Preparation of Chlorendic Acid Based Polyester Resins

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Four polyesters were prepared by stepwise condensation of isophthalic acid, chlorendic acid and maleic anhydride with propylene glycol using p-toluenesulphonic acid as catalyst and xylene as entrainer. The quantities of maleic anhydride and propylene glycol used were 1 and 2.2 moles respectively and the molar ratios of chlorendic acid to isophthalic acid were 0.2:0.8, 0.4:0.6, 0.6:0.4 and 0.8:0.2 for the four polyesters prepared. The polyesters obtained had better colour and relatively more uniform distribution of chlorendic acid over the polymer chain compared to the polyester made in one step. They were crosslinked using 30\% by weight of styrene and were characterized through the determination of viscosity, gel time, peak exotherm and acid value. They were evaluated by measuring Vicat softening point, heat distortion temperature, rate of flammability and rate of hydrolysis. The data reveal that the polyester obtained using chlorendic acid and isophthalic acid in molar ratio 0.6:0.4 is the best among the four polyesters prepared.

In an earlier work\(^1\) on chlorendic acid based polyesters reported from this institute, Gupta et al.\(^1\) identified the factors which contribute to thermal stability, flame resistance and chemical resistance by comparing chlorendic acid based polyesters with commercial polyesters. Gupta et al.\(^1\) did not discuss the selection of method for preparing chlorendic acid based polyesters and did not evaluate properties like thermal stability, flame resistance and chemical resistance thoroughly. Studies\(^2-6\) were also conducted at this institute on the synthesis of polyesters having the desired combination of properties like chemical resistance, heat and flame resistance, dimensional stability, good mechanical properties, high energy radiation stability and insulating property. This work necessitated thorough investigation of these aspects in order to meet the technical challenge posed by several strategical applications. In this paper, the results of studies arrived at by modifying the methods of preparing chlorendic acid based unsaturated polyesters, their characterization and evaluation with respect to Vicat softening point, heat distortion point, flame resistance and hydrolytic stability are reported.

Materials and Methods

**Chlorendic acid**—Chlorendic acid supplied by Hooker Chemical Corp. Ltd, U.S.A. was used. It had melting point (sealed tube) 208-210°C and melting point (open tube) 230-235°C, as it gets converted to anhydride in open tube. Its purity was 99.5%.

**Isophthalic acid**—Commercial isophthalic acid having melting point 352°C and purity 98% was used. The impurity was terephthalic acid.

Preparation of polyester based on chlorendic acid and isophthalic acid by one step condensation—To a 1 litre three-necked round bottomed flask, fitted with a Dean and Stark apparatus and condenser, thermometer pocket and a gas inlet, were added isophthalic acid (83 g, 0.5 mole), chlorendic acid (195 g, 0.5 mole), maleic anhydride (98 g, 1 mole), propylene glycol (167 g, 2.2 mole), p-toluene sulphonic acid (2 g) and xylene (100 ml). The mixture was refluxed at 140°C in an oil bath in a stream of carbon dioxide and 36 ml of water of esterification was removed by Dean and Stark apparatus under vacuum in CO\(_2\) atmosphere. The reaction mixture was heated at 180-190°C for 90 min under 50 mm Hg pressure in a stream of CO\(_2\), until the required acid number was reached. A black mass insoluble in styrene was obtained.

Preparation of polyester 1 based on chlorendic acid and isophthalic acid—To a 1 litre three-necked round bottomed flask, fitted with a Dean and Stark apparatus and condenser, thermometer pocket and a gas inlet were added isophthalic acid (132.8 g, 0.8 mole), propylene glycol (129.0 g, 1.7 mole) and p-toluene sulphonic acid (0.5 g). The mixture was refluxed at 160°C in an oil bath in a stream of carbon dioxide and 28.6 ml of water of esterification was removed by Dean and Stark apparatus. After this chlorendic acid (78 g, 0.2 mole), propylene glycol (32 g, 0.41 mole) and
xylene (100 ml) were added to the flask and the temperature was brought to 140°C; 7.2 ml water of esterification was removed. Then maleic anhydride (98 g, 1 mole) was added to the resulting solution and the temperature was again brought to 140°C; 18 ml water of esterification was removed. Xylene was removed under vacuum in CO₂ atmosphere. The reaction mixture was heated at 180-190°C for 90 min under 50 mm Hg pressure in a stream of CO₂, until the required acid number was reached. This resin (70 g) was mixed with styrene (30 g) in the presence of 0.02% p-tert.-butyl catechol, 0.02% UV light absorber and 0.005% hydroquinone.

