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Synthesis and Characterization of Pentaerythritol Phthalic Anhydride Resin from Soybean Oil

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Alkyd resins, a type of polyesters obtained through esterification of a polybasic acid and polyhydric alcohol (*e.g.*, pthalic anhydride and pentaerythritol). This study aimed to synthesize and characterize pentaerythritol phthalic anhydride resin by using soybean oil, pentaerythritol, phthalic anhydride and litharge (PbO) catalyst through alcoholysis method. FTIR and DS/TGA were used to characterize the freshly obtained pentaerythritol phthalic anhydride resin. Based on results, acid value 7.9 mgKOH/g is beneficial for the quality synthesis of pentaerythritol phthalic anhydride resin having high thermal stability even upto T_{max} = 670 ºC.

Keywords: Pentaerythritol phthalic anhydride resin, Acid value, Soybean oil, Esterification.

INTRODUCTION

Resins are complex oil modified polyesters that serves as film forming agent in selected type of paints and coatings. Mostly, the resins are hard, have good stability, gloss retention, weather resistance and fast drying characteristics [1,2]. Alkyd resin is used in solvent based paints and poly(vinyl acetate) resin (PVA) is used in water based paints. There are two types of alkyd resins *i.e.*, drying and non-drying. Both types are produced from carboxylic acids or anhydrides (phthalic anhydride or maleic anhydride) and polyols such as pentaerythritol. Resins have various benefits for paints such as increasing their flexibility, adhesiveness, brushing power, film hardness, durability and gloss retention. Moreover, the presence of resins in paints not only provides the resistance to water and abrasion effects but also helps to decrease the overall drying time. Alkyd resins could be produced from fatty acids and are most widely used in alcoholysis processes [3-6]. Pentaerythritol phthalic anhydride resin (PPR) is used as a binder in coating compositions, adhesive, plastics, varnishes, printing inks and floor coverings. The industrial finishes include primers and top coatings for refrigerators, furniture and electrical equipment [7]. The enhancing quality effects on the synthesized alkyd resin using methyl esters of rubber seed oil were indicated by the improvement in physico-chemical properties of the finished alkyds [8]. An oil modified alkyd based resin was synthesized using castor oil to have promising physico-chemical properties and high chemical resistance in formulating paint [9]. Hyper branched alkyd resins (HBRA) based on tall oil fatty acids were synthesized by acid catalysis and characterized to investigate their properties such as adhesion, flexibility, drying time, gloss and chemical resistance [10].

The current research work presents the synthesis of pentaerythritol pthalic anhydride with soyabean oil using catalyst. Acid value was measured to monitor the esterification reaction. The synthesized product was characterized using FTIR for the analysis of functional groups. Moreover, thermal degradation and differential scanning calorimetry was also performed simultaneously using SDTQ600 with moderate heating rate of 10 ºC/min in the presence of nitrogen.

EXPERIMENTAL

Alkali refined soybean oil was purchased from local brand (Shan oil Pakistan Ltd. ~100 % pure). The others lab grade reagent such as pentaerythritol, lead oxide, methanol (95%), KOH solution, phenolphthalein, phthalic anhydride and xylene (used as 5 % of oil wt.) were obtained from local vendor.

Initially, alkali refined soybean oil, pentaerythritol and PbO were charged to three neck flasks. The presence of PbO decreases the reaction time as it provides the complete alcoholysis to precede esterification reaction after reaction time for 2 h. The nitrogen flow (0.01ft^3/min) was maintained at 230 ºC for 2 h until 1 mL of the flask contents showed a clear solution with

2 mL anhydrous methanol. The acid value, the number of mg of KOH required neutralizing acids in 1 g of fatty material (mg KOH/g of sample), was determined by using titration method. A known amount of sample was dissolved in ethanol-toluene (1:1) solution and titrated with KOH solution using phenolphthalein as an indicator. Total acid number (TAN) was calculated using eqn 1:

$$\text{Total acid number (TAN)} = \frac{(A \times N \times 56.1)}{W} \quad (1)$$

where, A = Consumption of KOH solution (mL), N = Normality of KOH solution and W = Sample weight (g).

After the confirmation of esterification reaction, added phthalic anhydride and resin formation started. Both the apparatus and attached condenser assembly (cooling water flowing in the condenser to remove heat with stirring and use about 5 % of xylene (5 % of oil weight) as an azeotropic agent) to facilitate removal of water of esterification. Maintain temperature at 245 ℃ until the acid values of system falls below 10 mg KOH/g oil. The alcoholysis reaction is one of the two major reactions occurring during pentaerythritol phthalic anhydride resin (PPR), the other being is esterification.

