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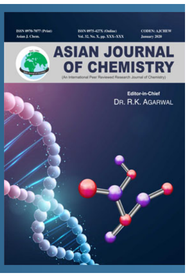

Structural and Thermal Characterization of Castor Oil Based Unsaturated Polyester Resin

A. CHOWDHURY*, S.K. SINGH and P. ANTHONY

Department of Chemistry, Faculty of Science, Sam Higginbottom University of Agriculture, Technology & Sciences, Prayagraj-211007, India

*Corresponding author: E-mail: abhishek.chowdhury2089@gmail.com

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In the present study, unsaturated polyester resins based on castor oil was synthesized. Structure elucidation of the synthesized unsaturated polyester resin was done by FTIR and ^{1}H NMR spectroscopy. Thermogravimetric analysis was used to evaluate the thermal stability of cured unsaturated polyester resin. Thermogram plot was further utilized to calculate various other parameters such as statistic heat-resistant index (Ts) and the integral procedural decomposition temperature (IPDT). Comparable properties with respect to commercial resins were reported for the synthesized polymers.

Keywords: Castor oil, Unsaturated polyester resin, Thermal decomposition, Renewable resource.

INTRODUCTION

Polymeric materials derived from petroleum derivatives possess volatile organic compound, which disconfirm the objectives of green chemistry [1-3]. Considering the increased petroleum price, exhaustion of fossil fuels and increase in environmental pollution, researchers have been forced to find an alternative source of raw materials which are not only eco-friendly but also meet the demand of polymers in regards to the variety of applications [1,4].

The use of several natural alternatives like chitin, polysaccharides, lignin, vegetable oils, *etc*. can minimize the dependence on petrochemicals as well as they will control the issues related with synthetic ones [5-8]. Vegetable oils are dominant and attractive alternative for the production of bio-based polymers due to its renewable nature, low cost and comparable performance with respect to petroleum based ones [4,9]. Mostly, semi and completely drying vegetable oils are being utilized in various industries like adhesives, inks, paints and coatings [10,11]. Non-edible oil such as castor oil is an interesting and unique naturally occurring triglyceride of ricinoleic acid. Its unusual structure can be easily tailored for versatile applications due to the presence of a secondary hydroxyl group and unsaturation [12].

Several studies have been focused on substitution of different vegetable oils. Sahoo *et al*. [13] synthesized epoxidized linseed and castor oil based epoxy resins cured with citric acid. They further compared its thermo-mechanical properties with respect to petro-based ones. Castor oil was epoxidized in the presence of different catalyst such as γ-alumina and formic acid and its oxirane oxygen content was further analyzed [14]. Castor oil has been converted to a series of phosphorus esters, which behave as effective flame retardants in diglycidal ether of bisphenol A (DGEBA) epoxy resin [15]. Several other oils such as karanja [16], yellow oleander [17], *Jatropha curcas* [18], nahar [19] seed oil based polyester resins were prepared and tested for coating applications.

In the present study, unsaturated polyester resin (UPR) based on castor oil was synthesized. Structure elucidation of the synthesized UPR was done by FTIR and ^{1}H NMR spectroscopies. Thermogravimetric analysis (TGA) was used to evaluate the thermal stability of the cured unsaturated polyester resin. Thermogram plot was further utilized to calculate various other parameters such as statistic heat-resistant index (Ts) and the integral procedural decomposition temperature (IPDT). Comparable properties with respect to commercial resins were reported for the synthesized polymers

EXPERIMENTAL

Castor oil was purchased from the local market of Prayagraj city, India. Phthalic anhydride (PA) was purchased from Merck, India. Succinic acid (SA) and maleic anhydride (MA) was purchased from Central Drug House (P) Ltd. and propylene glycol (PG) purchased from Rankem, were used without further purification. Styrene 98% was purchased from Avra synthesis Pvt. Ltd, Hyderabad, India. Methyl ethyl ketone peroxide and cobalt-octoate were used as received from Lilha & Company, Varanasi, India.

Synthesis of unsaturated polyester resins (UPR): The resin was synthesized by a two stage alcoholysis-polyesterification process using Dean & Stark type condenser [20]. Table-1 shows the composition of the synthesized resin.

