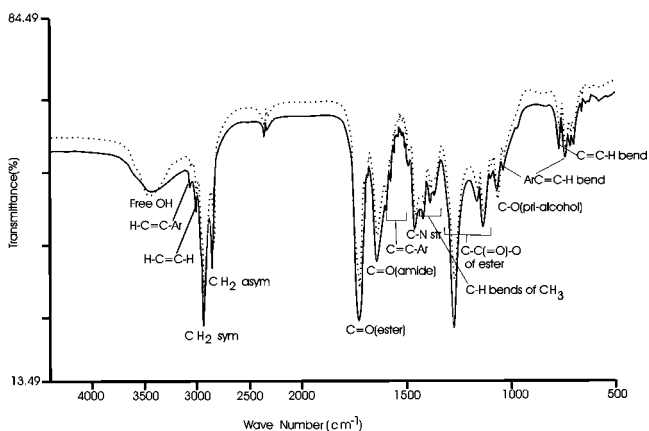


Figure 1 FTIR spectra of LPEA (···) and Sf-LPEA (—).

aromatic groups, respectively. Bands observed at 1605, 1595, and 1566  $\text{cm}^{-1}$  are because of the stretching of C=C phthalic ring while bands at 1050 and 750  $\text{cm}^{-1}$  are corresponding to C—H bending (in plane and out of plane) of phthalic ring. A weak band of C—H bending of aliphatic unsaturation is observed at 778  $\text{cm}^{-1}$  as well as weak bands observed at 1450 and 1378  $\text{cm}^{-1}$  are because of the C—H bending of  $\text{CH}_3$  asymmetric and  $\text{CH}_3$  symmetric vibrations.

The peaks in  $^1\text{H}$  NMR and  $^{13}\text{C}$  NMR spectra have been assigned to different groups in Figures 2 and 3.  $^1\text{H}$  NMR shows the peaks of  $\text{CH}_2$  attached to amide carbonyl ( $>\text{N}(\text{C}=\text{O})\text{—CH}_2$ ) at  $\delta = 2.35$  ppm, ester carbonyl ( $\text{CH}_2\text{—OC}=\text{O}$ ) at  $\delta = 4.4$  ppm, and amide nitrogen ( $(\text{—H}_2\text{C})_2 \text{N—C}=\text{O}$ ) at  $\delta = 3.71$  ppm. Likewise  $^{13}\text{C}$  NMR shows the peaks of  $\text{CH}_2$  attached to amide carbonyl ( $>\text{N}(\text{C}=\text{O})\text{—CH}_2\text{—}$ ) at  $\delta = 33.5$  ppm, ester carbonyl ( $\text{—CH}_2\text{—OC}=\text{O}$ ) at  $\delta = 61\text{--}64$  ppm, and amide nitrogen ( $(\text{—H}_2\text{C})_2 \text{N—C}=\text{O}$ ) at  $\delta = 44\text{--}48$  ppm. Peaks are observed at  $\delta = 173$  ppm,  $\delta = 171$  ppm, and  $\delta = 167$  ppm corresponding, respectively, to carbonyl groups of amide ( $>\text{N—C}=\text{O}$ ), free acid ( $\text{—COOH}$ ) and ester ( $\text{—OC}=\text{O}$ ). These observations confirmed the structure of the Sf-LPEA.

### Physico-chemical analysis

The physico-chemical properties of Sf-LPEA such as the hydroxyl, iodine, and saponification values are found lower whereas specific gravity, refractive index, and inherent viscosity higher than that of LPEA (Table I). These trends can be correlated to higher molar mass of the Sf-LPEA resin than the LPEA resin.

The solubility of the resin was observed in dimethylsulfoxide, dimethylformamide (DMF), ethanol, methanol, ethylmethylketone, carbontetrachloride, chloroform, ether, acetone, toluene, and xylene. Sf-LPEA resin has same solubility trends as those of LPEA resin,<sup>19</sup> that is, 80–100% solubility in xylene, toluene, chloroform, carbontetrachloride, ether, acetone, and DMF while 20–40% solubility in the rest of the solvents.

