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# SELF-CURED POLYMERS FROM NON-DRYING OIL

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**Abstract.** *Pongamia glabra* seed oil (PGSO) – a non-edible, non-drying oil; a sustainable resource has found application as alkyds, epoxies and polyesteramides in paints and coatings. Generally, PGSO based polymeric coatings are obtained by curing at elevated temperature. Efforts have been made to cure PGSO at room temperature by simple route modification.

Self-cured *Pongamia glabr*a oil based polyesteramide (APGPEA) resin was synthesized by the reaction between *Pongamia glabra* oil modified fatty amide diol (HEPGA) with poly(styrene-*co*-maleic anhydride) (SMA). After complete synthesis of APGPEA, phthalic anhydride modified polyesteramide (APGPEAPh) was synthesized *in situ* by a minor addition of phthalic anhydride (PA) to APGPEA in order to improve the performance of the latter. The effect of the SMA and PA introduction on properties of PGPEAPh film was also investigated. The physico-chemical characteristics of both resins were obtained by standard laboratory methods. The structural elucidation of these resins was carried out by FT-IR, ^{1}H-NMR and ^{13}C-NMR spectral techniques. The thermal behavior was studied by TGA. Curing was studied by DSC and FT-IR techniques. It was observed that APGPEA and APGPEAPh resins significantly improve the drying property in contrast to the previously reported polyesteramides cured at high temperature. Physico-mechanical and chemical/corrosion resistance tests of APGPEAPh coatings showed that the presence of phthalic anhydride in APGPEA enhanced the physico-mechanical and corrosion resistance considerably. The APGPEAPh resin appears to be a sustainable aspirant biomaterial for anticorrosive surface coatings which may substitute polymers obtained from petroleum, potentially scarce resource.

**Keywords:** *Pongamia glabra* oil, polyesteramide, mechanical and thermal properties, coating, corrosion.

## 1. Introduction

Development of polymers from sustainable resources has attracted the attention of researchers, who have focused on the use of readily available, inexpensive, biodegradable and seasonally renewable raw materials that can reduce dependence on petroleum and its negative impact on environment [1]. Bio-based materials such as carbohydrates, starch, proteins, vegetable oils, animal oils and fats are currently being investigated as the alternative resources of petro-based materials [2]. Vegetable oils and fatty acids are abundantly available resources. Their use as starting materials has numerous advantages including low toxicity, inherent biodegradability and high purity [2, 3]. Extensive work has been done to develop the bio-based polymers using these raw materials as the main components [1, 2, 4, 5]. Vegetable oil is a triglyceride with numerous active sites that help in the conversion of oils into useful polymeric materials. Specific oils has specific physical and chemical properties depending upon their fatty acid composition [5-7]. It is observed that the degree of unsaturation influences the oil physico-chemical and mechanical properties [5, 8, 9]. Depending on the iodine values (IV, $I_2$ mg/100 g sample) and drying index (DI = % linoleic acid + 2 X % linolenic acid), oils are divided into three groups: drying (IV > 130 and DI > 70), semi-drying (IV between 90 and 70, and DI between 65 and 70) and non-drying(IV < 90 and DI < 65) oils [5, 10, 11]. Generally, drying and semi-drying oils are used for the preparation of paints and coatings, since they contain sufficient reactive unsaturated fatty acids for curing with atmospheric oxidation [7, 8, 12-15]. Works reported on non-drying oil based paint and coating applications are very rare [8, 9, 15-17].

*Pongamia glabra* (common name *Karanj* of *Leguminaceae* family; IV 87; DI 14.5) oil is a non-drying oil (Fig. 1). Only a small percentage (7 %) of its total production has found application as soaps, leather tanning, lubricants, medicines and crosslinkers. Although it has a good potential for the synthesis of low molecular weight epoxies, polyurethanes and polyesteramides, which have a scope as antibacterial and anticorrosive coating materials [8, 9, 15-19]. India produces oil rich *Pongamia glabra* seeds (30–40 % oil content) twice a year, annual yield of seeds is being over 150000 and that of oil is being 50000 tons. Out of this only one forth is presently being utilized [20-22].
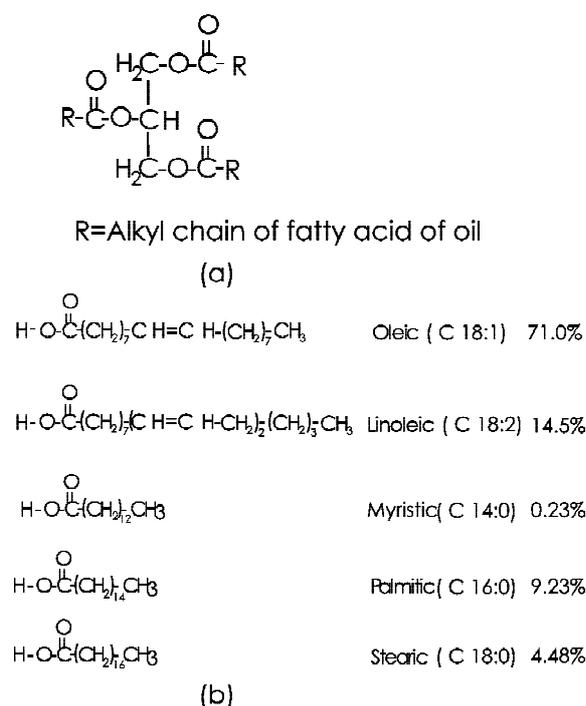
**Fig. 1.** Structure of oil (a) and different fatty acids (b) observed in *Pongamia glabra* seed oil

Earlier PGSO was utilized in the synthesis of high temperature cured *Pongamia glabra* oil polyesteramide (PGPEA), vinylated PGPEA (VPGPEA) and alumina incorporated PGPEA (Al-PGPEA) [10, 16-18]. Synthesis of this polyesteramide required higher temperatures (418–433 K) and products were used as baked coating materials [16, 18, 23]. The VPGPEA and Al-PGPEA exhibit a lower baked curing temperature and better physico-mechanical properties. However, the high temperature curing involved higher energy consumption as well as a multi-stage process [17, 23].