Preparation of polyester 2 based on chlorendic acid and isophthalic acid—A mixture of isophthalic acid (99.5 g, 0.6 mole), propylene glycol (99 g, 1.3 mole) and p-toluene sulphonamic acid (0.5 g) was refluxed at 160°C and 21.6 ml water of esterification was removed as above. After this, chlorendic acid (156 g, 0.4 mole), propylene glycol (64 g, 0.82 mole) and xylene (100 ml) were added to the flask and the temperature was again brought to 140°C; 14.4 ml water of esterification was collected. Maleic anhydride (98 g) was added to the resulting reaction mixture and the temperature was again raised to 140°C; 18.0 ml water of esterification was removed. Xylene was removed and the polycondensation was carried out to give a base resin of the required acid number. This resin (70 g) was mixed with styrene (30 g), as described earlier.

Preparation of polyester 3 based on chlorendic acid and isophthalic acid—A mixture of isophthalic acid (66.4 g, 0.4 mole), propylene glycol (64.5 g, 0.85 mole) and p-toluene sulphonamic acid (0.25 g) was refluxed at 160°C and 14.4 ml water of esterification was removed as described earlier. After this, chlorendic acid (234 g, 0.6 mole), propylene glycol (96 g, 1.26 mole) and xylene (150 ml) were added and the mixture was heated to 140°C; 21.6 ml water of esterification was collected. Maleic anhydride (98 g, 1 mole) was added to the resulting solution and the mixture was again refluxed at 140°C; 28 ml water of esterification was removed. Xylene was removed and polycondensation was done to get the polyester of the required acid number in the same manner as above. This resin (70 g) was mixed with styrene (30 g) as described earlier.

Preparation of polyester 4 based on chlorendic acid and isophthalic acid—In the same manner as above, a mixture of isophthalic acid (33.2 g, 0.2 mole), propylene glycol (32.25 g, 0.425 mole) and p-toluene sulphonamic acid (0.125 g) was refluxed at 160°C and 7.2 ml water of esterification was removed. After this, chlorendic acid (312 g, 0.8 mole), propylene glycol (128 g, 1.68 mole) and xylene (125 ml) were added and the temperature was brought to 140°C; 28.8 ml water of esterification was collected. Then maleic anhydride (98 g, 1 mole) was added to the resulting solution and the temperature was again raised to 140°C; 18 ml water of esterification was removed. Xylene was removed and polycondensation was carried out to give a base resin of the required acid number. This resin (70 g) was mixed with styrene (30 g) as above.

Determination of gel time and peak exotherm—A test tube (19 x 72.5 mm) was filled with the resin containing 1% benzoyl peroxide to a height of 3 cm. The test tube was placed in a constant temperature bath (180°C). The sulfonamide gel time, which is the time interval for the temperature of the resin to rise from 150°F to 190°F, was noted. The peak isotherm values obtained are given in Table 1.

Determination of acid value¹—About 2.5 g polyester resin was dissolved in 50 ml benzoyl alcohol. This solution was titrated against standard alcoholic KOH using methyl red as indicator. The acid value was calculated as follows.

\[
\text{Acid value} = \frac{56.1 \times NV}{W}
\]

where \(N\) is the normality of alcoholic KOH; \(V\), the volume (ml) of KOH used; and \(W\), the weight of the resin taken.

The results are given in Table 1.

Determination of viscosity²—The viscosity of 70% solution of resin in styrene was determined with the help of a Gardener tube. In this case, the Gardener tube was filled with the syrupy resin up to the lower mark on it. It was corked up to the upper mark and was kept vertically in a thermostat maintained at 30°C. The tube was inverted and the time taken for the air bubble to come up was recorded. Corresponding to this time, the viscosity of the resin was noted from the Gardener graph. The results are given in Table 1.

Rate of hydrolysis of base polyester resins²—Ten flasks of 100 ml capacity were charged with 0.5 g of the base resin each and were clamped in a thermostat maintained at 50°C. To each flask, 10 ml of a sodium hydroxide solution previously heated to 50°C was added with constant shaking. After known time intervals, the flasks were taken out and an excess of a standard sulphuric acid solution was added to stop the reaction. The excess of acid left was back titrated against standard alkali. From the amount of alkali consumed to hydrolyse the resin, the rate of hydrolysis was determined. The results are given in Table 1.

Preparation of test specimen for testing the rate of flammability, vicat softening point and heat distortion point—The resin mixture containing 70 g polyester resin, 30 g styrene, 1 ml methyl ethyl ketone peroxide, and 0.3 ml cobalt octoate was poured into suitable
over 55% chlorine by weight and is used in the preparation of self-extinguishing resins without additional fire retardant additives. Many halogen containing dicarboxylic acids or glycols can be prepared by Diels-Alder reaction in addition to chlorendic acid. However, chlорendic acid seems to have the greatest industrial significance because of the greater overall economy resulting from its use. The acid can be incorporated into an unsaturated polyester resin by conventional polycondensation, although the reaction temperature is best maintained below 180°C because of the tendency to develop colour at high temperature. The double bond in chlорendic acid does not enter into the crosslinking reaction.