TABLE-1
COMPOSITION OF THE SYNTHESIZED RESIN

Oil	Propylene glycol	Succinic acid	Maleic anhydride	Phthalic anhydride
0.16 M	0.24 M	0.058 M	0.28 M	0.11 M

A mixture of oil and propylene glycol was firstly heated with continuous stirring in order to convert oil into a monoglyceride which was confirmed by methanol solubility test. Complete dissolution of a mixture of resin and methanol (1:3) indicates the monoglyceride formation [21]. Further, after cooling the reaction mixture finely divided form of acid anhydride and succinic acid was added. It was again heated with continuous stirring till a minimum constant acid value was achieved. Styrene (35 wt%) was added in the synthesized resin. In order to cure the resin, methyl ethyl ketone peroxide (2 wt%) as initiator and cobalt-octoate (0.2 wt%) as accelerator were added with continuous stirring [22].

Characterization: Perkin Elmer spectrum RX-I was used to record FT-IR spectra of the resin. The absorption peaks in between 4000 to 400 cm^{-1} were evaluated. Bruker Avance II spectrometer was used to scan the synthesized polymer samples for ^1H NMR spectra at 400 MHz, 293 K in $CDCl_3$. The chemical shifts (δ) were expressed in ppm. EXSTAR TG/DTA 6300 was used for thermogravimetric analysis. All materials were heated from 35 to 1000 ºC in a 200 mL/min flow of air at heating rate of 10 ºC/min. Continuous recording of sample temperature, weight and heat flow were performed.

The statistic heat resistant index temperature (Ts) was calculated by eqn 1 [23-25] values of T_{d5} & T_{d30} from the TGA data are used to calculate Ts.

$$Ts = 0.49[T_{d5} + 0.6 \times (T_{d30} - T_{d5})] \quad (1)$$

Integral procedural decomposition temperature (IPDT) Doyle′s method as proposed earlier [25-27] was used to calculate the IPDT.

$$IPDT\ (°C) = AK \times (T_f - T_i) + T_i \quad (2)$$

$$A = \frac{S_1 + S_2}{S_1 + S_2 + S_3};\ K = \frac{S_1 + S_2}{S_1}$$

where A is the area ratio of total experimental curve divided by total TGA thermogram; T_i is the initial temperature (500 ºC); T_f is the final temperature (800 ºC); K is the coefficient of A; and S_1, S_2 & S_3 values were determined by earlier studies.

RESULTS AND DISCUSSION

Synthesis of unsaturated polyester resin (UPR): Castor oil on being heated with propylene glycol, yields a mixture of products when it is subjected to transesterification. The product mainly comprises of monoglyceride, diglyceride, triglyceride and propylene glycol. The mixture is generally referred to as monoglyceride [28]. On being treated with succinic acid, maleic anhydride and phthalic anhydride, it forms an unsaturated polyester resin as a result of polyesterification reaction.

The reaction is kept under control by checking the acid value at different time intervals. As the reaction advanced, a drop was observed in the acid value. The acid value dropped quickly during the former stages of the reaction as compared to the latter stages. The variations in the acid value during the polycondensation reaction have been accounted for the different reactivities of primary hydroxyl and secondary hydroxyl groups of propylene glycol [29].

A primary hydroxyl group helps the reaction to advance faster than a secondary hydroxyl group. Therefore, it is concluded that the drop in the acid value during the former stages of the reaction is equivalent to the period when the primary hydroxyl group reacts, while the latter stage correlates to the period when the secondary hydroxyl group react [30]. It has been observed that the part of the reaction where the decrease in acid value is less rapid indicates the crosslinking of alkyd chain with the production of three dimensional networks [31]. Hence from these results it can be deduced that the crosslinking of alkyd chains takes place during the latter stage of the reaction when the secondary hydroxyl group reacts and this result in the increased viscosity of the reaction medium. Moreover, towards the end of the reaction it is observed that rate of polyesterification also decreases due to decrease in the concentration of free acids [32].

FTIR spectra: Existence of various characteristic peaks and important linkages such as olefinic double bonds, ester groups are indicated by the FT-IR spectra of the synthesized resin (Fig. 1). Polyesterification reaction was confirmed by FT-IR analysis.