To overcome the high temperature curing, we attempted the synthesis and characterization of room temperature self-cured *Pongamia glabra* oil based polyesteramides (APGPEA and APGPEAPh). APGPEA was synthesized *via* the reaction of *Pongamia glabra* oil modified fatty amide diol (HEPGA) with poly(styrene-*co*-maleic anhydride) (SMA) copolymer [22], while APGPEAPh was synthesized by minor inclusion of phthalic anhydride (PA) in the APGPEA. Latter resin was synthesized to investigate the effect of PA on film properties of APGPEA, since PA based resins show good solubility and good film forming property [23]. The structure of the newly developed room temperature cured polyesteramides (APGPEA and APGPEAPh) was

confirmed by FT-IR, $^1$H-NMR and $^{13}$C-NMR spectral analysis. The thermal stability was studied using TGA and DSC techniques. The physico-chemical, mechanical and chemical/corrosion resistance studies were analyzed by standard laboratory methods. The above mentioned properties of APGPEA and APGPEAPh coatings were compared with each other and with those of baked virgin PGPEA coatings, as well as ambient cured linseed oil based polyesteramide (ALPEA) [17, 23, 24]. The APGPEA coatings show better performance than the reported baked virgin PGPEA coatings, comparing with ALPEA. The APGPEAPh resin has been found to show better performance than APGPEA.

## 2. Experimental

### 2.1. Materials

Oil was extracted from *Pongamia glabra* seeds (PGO) (procured from local market, New Delhi, India) through a Soxhlet apparatus, using petroleum ether (boiling range 333–353 K) as a solvent. The compositions of different fatty acids forming the oil were determined by GC (111/8 s.s. column. FID detector, Fig. 1) [17]. Sodium methoxide and xylene (Merck, India), diethanolamine and phthalic anhydride (S.D Fine Chemicals, India) were of analytical grade along with the SMA copolymer an Aldrich product with an average molecular weight of 1600 Da.

### 2.2. Synthesis of HEPGA and PGPEA

HEPGA and PGPEA were prepared by reported methods [16].

### 2.3. Synthesis of APGPEA and APGPEAPh

APGPEA was synthesized by reaction between HEPGA and SMA copolymer in molar ratio 1:0.084. HEPGA was loaded in a four necked conical flask equipped with Dean-Stark trap, nitrogen inlet tube, thermometer and mechanical stirrer, then heated at 373±378 K under continuous stirring in nitrogen atmosphere. SMA copolymer was added in the presence of acid catalyst over a period of 30 min. After the complete addition of SMA copolymer, the temperature was raised to 413±418 K and 10 % v/w xylene was further added which formed an azeotropic solvent. Acid value and thin layer chromatography (TLC) were used to monitor the progress of the reaction. The reaction was carried out till the product has the desired acid value. The reaction was stopped at this point, the products were cooled and xylene was removed from the resin in a rotary vacuum evaporator under reduced pressure to obtain highly viscous APGPEA resins. Their characteristics are following:

FT-IR (cm$^{-1}$): 3400 (broad, –OH), 3050 ($v$, ArC=C–H), 3008 ($v$, C=C–H), 2926 ($v$, –CH$_2$ asym), 2853.9 ($v$, –

CH$_2$ sym), 1735 ($v$, > C=O ester), 1592, 1512, 750, 702 ($v$ and bending, Ar–C=C), 1635 (> C=O, amide), 1454 ($v$, C–N), 1250 ($v$, C–C(=O)–O–C).

$^1$H-NMR (CDCl$_3$, ppm): $d$ = 7.33–7.15 (styrene ring proton), 5.3 (C$\underline{H}$=C$\underline{H}$), 4.21 {C$\underline{H}_2$ –O–C(=O)–}, 3.855 (C$\underline{H}_2$–N), 3.49 (C$\underline{H}_2$–OH), 2.7–2.6 (–C$\underline{H}$ of maleic anhydride), 2.30–2.26 {C$\underline{H}_2$–C(=O)–N–}, 2.26–2.24 (–C$\underline{H}$ of styrene), 2.1 (C$\underline{H}_2$–CH=CH), 1.25–1.35 (fatty acid chain C$\underline{H}_2$), 1.12 (–C$\underline{H}_2$ of styrene), 0.88 (–C$\underline{H}_3$).

$^{13}$C-NMR (CDCl$_3$, ppm): $d$ = 144.5 (quaternary carbon of styrene), 130–127.7(–$\underline{C}$=$\underline{C}$–; olefinic carbon), 127.6, 126.66 and 125.8 (other styrene ring carbon), 96 {$\underline{C}H_2$–O–C(=O)–}, 59.376 ($\underline{C}H_2$–OH), 47–40 ($\underline{C}H_2$–N as well as $\underline{C}H_2$ and $\underline{C}H$ of SMA), 33.69 {$\underline{C}H_2$–C(=O)–N–}, 29 ($\underline{C}H_2$ fatty acid chain), 24.8 [$\underline{C}H_2$CH$_2$C(=O)–N], 27.2 ($\underline{C}H_2$–C=C–).

After complete addition of SMA copolymer and at desired acid value the reaction temperature was allowed to come down to about 373±378 K. PA (0.135, 0.3276 and 0.504 moles) was then added during 15 minutes. The temperature was then raised to 423±418 K for the post-polymerization. The progress of the reaction was again monitored by TLC and acid value. At desired acid value the reaction product was allowed to cool down. Xylene was then removed as described previously to obtain APGPEAPh-6, APGPEAPh-12, and APGPEAPh-18 resins designated respectively for 0.135 moles, 0.3276 moles and 0.504 moles addition of PA.