Unsaturated polyester having structures similar to those of polymers obtained by the esterification of chlорendic acid or anhydride can be obtained by reacting hexachlorocyclopentadiene with a highly

stainless steel moulds of 12.7 x 1.27 x 1.27 cm and 12.7 x 1.27 x 0.32 cm sizes. Then the resin was allowed to cure at room temperature and later post-cured at 100°C by infrared lamps for 30 min.

**Discussion**

The best known and most widely used of the fire retardant polyester resins are based on chlорendic acid or anhydride. The anhydride is prepared by Diels-Alder reaction of hexachlorocyclopentadiene with maleic anhydride (Eq. 1). Chlорendic acid contains

\[
\text{Cl}_2 \text{C} = \text{O} + \text{CH}_2 = \text{O} \rightarrow \text{Cl}_2 \text{C} = \text{O} \text{Cl} \text{C}-\text{CCl}_2 \text{C} \text{OH} \ldots (1)
\]

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**Table 1—Composition and Characteristics of Polymers Based on Chlorendic Acid and Isothiophenic Acid**

<table>
<thead>
<tr>
<th>Composition</th>
<th>Characteristics</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acid Chloride</td>
<td>Molar ratio</td>
</tr>
<tr>
<td>Chlорendic acid</td>
<td>0.2</td>
</tr>
<tr>
<td>Isothiophenic acid</td>
<td>0.6</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Polyester No.</th>
<th>Acid Chloride mole</th>
<th>Molar ratio</th>
<th>Acid to unsaturated molecule</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.2</td>
<td>1.7</td>
<td>1.7</td>
</tr>
<tr>
<td>2</td>
<td>0.4</td>
<td>0.4</td>
<td>0.4</td>
</tr>
<tr>
<td>3</td>
<td>0.6</td>
<td>0.6</td>
<td>0.6</td>
</tr>
<tr>
<td>4</td>
<td>0.8</td>
<td>0.8</td>
<td>0.8</td>
</tr>
</tbody>
</table>

*All four resins contained 1 mole of maleic anhydride and 2.2 moles of propylene glycol along with ingredients tabulated above.*
unsaturated polyester, such as polypropylene maleate

\[
\text{Cl}_2\text{C}_2\text{Cl}_2 + \left[ \text{CH}_2\text{CH}_2\text{OOCH} + \text{CH}_2\text{COOCH}_2 + \text{CH}_3 \right]
\]

Enough residual unsaturation is allowed to remain in the polymer backbone, so that the unsaturated polyester may be cured in the conventional manner with styrene or other monomers to yield compositions having satisfactory physical properties. But the solubility of the polyesters thus prepared in vinyl monomers like styrene is very low due to non-similarity of the structure of styrene to that of the polyester. Therefore, for making a homogeneous solution, more of styrene is required. Thus, the fire retardancy of these polyesters decreases with increase in styrene content. The other inherent disadvantages of polyesters based on chlorendic acid are their rather poor light, weather and thermal stability. To a certain extent, these drawbacks have been overcome by the addition of additives like antimony trioxide and stabilizers. But these impair the physical properties. Efforts have been directed to modify the structure of chlorendic acid to overcome these drawbacks. Roberts et al.\textsuperscript{10} postulated that the poor stability of chlorendic acid based polyesters is due to the two carbonyl activated alpha hydrogens. Attack on these hydrogen atoms would lead readily to the elimination of hydrogen chloride and splitting up of the endo methylene bridge. In the presence of oxygen, this bridge would yield phosgene and also eventually hydrogen chloride. It was further postulated that if the hydrogen could be removed or substituted by some non-reactive species, greater thermal and oxidative stability should result. It was pointed out that in the adduct of tetrahydrophthalic anhydride and hexachlorocyclopentadiene, the two alpha hydrogens would not be activated by the carbonyl groups or be adjacent to bridge-head chlorine atoms and thus polyesters of improved stability should result. Robert and coworkers prepared a series of resins from tetrahydrophthalic anhydride hexachlorocyclopentadiene adduct and compared their thermal properties. The effect of thermal treatment at 200°C for 7 days on weight loss and thermal strength of castings prepared from resins based on the adduct and THPA-BCP are evident from the data presented in Table 2.

The result in Table 2 indicate that there is no improvement in thermal stability with the addition of the adduct. To overcome the above-mentioned drawbacks of chlorendic acid based polyesters, in the present study, part of the chlorendic anhydride in the polyester chain was replaced by isophthalic acid. Isophthalic acid-containing polyesters are known for their thermal stability, light stability, chemical resistance and weatherability. For finding the optimum level of replacement of chlorendic acid by isophthalic acid for attaining high thermal stability, four different formulations were made by varying the molar ratio of chlorendic acid to isophthalic acid.