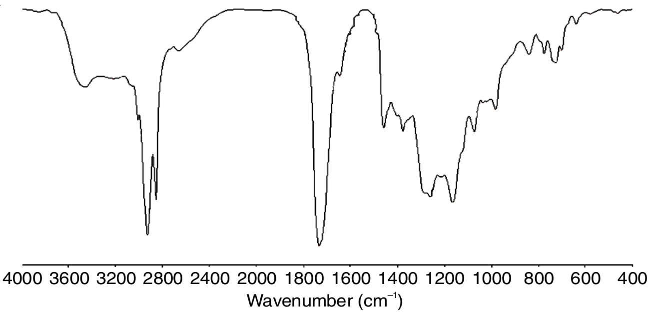

Fig. 1. FTIR spectra of the synthesized resin

A broad singlet peak at 3451.4 cm^{-1} confirms the presence of -OH group. Aromatic C-H stretching as well as olefinic C-H stretching is confirmed by the peak at 3009.4 cm^{-1}. Peaks around 2856.5-2928.9 cm^{-1} corresponds to aliphatic C-H stretching vibrations. A characteristic peak at 1733.5 cm^{-1} confirms the presence of ester linkages (C=O). Presence of aromatic

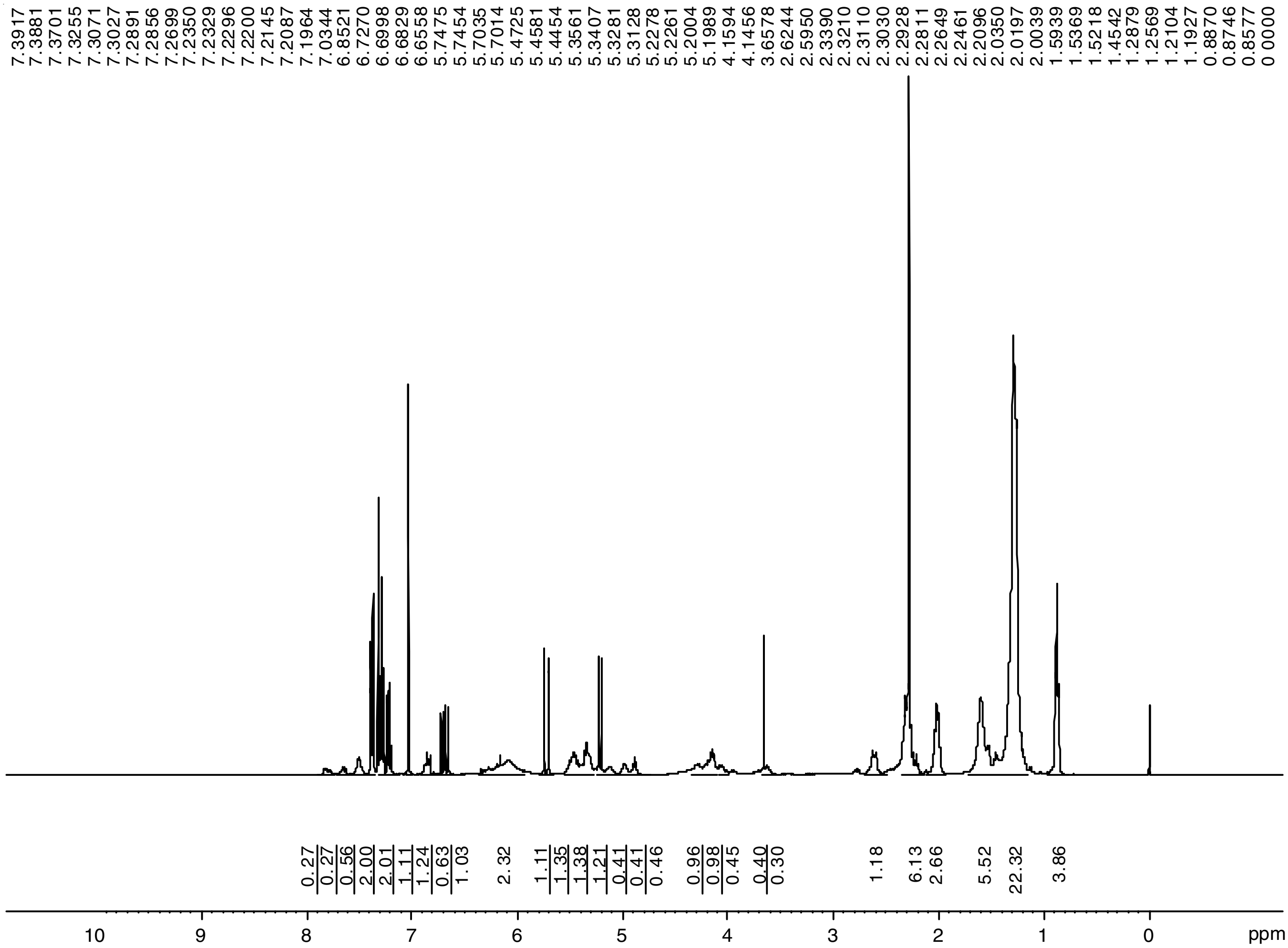

Fig. 2. ^{1}H NMR spectra of the synthesized resin

C=C were confirmed by peaks in 1601.7-1580.7 cm^{-1} region. Stretching of (-C-O-C-) is confirmed by the peaks around 1260.8-1074.4 cm^{-1}. A peak at 1165.6 cm^{-1} confirms the C-O stretching frequency of ester. Presence of C-C stretching is confirmed by the peak at 983.3 cm^{-1} while the peaks around 776.8-702.2 cm^{-1} correspond out of plane aromatic C-H bending vibration [33,34].

^{1}H NMR spectra: Fig. 2 depicts the ^{1}H NMR spectra of the synthesized resin. A peak at δ 0.8577-0.8870 ppm are for the protons of terminal -CH_3 group of the fatty acid