FT-IR (cm$^{-1}$): 3400 (broad, –OH), 3050 ($v$, ArC=C–H), 3008 ($v$, C=C–H), 2926 ($v$, –CH$_2$ asym), 2853.9 ($v$, –CH$_2$ sym), 1730 ($v$, > C=O ester), 1592, 1512, 750, 702 ($v$ and bending, Ar–C=C), 1635 (> C=O, amide), 1454 ($v$, C–N), 1250 ($v$, C–C(=O)–O–C).

$^1$H-NMR (CDCl$_3$, ppm): $d$ = 7.33–7.15 (styrene ring proton), 7.15–6.9 (phthalic ring proton), 4.48 {C$\underline{H}_2$–OC(=O)–Ar}, 4.21 {C$\underline{H}_2$–O–C(=O)–}, 3.855 (C$\underline{H}_2$–N), 3.49 (C$\underline{H}_2$–OH), 2.7–2.6 (–C$\underline{H}$ of maleic anhydride), 2.30–2.26 {C$\underline{H}_2$–C(=O)–N–}, 2.26–2.24 (–C$\underline{H}$ of styrene), 1.12 (–C$\underline{H}_2$ of styrene).

$^{13}$C-NMR (CDCl$_3$, ppm): $d$ = 144.5 (quaternary carbon of styrene), 131.8 (quaternary carbon of phthalic ring), 133.7, 132.7, 130.1 and 129.7 (other phthalic ring

carbon), 130–127.7(–$\underline{C}$=$\underline{C}$–; olefinic carbon), 127.6, 126.66 and 125.8 (other styrene ring carbon), 96 {$\underline{C}H_2$–O–C(=O)–}, 59.376 ($\underline{C}H_2$–OH), 47–40 ($\underline{C}H_2$–N as well as $\underline{C}H_2$ and $\underline{C}H$ of SMA), 33.69 {$\underline{C}H_2$–C(=O)–N–}, 32–30 ($\underline{C}H_2$ fatty acid chain).

## 2.4. Test Methods

FT-IR, $^1$H-NMR, and $^{13}$C-NMR were used for the characterization of chemical structures. FT-IR spectra of synthesized resins were taken on Perkin-Elmer 1750 FT-IR spectrophotometer (Perkin Elmer Instruments, Norwalk, CT) using a NaCl cell. $^1$H-NMR and $^{13}$C-NMR spectra were recorded on JEOL GSX 300MHz FX-1000 spectrometer using deuterated chloroform as a solvent, and tetramethylsilane (TMS) as an internal standard. The thermo gravimetric analysis (TGA) was done with the help of thermo gravimetric analyzer TA-51 (T.A. Instruments U.S.A.) at 293 K/min in nitrogen atmosphere. Differential scanning calorimetric (DSC) analysis was done by Dupont 910 model at 283 K/min in nitrogen atmosphere. Solubility of these resins were tested in various polar and non-polar solvents by taking 25 mg of each resin in 5 ml of different solvents in a closed test tube and set aside for a day. Iodine value, hydroxyl value, saponification value, inherent viscosity, specific gravity and refractive index were determined by standard laboratory methods (Table 1).

## 2.5. Preparation of Coatings

The coatings were prepared by brush technique using solution containing 60 % resin in xylene and applied on mild steel strips. The strips were polished on various grade 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 strips of 30×10×1 mm size were placed in 3 inch diameter porcelain dishes for chemical resistance test in water, acid (5 wt % HCl), alkali (5 wt %) and xylene solvent. The strips of 70×25×1 mm size were taken to evaluate coating physico-mechanical properties, such as scratch hardness (BS 3900), bending (ASTM D3281–84), impact resistance

*Table 1*

**Physico-chemical characteristics of PGPEA, APGPEA and APGPEAPh**

| Resin code | Hydroxyl value, % | Saponification value, mg KOH/g | Iodine value, g I$_2$/100 g | Specific gravity, g/ml | Refractive index | Inherent viscosity, dl/g |
|---|---|---|---|---|---|---|
| PGPEA | 5.08 | 106.00 | 28.00 | 1.0120 | 1.524 | 0.714 |
| APGPEA | 2.00 | 60.00 | 16.54 | 1.0492 | 1.598 | 0.792 |
| APGPEAPh-6 | 0.77 | 60.14 | 10.52 | 1.0520 | 1.609 | 0.806 |
| APGPEAPh-12 | 1.08 | 60.18 | 12.82 | 1.0499 | 1.606 | 0.801 |
| APGPEAPh-18 | 1.50 | 60.20 | 15.44 | 1.0494 | 1.604 | 0.796 |

*Table 2*

**Physico-mechanical and corrosion/chemical resistance properties of PGPEA, APGPEA and APGPEAPh coatings**

| Resin code | Drying time, min | Scratch hardness, Kg | Impact resistance passes, lb/in | Gloss at 45c | Bending 1/8 inch | Chemical resistance | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | | $H_2O$ 10 days | NaOH (5 %) 2 h | HCl (2 %) 10 days | NaCl (3.5 %) 10 days | Xylene 10 days |
| PGPEA[1] | 6[2] | 3.5 | 100 | 90[3] | passes | e | a[4] | d[5] | d[6] | d |
| APGPEA | 30 | 3.0 | 150 | 66 | passes | b | f | e | c | f |
| APGPEAPh-6 | 15 | 3.2 | 150 | 70 | passes | f | c | f | f | f |
| APGPEAPh-12 | 16 | 3.3 | 150 | 69 | passes | f | a | c | d | f |
| APGPEAPh-18 | 20 | 3.5 | 150 | 68 | passes | d | a | c | d | f |

Notes: a – film was completely removed; b – loss in gloss; c – slight loss in gloss and adhesion; d – slight loss in gloss; e – colour change; f – unaffected and slight loss in adhesion.