For preparing these isophthalate resins, first a diester of isophthalic acid and 1,2-propylene glycol was prepared using 0.2% p-toluenesulphonic acid as catalyst and heating the mixture to 160°C. In this manner, the whole of isophthalic acid having very low reactivity could be made to react. The monomeric diester was reacted successively with chlorendic anhydride and maleic anhydride in the presence of the required amount of propylene glycol, xylene as entrainer and p-toluenesulphonic acid as catalyst. It gave a pale amber coloured solid which was readily soluble in the styrene monomer. At the same time, the above polyester was prepared in one step. It did not dissolve in styrene easily and had black colour. This was corroborated by Lopatik et al.\textsuperscript{11}. It may be attributed to uniform distribution of various monomers in the chain, completion of the reaction of raw materials and reduction in the period of heating of the heat sensitive monomers like chlorendic acid by stepwise condensation. In this manner, polyesters 1, 2, 3 and 4 were synthesized keeping the molar ratio of chlorendic acid to isophthalic acid as 1:4, 2:3, 3:2 and 4:1 respectively.

Seventy parts by weight of the above polyesters were dissolved in 30 parts by weight of styrene. They were studied for viscosity, gel time and peak exotherm (Table 1). Their solubility in styrene varied, depending on the percentage of chlorendic acid in the polyester. It was observed that the molar proportion of styrene used to give a solution of a suitable viscosity range (800-1300 cp) and to overcome unsaturation of the polyester increased with increase in chlorendic acid content. This
may be attributed to the non-similar structure of the base polyester containing chlorendic acid as compared to that of styrene.

The SPI gel time of these resins does not vary appreciably. But their peak exotherms vary from 132 to 145°C. The peak exotherms of polyesters 1, 2, 3 and 4 are 132.2, 135, 145 and 137.7°C respectively. The heat distortion points of these resins after crosslinking and curing are also in the same order as the peak exotherm; for polyesters 1, 2, 3 and 4 they are 68.5, 75, 88 and 84°C respectively. According to Parker and Moffett, the heat distortion point and the peak exotherm increase with increase in the mole % unsaturation and the quantity of styrene. Johnson et al. pointed out that excess of styrene lowers the heat distortion point. Funke and Hamman consolidated the ideas of various workers about crosslinking density and stated that there is an optimum molar ratio of the unsaturated monomer to unsaturation in the polyester for optimum crosslinking and the resultant cured products have high peak exotherms and heat distortion points. It is usually less than 2. Therefore, the above mentioned data for peak exotherm and heat distortion point lead to the conclusion that the optimum molar ratio of styrene to unsaturation in polyesters based on chlorendic acid is 2.1 to give the maximum peak exotherm and heat distortion point for polyester 3. This is further corroborated by the value of vicat softening point and the rate of flammability data (Table 1). The vicat softening points for polyesters 1, 2, 3 and 4 are 220, 250, 280 and 276°C respectively. The rates of flammability for polyesters 1, 2, 3 and 4 are 0.55, 0.43, 0.21 and 0.21 in/mil respectively.

For polyester 3, vicat softening point and rate of flammability are optimum. The high rate of flammability of polyesters 1 and 2 may be due to less crosslinking because of the insufficient quantity of styrene and low chlorine content compared to polyester 3.

The rates of hydrolysis of the base polyesters 1, 2, 3 and 4 are $3.0 \times 10^{-2}$, $1 \times 10^{-2}$, $8.93 \times 10^{-3}$ and $9.0 \times 10^{-3}$ 1 mol$^{-1}$ sec$^{-1}$ respectively. The rate of hydrolysis decreases as the chlorendic acid content increases in the polyester chain. This may be attributed to the steric protection of ester linkage by the bulky chlorendic acid group.

**Conclusion**

The results of the present study indicate that stepwise condensation helps in improving the colour of the resin by reducing the heating period of a heat sensitive monomer like chlorendic acid; in ensuring uniform distribution of the monomers over the length of the polyester chain, and in making the monomer of high melting point, low solubility and low reactivity to react fully by reacting it first with another relevant monomer taken in excess, e.g. for incorporating isophthalic acid in the resin, it can be reacted completely with 1,2-propylene glycol taken in excess as the first step.

Besides the selection of proper monomers for making heat and flame resistant polyesters, optimization of crosslinking and elimination of the formation of homopolymer by vinyl monomer also help. Therefore, it is essential to establish the optimum molar ratio of the vinyl monomer to the unsaturation present in the polyester chain. It is 2.1 for chlorendic acid based polyesters.

Incorporation of a bulky monomer like chlorendic acid in the polyester chain helps in imparting hydrolytic stability to the polyester.

On the whole, polyester 3 has the best combination of properties with respect to thermal stability, flame resistance and hydrolytic stability in the present series of polyester resins.

**References**