chains. Peak at δ 1.5939 ppm correspond to the protons of CH_2 groups attached next to above terminal methyl group. Peak at δ 1.2569-1.2879 ppm were observed for all the internal -CH_2 groups present in the fatty acids chains. Characteristic peak at δ 5.3407 ppm was also observed for protons of unsaturated carbon. For methylene protons of propylene glycol moiety were observed at 3.6578-4.1594 ppm. Due to the deshielding effect by anhydride group (PA/MA), the protons for CH of propylene glycol moiety shows the characteristic peaks at 6.72-6.85 ppm. The peaks at 7.2891-7.391 ppm were observed for aromatic protons of phthalic anhydride [33,34].

Thermal analysis: Applicational aspects of unsaturated polyester resins is determined by thermooxidative stability [35]. Thermogravimetric analysis was performed at the heating rate of 10 ºC/min. Fig 3a represents the TGA curve and Fig. 3b represents DTG of the commercial resin (CR-1) and synthesized resin (CR-4). The weight loss of cured polyester resin

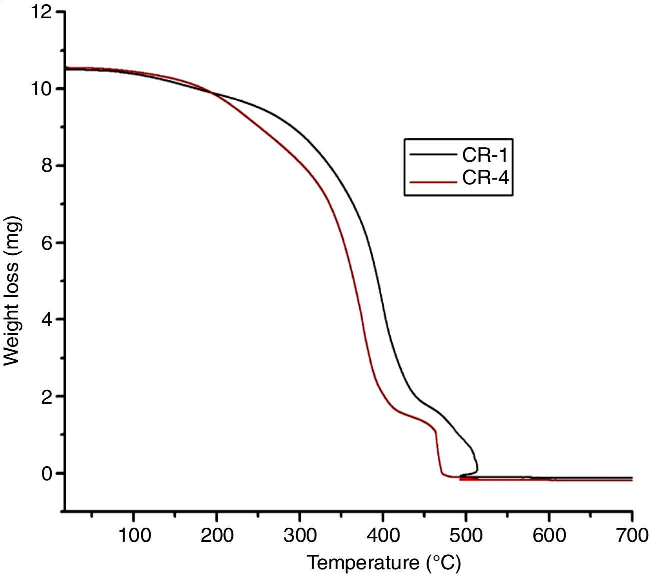

Fig. 3(a). TGA curve of the commercial resin (CR-1) and synthesized resin (CR-4)