The condition of reaction is critical factors in the alcoholysis procedure. Though, high temperatures facilitate the reaction but often are avoided because of possible development of highly colored products. Both alkaline and acidic reagent can be used to catalyzed the alcoholysis but it has been determined that the acidic catalyst frequently contribute to dark colours in the reaction product. Some factors affecting the colours of an alcoholysis mixture are: contact with air, choice, and concentration of catalyst and temperature of the reaction. Alcoholysis is preferably carried out in the presence of an inert gas to prevent contact with oxygen and by using the least quantity of catalyst and lowest temperature necessary to accomplish the reaction within a reasonable period of time. The prepared PPR was characterized using FTIR (IRPrestige-21/DRS-8000 Shimadzu, Japan) and simultaneous thermal analysis *i.e.*, DSC/TGA using SDT (Q600 TA instrument, USA) at heating rate of 10 ℃/min under the nitrogen atmosphere.

RESULTS AND DISCUSSION

Synthesis of pentaerythritol phthalic anhydride resin (PPR): The acid values were determined to follow the progress of esterification reaction with time as shown in Fig. 1. It revealed that acid values (mg KOH/g) decreases with the progress of reaction time (min). A rapid decrease in acid values was observed at early stages of esterification reaction due to the high consumption of fatty acids. However, low changes of acid values at the later stages of esterification reaction revealed that the consumption of fatty acid amount decreased with the passage of time.

The acid value of the synthesized resin was found to be 7.9, which is within the standard range of (< 10 as per ASTM). Resins with high acid values are not suitable for paints manufacture as the extender pigments would be decomposed which could impart significant impact on paint properties. A methanol test to determine the solubility of alcoholysis mixture with anhydrous methanol (1 mL sample + 2 mL methanol), was performed to confirm the completion of alcoholysis reaction. The results of methanol test are summarized in Table-1. The solubility

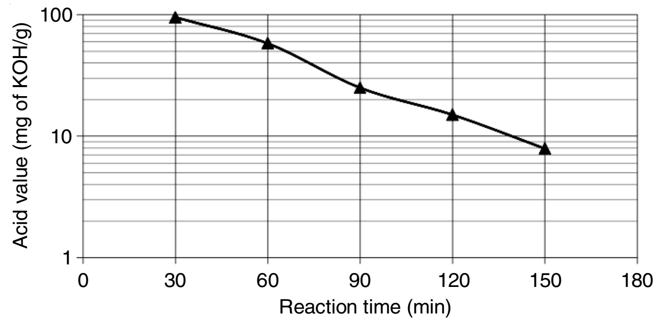

Fig. 1. Acid value *versus* esterification reaction time

TABLE-1
METHANOL TEST FOR THE CONFIRMATION OF ALCOHOLYSIS REACTION COMPLETION

Time (min)	Temperature (°C)	Physical state
0	200	Immiscible
30	210	Immiscible
60	220	Immiscible
90	228	Partially miscible
120	230	Soluble
150	235	Soluble

of methanol with final mixture confirms the completion of reaction after 150 min.

Chemical resistance of pentaerythritol phthalic anhydride resin (PPR) film: The chemical resistance of synthesized resin for the solvent media (distilled water and sulfuric acid) is summarized in Table-2. The results suggested that the distilled water has no effect on the dry film even after the immersion for 18 h. However, when PPR film was immersed in H_2SO_4 (pH = 3), the film got white appearance after 8 h, blistering after 16 h and removal after 24 h. This is the clear indication of good quality resin fully capable of being used in paints as a resistant to acid rain as well as humidity in air.

TABLE-2
CHEMICAL RESISTANCES OF PENTAERYTHRITOL PHTHALIC ANHYDRIDE RESIN

Media	Immersion time (h)	Appearance of film*
Distilled water	18	No effect
H_2SO_4 (pH = 3)	8	Whitening
	16	Blistering
	24	Removal

*Examined after 30 min of air drying

FT-IR adsorption of pentaerythritol phthalic anhydride resin (PPR): The FTIR adsorption key bands of PPR synthesized from soybean oil are shown in Table-3. The FTIR spectrum (Fig. 2) exhibited the characteristic of aromatic ring ester band at 1730.15 cm^{-1}. The appearance of CH_2, -CH- confirms the presence of methyl group at 1460.11 and 2854.65 cm^{-1}. According to the literature [11-13], the adsorption band at 2924.09 cm^{-1} is the characteristics of alkenes carbon (=C-H).