[1] – baked at 483 K for 20 min; [2] – after 6 days; [3] – at 60°; [4] – after 1 h; [5] – after 48 h and [6] – after 2 h.
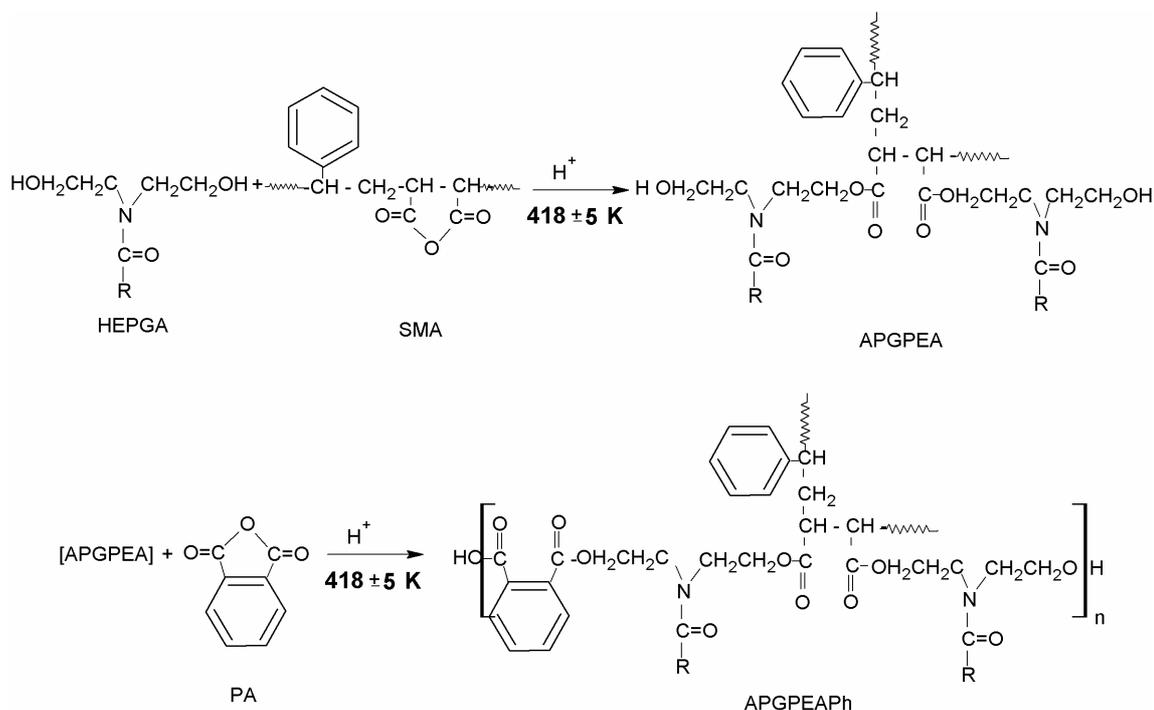


**Scheme 1.** Synthesis of self-cured *Pongamia glabra* oil based polyesteramide, R = alkyl chain

(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 the coating was between 75–100 μm as measured by Elcometer (Model 345; Elcometer Instrument, Manchester, UK). Salt spray test (ASTM B177-94) in 3.5 wt % NaCl solution was also carried out for a period of 10 days in a salt mist chamber. Coatings were self-cured/dried at room temperature; curing/drying time is given in Table 2.