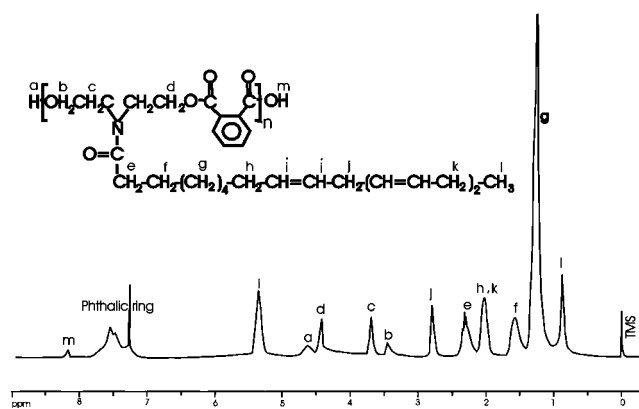


Figure 2  $^1\text{H}$  NMR spectra of Sf-LPEA.

### Coating properties

Physico-mechanical and chemical resistance properties of Sf-LPEA and LPEA are summarized in Table II. It is observed that optimum curing temperatures for Sf-LPEA and LPEA are 1900 and 220°C, respectively. The lowering of curing temperature of Sf-LPEA can be attributed to the formation of higher crosslinking at lower temperature because of high molar mass.

It is observed that curing of polyesteramide resin involves evaporation of solvent followed by chemical reactions between functional groups. Evaporation of solvent occurring at room/low temperature results into chain entanglement. Further heating causes polyesterification of polyesteramide through the reaction of free acid and hydroxyl groups at  $100 \pm 5^\circ\text{C}$ , as well as thermal polymerization of unsaturated fatty acid chains at still higher temperature ( $\approx 170^\circ\text{C}$ ). These chemical reactions produce hard film through the formation of high molecular weight three-dimensional network.<sup>8,26</sup>

Sf-LPEA film has higher scratch hardness (2.5 kg) and impact resistance (150 lb/in.) properties than LPEA film. The scratch hardness and IS of the film generally depends upon number of crosslinks and

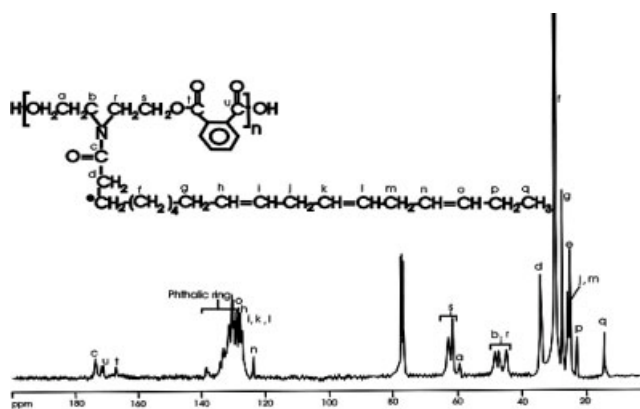


Figure 3  $^{13}\text{C}$  NMR spectra of Sf-LPEA.

**TABLE III**  
**Thermal Stability of LPEA and Sf-LPEA**

Polymer	$T_5$ (°C)	$T_{20}$ (°C)	$T_{50}$ (°C)	$T_{80}$ (°C)
LPEA	255	315	370	470
Sf-LPEA	285	350	415	500

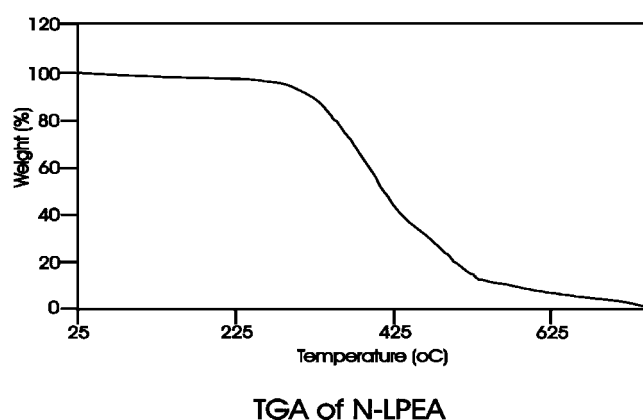
The  $T_5$ ,  $T_{20}$ ,  $T_{50}$ , and  $T_{80}$  are temperature at 5 wt %, 20 wt %, 50 wt %, and 80 wt % decomposition respectively.