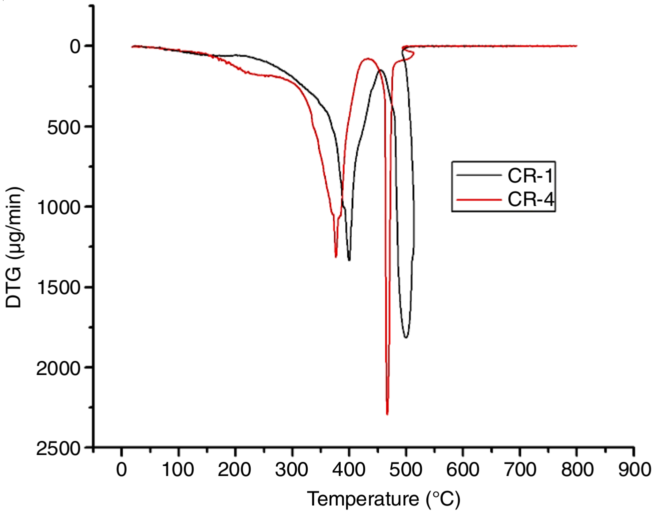

Fig. 3(b). DTG curve of the commercial resin (CR-1) and synthesized resin (CR-4)

usually occurs at two main temperature ranges. Evaporation of unreacted soluble components and degradation of low molecular weight oligomeric component occur around 100-250 ºC, whereas the degradation and char formation of the cross linked polymer structure takes place rapidly around 250-450 ºC [22,36,37]. Thermal degradation temperatures of the resin are tabulated in Table-2.

TABLE-2
THERMAL STABILITY DATA OF CR-1 AND CR-4

Sample code	T_{onset} (°C)	T_{d5} (°C)	T_{d30} (°C)
CR-1	97.4	180.5	354.4
CR-4	115.0	187.0	328.0

T_{onset} = Onset temperature; T_{d5} = Temperature of 5% weight loss; T_{d30} = Temperature of 30% weight loss; Ts = Statistic heat resistant index temperature

The onset thermal degradation temperature (T_{onset}) of CR-1 was around 97.4 ºC whereas for CR-4 was at 115 ºC, which may be due to loss of water and other volatile substances [38]. The early degradation of CR-1 could be explained by the assumption that the solvent used is more volatile than the one used for CR-4 [39]. The temperature of 5% weight loss (T_{d5}) are almost comparable for both CR-1 and CR-4 *i.e.* at 180.5 ºC for CR-1 and for CR-4 at 187 ºC. About 30% weight loss (T_{d30}) temperatures for CR-1 and CR-4 are 354.4 ºC and 328 ºC, respectively which correspond to degradation of ester linkages.

The statistic heat-resistant index (Ts) and the integral procedural decomposition temperature (IPDT) are the specific parameters to explain the thermal stability of the cured resins. Parameters of thermal stability of cured resins are shown in Table-3. The value of IPDT for CR-4 is found to be 507 ºC, which is at par with CR-1 *i.e.* 525 ºC, whereas the value of statistic heat-resistant index (Ts) of CR-4 is 121 ºC, which is lower than CR-1 *i.e.* 140 ºC. These data clearly indicated that the properties of the synthesized resin (CR-4) are comparable to the commercially available one (CR-1).

TABLE-3
PARAMETERS OF THERMAL STABILITY OF CURED RESINS

Sample code	IPDT (°C)	Ts (°C)
CR-1	525	140
CR-4	507	121

Conclusion

Unsaturated polyester resins based on a castor oil and a mixture of phthalic anhydride, maleic anhydride, propylene glycol and succinic acid in varying amounts by a two stage alcoholysis-polyesterification process have been successfully synthesized. The FTIR and ^{1}H NMR spectra confirmed the structure of the resin and TGA studies along with the values of statistic heat-resistant index (Ts) and the integral procedural decomposition temperature (IPDT) confirmed the thermal stability. On comparison, it is being found that the values of T_{onset} of CR-1 is around 97.4 ºCwhereas for CR-4 is at 115 ºC. T_{d5} and Td_{30} are almost comparable for both CR-1 and CR-4 samples. Whereas the values of IPDT and Ts are higher for commercial resins. Based on these results, it can be concluded that UPRs based castor oil are thermally stable and has tremendous potential to be a good alternative for fossil fuel based polymers.

CONFLICT OF INTEREST

The authors declare that there is no conflict of interests regarding the publication of this article.

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