## 3. Results and Discussion

### 3.1. Synthesis

Flow charts of the synthesis of APGPEA and APGPEAPh are given in Scheme 1 and their probable reaction mechanisms are shown in Scheme 2. It is clear from Scheme 1 that APGPEA was obtained simply by the reaction between HEPGA and SMA in the presence of
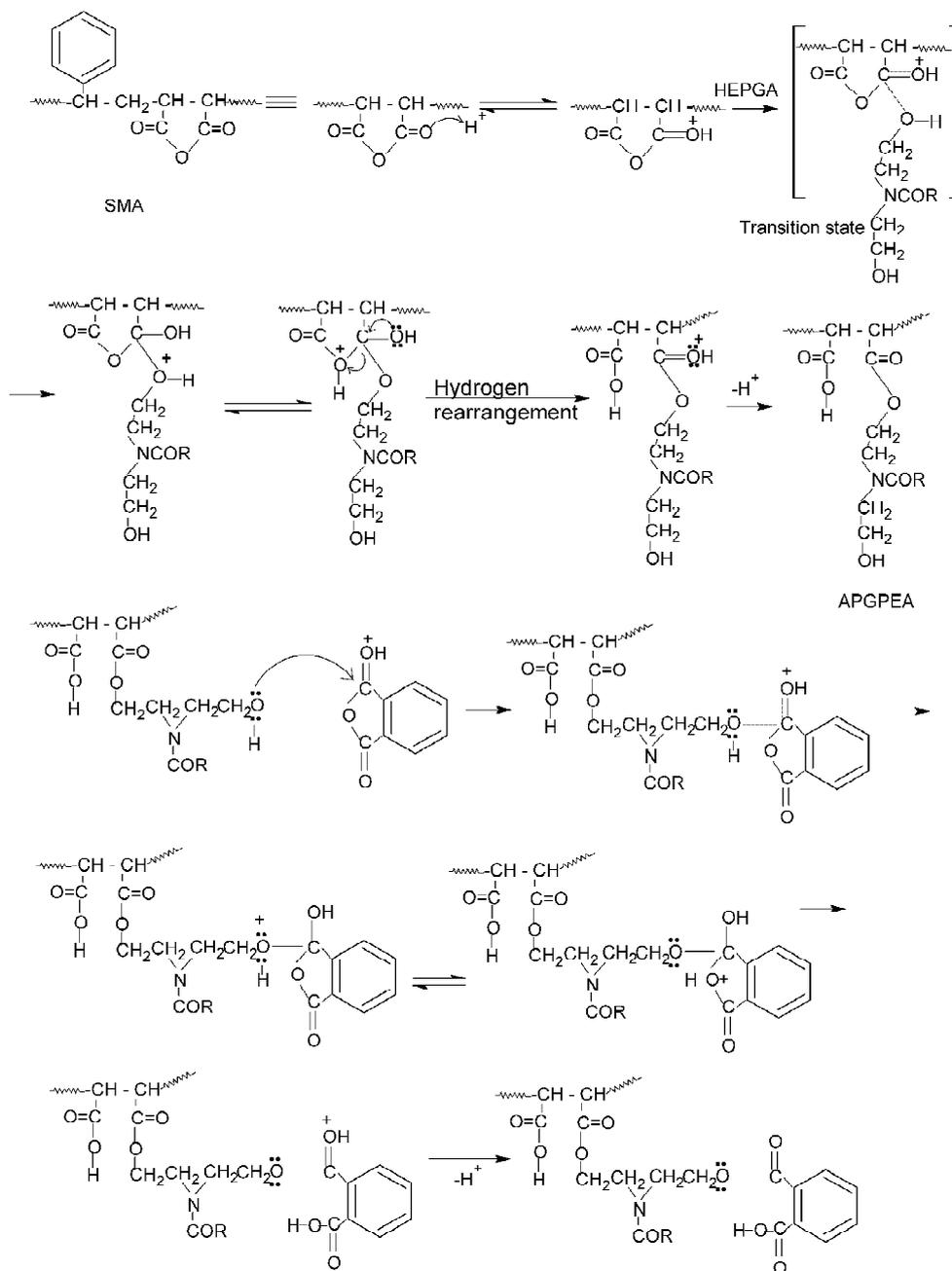
**Scheme 2.** Reaction mechanisms involved acid-catalyzed nucleophilic acyl substitution (addition and elimination)

acid as a catalyst, while APGPEAPh was synthesized *in situ* by addition of PA into APGPEA in the presence of an acid. The mechanism (Scheme 2) involved in these reactions is acid catalyzed nucleophilic acyl substitution. The presence of acid in this reaction facilitates the substitution of nucleophile at a carbonyl carbon of an acid group [25].

For APGPEA synthesis the optimum mole ratio of HEPGA and SMA copolymer was investigated [24]. The resin showed higher yield when the PEPGA to SMA ratio

was higher. Therefore the reaction was carried out at HEPGA to SMA copolymer ratio 1:0.084.

## 3.2. Solubility

The test for solubility behavior of APGPEA and APGPEAPh resins has been carried out with various solvents, *viz.* xylene, toluene, chloroform, carbon tetrachloride, diethyl ether, petroleum ether, acetone, ethanol, methanol, dimethylsulfoxide (DMSO),

dimethylformamide (DMF). The resins showed 80–100 % solubility in xylene, toluene, chloroform, carbon tetrachloride, ether, acetone, DMSO and DMF. However, only 20–40 % solubility was found for the rest of the solvents. The solubility behavior of resin can be correlated to the presence of long fatty acid hydrocarbon chains.

## 3.3. Spectral Analysis

In IR spectral analysis, the appearance of characteristic bands of amide and ester moieties confirmed the presence of ester and amide linkages in the same polymeric chain [23, 24, 26]. Shifting of 20.5 cm$^{-1}$ (C–C(=O)–O str.), 5.7 cm$^{-1}$ (C–N str.), 20 cm$^{-1}$ (–OH; broad) and 30 cm$^{-1}$ (ArC=C–H str) was observed in the formation of APGPEAPh from those of APGPEA. In $^1$H–NMR and $^{13}$C–NMR spectra the appearance of characteristic bands of amide and ester also confirmed the esterification reaction between HEPGA and SMA copolymer resulting in the formation of APGPEA, as well as the reaction of latter one with PA to form APGPEAPh. A sharp peak with high intensity appeared at $d = 96$ ppm for –CH$_2$ attached to –OC=O of maleic anhydride group of the copolymer [22-24]. The additional peaks in aromatic region, the peak associated to CH$_2$ attached to –OCOAr in $^1$H–NMR and $^{13}$C–NMR spectra, also a new peak of C=O of ester group in $^{13}$C–NMR spectra were also observed in APGPEAPh, which confirmed the incorporation of PA in APGPEA [23].

## 3.4. Physico-Chemical Characterization

Physico-chemical characterization data of APGPEA and APGPEAPh resins summarized in Table 1 indicate the decrease in hydroxyl value, saponification value and iodine value as well as the increase in specific gravity, refractive index and inherent viscosity from APGPEA to APGPEAPh. The opposite trend of aforementioned values is also observed from APGPEAPh-6 to APGPEAPh-18. The above mentioned behavior confirms the reaction between HEPGA and SMA as well as the reaction between APGPEA and PA.

## 3.5. Self-Curing/Drying of Films

The PGPEA coating cured in 6 days at room temperature and in 20 min when baked at 493 K/20 min. The coating of APGPEA and APGPEAPh resins were found to be self-cured/dried at room temperature within 30–15 min. It is observed that the fast curing/drying of the film of these resins (APGPEA and APGPEAPh) is due to the presence of SMA. Both styrene and maleic anhydride are known to facilitate self-curing/drying of the resin at room temperature [23, 24]. The curing/drying time increases after addition of 6–18 % PA. APGPEA-6 and APGPEA-12 have lower curing/drying time in comparison with APGPEA-18 correlated to higher SMA copolymer content.