The adsorption band at 3396.64 and 1068 cm^{-1} shows the presence of hydroxyl group (-OH) an indication of increased stretching power of the resin.The presence of C=O in the resin (characteristic of ester) at 1730.15 cm^{-1} is attributed to the stretching power in fatty acid, which indicates the possibility of polyesterification reaction during the transformation of the carboxylic acid in ester [9].

TABLE-3
KEY FTIR BANDS OF ABSORPTIVE
PENTAERYTHRITOL PHTHALIC ANHYDRIDE RESIN

Frequency (cm^{-1})		Remarks
Experimental	Literature	
1068.00	Near 1100	O-H
1460.11	1440-1485	CH_2
1730.15	1717-1730	COO
2854.65	2850-2926	C-H
2924.09	Near 3030	=C-H
3396.64	3200-3570	O-H

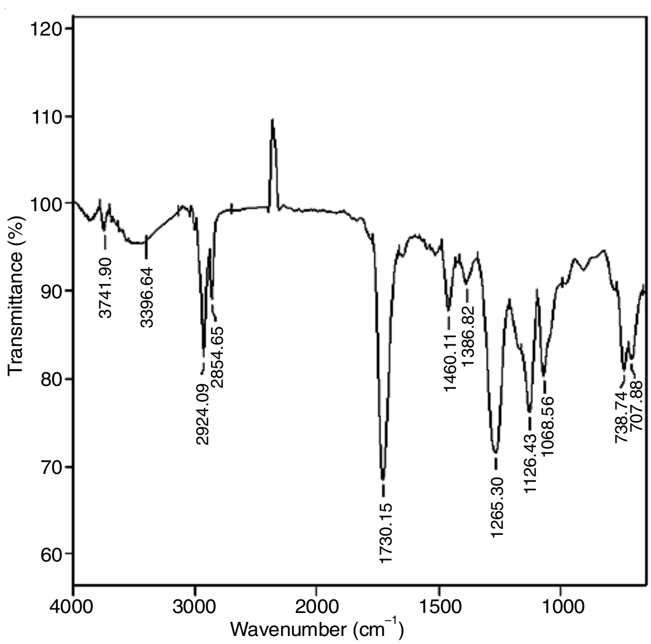

Fig. 2. FTIR spectrum of pentaerythritol phthalic anhydride resin (PPR)

Thermal analysis: The results of differential scanning calorimeter (DSC) and thermogravimetric analysis (TGA) for synthesized PPR are shown in Fig. 3. TGA results suggested that the thermal degradation of PPR is initiated (with 1% wt. loss of the resin) at 167 ºC and the final decomposition temperature

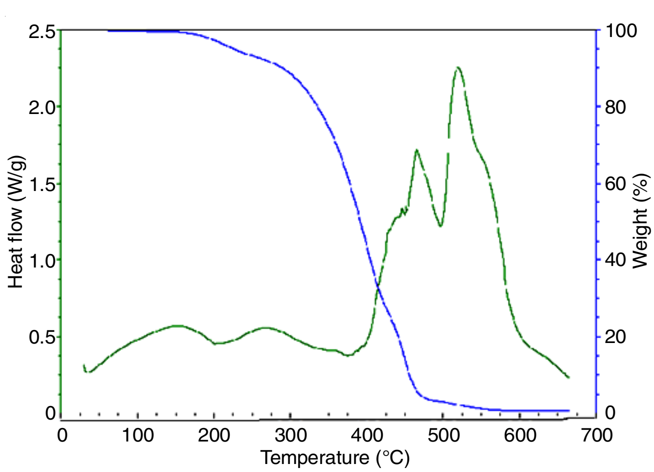

Fig. 3. DSC/TGA curves of synthesized pentaerythritol phthalic anhydride resin (PPR)

at (100 % wt. loss) was 670 ºC which is comparable to the values reported for artists' alkyd paints (470 ºC) and considered to be thermally stable [12] and for PET based alkyd resin (500 ºC) [13,14]. An indication of the presence of large number of hydroxyl (-OH) groups in the synthesized PPR, which increased the stretching power and overall strength that improved its thermal stability.

Conclusion

Alkali refined soybean oil, due to the presence of relatively high proportion of oxidation-prone linolenic acid, has shown to be good for the synthesis of pentaerythritol phthalic anhydride resin (PPR) (having acid value 7.9 mgKOH/g) in the presence of lead oxide as catalyst by alcoholysis process. The synthesized PPR presented a high chemical resistance when immersed in sulfuric acid for a longer time, which implies its utilization for paints to withstand for acid rain as well as humidity in the air. As, newly synthesized entaerythritol phthalic anhydride resin has high thermal stability, therefore, the pentaerythritol phthalic anhydride resin could be used in paints to decrease their overall drying time and to enhance their quality by layer formation.

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