presence of hard moieties in the resin. The higher value of scratch hardness of Sf-LPEA resin can be attributed to the formation of a highly crosslinked network. LPEA and Sf-LPEA films were show good adhesion strength (100%) as per crosshatch tape test and good flexibility passing 1/8 in. conical mandrel test. Adhesion of film may be due to the higher valence forces and interlocking action of polar groups of the resin on the metal surface. Oil based coatings are well known for good flexibility.<sup>27</sup> The gloss values at 45° for Sf-LPEA and LPEA are comparable being, respectively, 55 and 50. This property generally depends upon uniformity and denseness of the film.

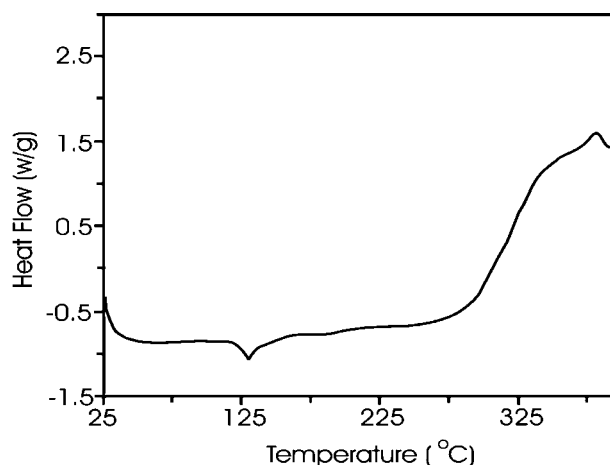
The chemical resistance performance of Sf-LPEA coating has been found to be better than LPEA coating (Table II). Sf-LPEA coating was unaffected after immersion for 7 days in HCl (2%), NaCl (3.5%), and xylene whereas LPEA coating showed loss in gloss in HCl (2%) and NaCl (3.5%). However slight loss in gloss was observed in xylene. Alkali resistance of Sf-LPEA observed in 5% NaOH, was not much improved. Sf-LPEA film cracked and was partially removed while LPEA film was completely removed in after 1 h. Improved chemical properties of Sf-LPEA may be attributed to the factors, such as higher molar mass and high crosslinked density.

### Thermal analysis

TGA data thermogram of LPEA and Sf-LPEA are reported in Table III and Sf-LPEA is shown in Figure 4. It is observed that Sf-LPEA has higher thermal sta-



**Figure 4** TGA thermogram of Sf-LPEA.



**Figure 5** DSC thermogram of Sf-LPEA.

bility, which can be attributed to the higher crosslink density and higher molar mass of Sf-LPEA resin than that of LPEA. Figure 4 shows two decomposition events, respectively, in the temperature range 290–450°C and 450–550°C. The first event involves the weight loss around 65%, which is equivalent to the aliphatic diol portion (HELA) in the polyesteramide. The second event shows much lower weight loss than the first decomposition event. The first decomposition event, therefore, involves a main chain scission through the ester linkages between the HELA and PA moieties, whereas the second event corresponds to the decomposition of hydrocarbons of the resin.

The DSC thermogram of Sf-LPEA (Fig. 5) shows an endothermic peak in the temperature range 115–150°C centered at 135°C. The TGA thermogram does not show any noticeable change in this temperature range. This peak can, therefore be attributed to the melting of the resin. The melting temperature of Sf-LPEA is lower than that of LPEA (150°C).<sup>19</sup> This can be correlated to the increase in the pendant fatty acid chain in the resin. The fatty acids chains are known to impart flexibility to the polymer. The curing temperature of Sf-LPEA is found between 150 and 285°C, beyond this temperature decomposition starts. This matches with the TGA (Fig. 4). Hence Sf-LPEA coating can be used safely up to 285°C.

### CONCLUSIONS

The synthesis of linseed oil based polyesteramide in a solvent free medium at lower temperature provides a route for the same in absence of toxic organic solvents. It also yields a resin with improved physico-mechanical and chemical resistance properties along with thermal stability as compared with other commercially synthesized vegetable oil based polyesteramides.

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