As a result, they have a higher molar mass. The higher molar mass of APGPEAPh-6 compared to APGPEA is attributed to the presence of phthalic anhydride. The higher copolymer content as well as the presence of phthalic anhydride provides a reasonably longer chain length and a higher crosslink density for the resins through condensation polymerization. The resin becomes denser and more compact conferring rapid self-curing tendency to the resin. The curing/drying time for APGPEAPh-18 and APGPEA was found to be the same while those for APGPEAPh-12 and APGPEAPh-6 were lower (Table 2). This fact confirms that the amount of copolymer directly influences the curing/drying properties of the resins. The presence of copolymer as well as phthalic anhydride causes entanglement of the chains through the condensation polymerization. Further this increases the efficiency of film formation and reduces the drying time. The coating specimens were refluxed in CHCl$_3$ or THF for 12 h to dissolve and extract any soluble component. No soluble fractions were detected in the treated solvent suggesting that the crosslinking reaction had occurred in the resins which had made the cured resins insoluble. Fig. 2 shows FT-IR spectra of the resin before and after curing/drying of film. The resin had characteristic peak at 3400 cm$^{-1}$ and 3008 cm$^{-1}$ ascribed to –OH str and C=C–H str. After curing/drying of the film the peak of –OH completely disappeared while C=C –H peak at 3008 cm$^{-1}$ still appeared. This can be correlated to curing of the film obtained through the reaction between –OH and –COOH groups. It also confirms that the double bonds in the resin are not involved in curing process. The broadening and shifting of ester C=O peaks are also observed confirming the hydrogen bonding [26]. This observation shows that drying of the film involves 2 steps (Fig. 3). 1$^{st}$ step is the evaporation of solvent that causes chain entanglement (physical process) that leads to dry-to-touch of the coating. 2$^{nd}$ step involves esterification reaction that occurs between free –OH groups of one chain and free –COOH groups of another chain or between these groups within a chain. This is due to the increased reactivity of each free group after evaporation of a solvent. Along with these two steps an important electrostatic process of interaction also takes place through hydrogen bonding shown in Fig 3. Both intermolecular and intermolecular hydrogen bonds are involved [27].

## 3.6. Coating Properties

The coating property resulting in APGPEA, APGPEAPh-6 to APGPEAPh-18 are summarized in Table 2. Remarkable change in the film properties of the resin was observed with minor inclusion of PA in APGPEA resin. The coatings have been found to be self-cured/dried at room temperature. The coating of APGPEA and all compositions of APGPEAPh passed 1/8 inch conical
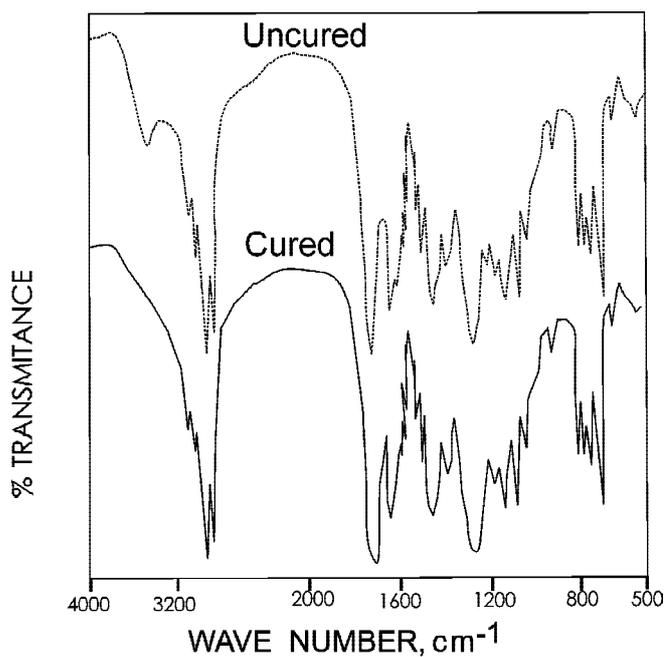
**Fig. 2.** FT-IR spectra of uncured and cured film of APGPEAPh
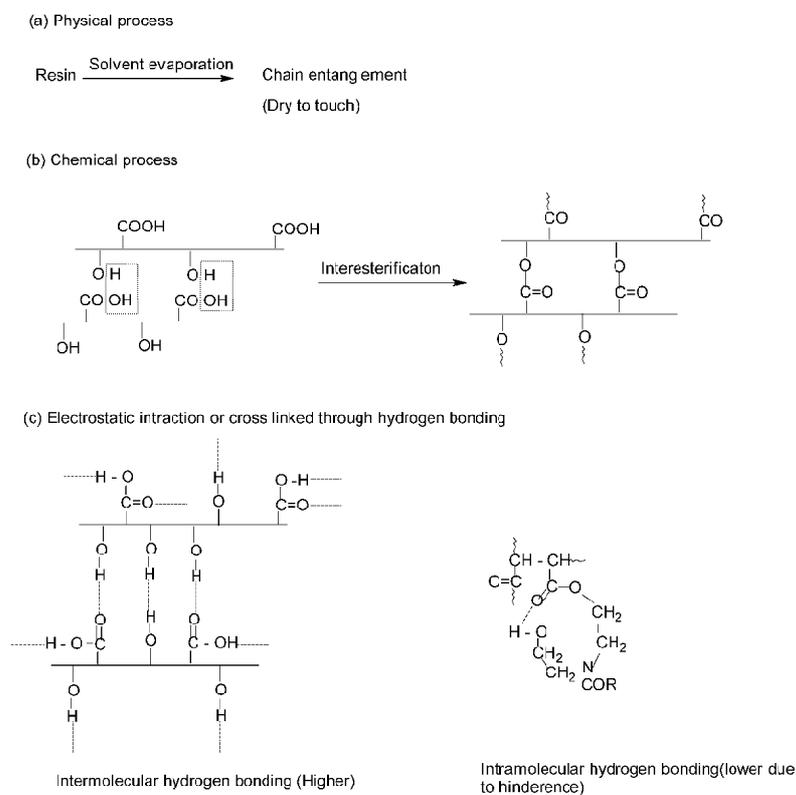


**Fig. 3.** Self-curing of the film

mandrel bend test and 150 lb/inch impact resistance test. These values are comparable to ALPEA coatings, but show considerable improvement compared to PGPEA coatings (100 lb/inch, bend test passed). The coatings were found to have higher gloss values in comparison with PGPEA while they were almost the same to compare with ALPEA. The reason may be SMA content and fatty acid chains [24]. Gloss value increased after loading of 6 wt % PA. The further addition of PA caused reduction of gloss value. It is attributed to the decrease of SMA content. Scratch hardness value of APGPEA was found to be lower in comparison with the baked PGPEA. Higher value of PGPEA was obtained due to the thermal curing of double bonds [16]. The addition of PA to APGPEA leads to the increase of scratch hardness. It is correlated to the enhanced crosslinked structure of the resin. Scratch hardness of APGPEA and APGPEAPh is higher than ALPEA and comparable to that of baked PGPEA. Linseed oil polyesteramide having higher linolenic acid (46 %) and lower oleic acid (22 %) yields more rigid films due to higher crosslinking between the chains through autoxidation. Contrary to this *Pongamia glabra* oil based polyesteramides possess oleic acid (71 %) which is insufficient for autoxidation and resultant crosslinking. Therefore these films are uniform and strain free [9, 17, 14, 28].

Chemical resistance of APGPEA was found to be higher in comparison with PGPEA coatings and comparable to ALPEA coatings [17, 24]. After 6 wt % loading of PA, alkali resistance decreases while water, acid, xylene and NaCl resistance increases. The APGPEAPh coatings are more corrosion resistant especially in water, NaCl (3.5 wt %) and acid (2 wt %) but have lower alkali (5 wt %) resistance than APGPEA coatings. It is observed that beyond 6 wt % loading of PA in the resin, chemical resistance decreases in all corrosive mediums except xylene. The lower alkali resistance is correlated to the amount increase of the ester groups that are easily hydrolysable [27, 28]. Best chemical resistance of APGPEAPh-6 was obtained because of the smaller amount of PA, as well as an optimum amount of SMA that provides a uniform and firmly adhered coating on the surface of the substrate which prevents the ingress of corrosive ions.

## 3.7. Thermal Analysis

Fig. 4 shows the TGA thermograms of PGPEA, APGPEA and APGPEAPh-6 which reveals that the thermal stability of APGPEA and APGPEAPh-6 polymers is comparable to each other while they have higher thermal stability than PGPEA. The 10 wt % loss for PGPEA is observed at 508 K, while in case of APGPEA and APGPEAPh-6 – at 558 K. This weight loss can be correlated to moisture and entrapped solvent. The 50 wt % loss is observed at 643, 658 and 673 K while

80 wt % losses – at 688, 753 and 823 K for PGPEA, APGPEA and APGPEAPh-6 respectively. DSC thermograms of PGPEA, APGPEA and APGPEAPh-6 resins show endothermic peaks at 453, 448 and 428 K respectively (Fig. 5). At this temperature no weight loss is observed in the TGA thermogram of the same sample. These temperatures can therefore be correlated to the melting temperatures $(T_m)$ of these resins. The $T_m$ of APGPEAPh-6 was found to be lower than that of PGPEA [17] and APGPEA. This can occur due to the increase in the pendant fatty acid chains in the resin. The fatty acids chains are known to impart flexibility to the polymer [29]. DSC thermogram also shows the initial decomposition event at temperature around 473 K in PGPEA and at 503 K in APGPEA and APGPEAPh-6. This matches with the initial decomposition temperature observed in TGA thermogram.
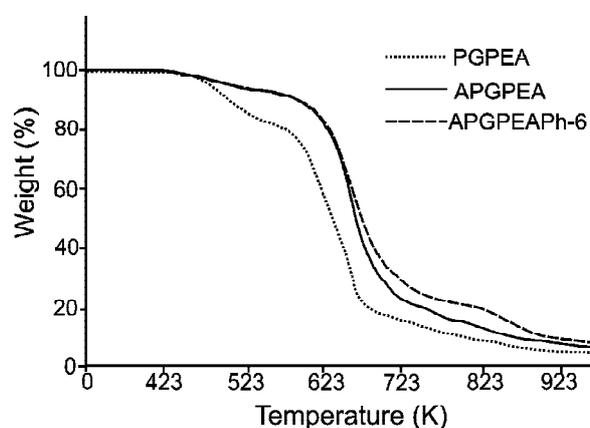


**Fig. 4.** TGA thermogram
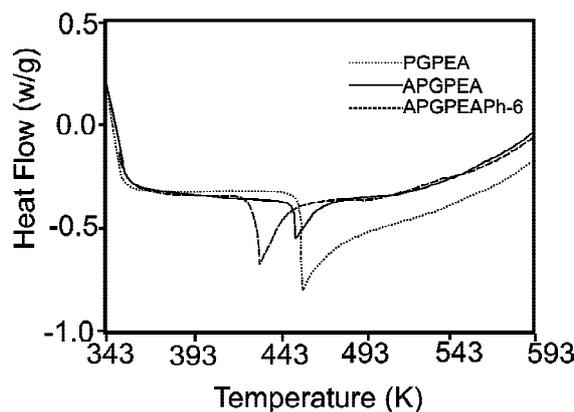


**Fig. 5.** DSC thermogram

## 4. Conclusions

The present study reveals that coating of APGPEAPh resin exhibits room temperature self-curing along with enhanced physico-mechanical, thermal and corrosion resistance properties compared to those of

APGPEA coatings. It is also observed that the APGPEAPh-6 resin shows noticeable increase of aforementioned properties. APGPEAPh-6 coatings were found to be thermally stable up to 503 K. By synthesis cured at room temperature APGPEAPh, we have an opportunity to convert non-drying oils to room temperature self-cured polymeric materials for eco-friendly protective coatings.

## Acknowledgements

## References

[1] Lligadas G., Ronda J., Galia M. and Cadiz V.: Biomacromolecules, 2007, **8**, 686.
[2] Andjelkovic D. and Lorock R.: Biomacromolecules, 2006, **7**, 927.
[3] Narine S., Yue J. and Kong X.: J. Am. Oil. Chem. Soc., 2007, **84**, 173.
[4] Czub P.: Macromol. Sym., 2006, **245**, 533.
[5] Guner F., Yagci Y. and Erciyes A.: Prog. Polym. Sci., 2006, **31**, 633.
[6] Petrovic Z., Zhang W. and Janvi I.: Biomacromolecules, 2005, **6**, 713.
[7] Derksen J., Cuperus F. and Kolster P.: Prog. Org. Coat., 1996, **27**, 45.
[8] Sharmin E., Ashraf S. and Ahmad S.: Int. J. Bio. Macromol., 2007, **40**, 407.
[9] Ahmad S., Ashraf S., Naqvi F. *et al.*: J. Macromol. Sci. Part A: Pure Appl. Chem., 2006, **43**, 1409.
[10] Bailey A.: Bailey's industrial oil and fat product. Wiley, New York 1996.
[11] Deffar D., Teng G. and Soucek M.: Surf. Coat. Int. Part B: Coat. Trans., 2001, **84 (B2)**, 147.
[12] Gorkum R. and Bouwman E.: Coord. Chem. Rev., 2005, **249**, 1709.
[13] Kabasakal O.: Prog. Org. Coat., 2005, **53**, 235.
[14] Erich S., Vander Ven L., Huinink H. *et al.*: J. Phys. Chem. B., 2006, **110**, 8166.
[15] Ahmad S., Ashraf S., Naqvi F., *et al.*: Prog. Org. Coat., 2006, **56**, 1.
[16] Zafar F., Ashraf S. and Ahmad S.: Bhart. Viag. Odhyo. Anusan. Patri., 2007, **1**, 44.
[17] Ahmad S., Ashraf S., Naqvi F. *et al.*: Prog. Org. Coat., 2003, **47**, 95.
[18] Kaul S., Saxena R., Kumar A. *et al.*: Fuel Proc. Technol., 2007, **88**, 303.
[19] Raval D. and Patel V.: Paintindia, 2005, **LV (3)**, 51.
[20] http://www.google.com/search?hl=en&lr=&q= H+S+Mukunda%2C+100+%25+Of+Energy+From+ Renewables+%E2%80%93+Is+This+An+Achievable+%2C +Goal+Or+An+Improbable+Slogan%3F+Department+Of+ Aerospace+Engineering+Indian+Institute+Of+Science%2C+ Bangalore+560+012+&btnG=Search
[21] Zafar F., Ashraf S. and Ahmad S.: J. Appl. Polym. Sci., 2007, **104**, 1143.
[22] Zafar F., Sharmin E., Ashraf S. and Ahmad S.: J. Appl. Polym. Sci., 2004, **92**, 2538.
[23] Zafar F., Ashraf S. and Ahmad S.: Prog. Org. Coat., 2004, **51**, 250.
[24] Zafar F., Sharmin E., Ashraf S. and Ahmad S.: J. Appl. Polym. Sci., 2005, **97**, 1818.
[25] Morrison R. and Boyd R.: Organic Chemistry, 6th edn. Prentice Hall, India 2000.
[26] Silverstein R., Bassler G and Morril T.: Spectrometric Identification of Organic Compounds, 5th edn. John Wiley and Sons, New York 1991.
[27] Paul S.: Surface Coatings Science and Technology, 2nd edn. John Wiley and Sons, New York 1996.
[28] Nylen P. and Sunderland E.: Modern Surface Coating, 1st edn. Wiley, London 1965.
[29] Gwariker V., Viswanathan N. and Sreedhar J.: Polymer Science. New Age International Publisher, New Delhi, India 2006.

## САМОСТРУКТУРУЮЧИЙ ПОЛІМЕР З НЕВИСИХАЮЧОЇ ОЛИВИ

**Анотація.** *Нехарчова, невисихаюча олива Pongatia glabra (ПГО) знаходить застосування для одержання алкідів, епоксидів і поліестерамідів, які використовуються при виробництві фарб і покриттів. Самоструктуруюча поліестерамідна смола на основі ПГО була синтезована за реакцією ПГО, модифікованої жирним амідним діолом, з полікополімером на основі стиролу і малеїнового ангідриду. Синтезовано також поліестерамід, модифікований фталевим ангідридом. Для обох смол стандартними методами визначено їх фізико-хімічні характеристики з використанням Фур'є-спектроскопії, *1H-ЯМР і 13C-ЯМР*. Встановлено, що синтезовані смоли мають кращі властивості порівняно з поліестерамідами, затвердженими при високих температурах. Показано, що присутність фталевого ангідриду значно покращує фізико-механічні і корозійні властивості покрить.*

***Ключові слова:*** *олива Pongatia glabra, поліестерамід, механічні та термічні властивості, покриття, корозія.*