Thermal Stabilisation of Polyvinylchloride: Effect of Rubber Seed Oil Derivatives on the Thermal Degradation of Polyvinylchloride

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Thermal degradation of polyvinylchloride is studied under non-oxidative and oxidative conditions in the presence of epoxidised rubber seed oil and metal soaps of the oil. Changes in intrinsic viscosity and in the levels of unsaturation in the degraded polymer samples are used to assess the effect of the rubber seed oil derivatives on the thermal degradation of polyvinylchloride. It is found that the metal soaps of epoxidised rubber seed oil markedly reduce the level of unsaturation in the degraded polymer sample and the extent of polymer chain scission which is accompanied by dehydrochlorination. The stabilising ability of the rubber seed oil derivatives is compared with that of Jatropha seed oil.

Introduction

Polyvinylchloride (PVC), is an important commercial polymer. A major disadvantage in the manufacture and use of PVC is its low thermal stability. At elevated temperatures well below its decomposition temperature, PVC loses HCl and discolours, leading to deterioration in the properties of the polymer. Several workers have reported on the degradation and stabilisation of PVC. Thermal degradation of PVC is generally considered to be initiated at unstable sites, particularly tertiary and allylic chlorides, within the polymer. Although structural irregularities within PVC considerably increase the initial rate of elimination of HCl it has been argued that on account of the low concentration in normal PVC of these structural irregularities that initiation of thermal degradation also takes place at regular monomer sequence.

The poor thermal stability of PVC requires the use of heat stabilisers in the processing of the polymer. Heat stabilising additives have been suggested to prevent or retard dehydrochlorination in a several ways. Their proposed mechanism of action includes HCl scavenging and the replacement of labile chloride atoms within PVC with stabiliser moieties that are more stable to heat treatment. The latter mechanism was first proposed by Frye and Horst. Additives that have found practical application as thermal stabiliser for PVC include metal soaps of carboxylic acids, organometallic compounds and inhibitors of radical chain reactions. More recently, interest has been shown in the use of epoxides as co-stabiliser in PVC formulations. This study is a part of an on-going study aimed at the development of value-added products from local resources and evaluates the application of epoxidised rubber seed oil and its metal soaps as thermal stabiliser for polyvinylchloride.

Materials and Methods

Polyvinylchloride (BDH) (Mn 1.0 x 10^5; particle size 100 per cent pass BS 60 mesh, 74 per cent pass BS 200 mesh) was purified by solution in THF/acetone mixture and precipitation with constant stirring in excess of methanol. The precipitated polymer was filtered off after 24h, washed with methanol and air-dried. Rubber seed oil (RSO) was obtained from the Rubber Research Institute of Nigeria, Benin. The oil was mechanically extracted from seeds collected within a period of 1y. The physico-chemical and fatty acid composition of RSO is shown in Table 1.

Epoxidation of Rubber Seed Oil

Epoxidation of RSO was carried out at 29°C using peracetic acid prepared in situ by reacting hydrogen peroxide (30 per cent v/v) with glacial acetic acid. The level of epoxidation was determined using the method described by Durberaki. The epoxidised
rubber seed oil, (ERSO), was stored at 7°C until required. Detailed kinetic studies on the epoxidation of RSO and subsequent cleavage of the oxirane ring by acetic acid have been reported by Aigbodion et al.25.

Preparation of Metal Soaps of Rubber Seed Oil

Metal soaps were prepared from RSO and ERSO by metathesis in alcohol solution23,24. The sodium soaps of the oils were first prepared by dissolving the oil sample (9.2 g) in 50 ml of hot ethanol followed by treatment with 20 ml of 20 wt per cent sodium hydroxide solution. To this mixture, 100 ml of 30 wt per cent solution of the metal salt were slowly added with continuous stirring. The precipitated metal soap was washed with hot water and air-dried.

Degradation

Thermal degradation was carried out using PVC powder in the presence of 10 wt per cent RSO and ERSO and 3 wt per cent of the metal soaps of the oils. The polymer sample (1.5 g) was mixed thoroughly with the appropriate amount of the additive and transferred to a degradation tube. The tube was connected to a source of nitrogen maintained at a flow rate of 60 ml/min. The degradation tube was immersed in a thermostat oil bath controlled at 190 ± 1°C. Degradation was allowed to proceed for 30 and 60 min at the end of which the degradation tube was cooled and the contents dissolved in cyclohexanone and poured into excess of methanol. The precipitated PVC was filtered off, washed several times with methanol, dried in a vacuum at room temperature, and stored in the dark.

Thermoxidative degradation studies were carried out in air as described for non-oxidative degradation.

Viscosity Measurements

Viscosity measurements of undegraded and degraded PVC samples were carried out in cyclohexanone solution at 30°C. The intrinsic viscosities and Huggins’ interaction constant of the polymer samples were determined using the relationship:

\[ \eta_0/ C = [n] + K_1[n]^2 C \]

The ratios of the intrinsic viscosity of PVC samples degraded in the presence of the rubber seed oil derivatives to the viscosity of the undegraded polymer sample, \([\eta]/[\eta]_0\), were used to assess the effect of the additives on the degradation of PVC.

Levels of Unsaturation in Polymer Samples

The levels of unsaturation in the undegraded and degraded PVC samples were estimated from their iodine values determined by the Wij’s method25.

Results and Discussion

Non-oxidative Degradation

The values of intrinsic viscosity and Huggins’ interaction constant for the degraded PVC samples are shown in Table 2. It has been reported26 that the intrinsic viscosity of PVC undergoing thermal degradation decreases initially to a minimum and then increases with further increase in the number of conjugated double bonds in the polymer. Therefore, if the extent of dehydrochlorination is kept low, changes in the value of intrinsic viscosity can be taken as estimates of the extent of degradation in which case, the values of relative intrinsic viscosity \([\eta]/[\eta]_0\), where \([\eta]_0\) is the intrinsic viscosity of undegraded PVC, can be used to assess the effect of rubber seed oil derivatives on the degradation process. The reactions that may accompany thermal dehydrochlorination of PVC include chain scission and cross-linking; the latter leading to \([\eta]/[\eta]_0\), values > 1 and the former to values < 1. Thus, closer the values of relative intrinsic viscosity to unity the greater the stabilising ability of the additive. The results in Table 2 show that the values of \([\eta]/[\eta]_0\) are < 1, suggesting that chain scission is the predominant reaction accompanying thermal
Table 2 — Viscosity parameters for PVC degraded at 190°C in the presence of rubber seed oil derivatives

<table>
<thead>
<tr>
<th>Additive</th>
<th>Period of degradation (min)</th>
<th>Intrinsic viscosity $[\eta]$ (dl/g)</th>
<th>Huggins' constant $K$</th>
<th>Relative intrinsic viscosity $[\eta]/[\eta]_0$</th>
</tr>
</thead>
<tbody>
<tr>
<td>None</td>
<td>30</td>
<td>0.45</td>
<td>35.70</td>
<td>0.41</td>
</tr>
<tr>
<td></td>
<td>60</td>
<td>0.56</td>
<td>39.54</td>
<td>0.33</td>
</tr>
<tr>
<td>RSO (10 wt per cent)</td>
<td>30</td>
<td>0.67</td>
<td>18.80</td>
<td>0.61</td>
</tr>
<tr>
<td></td>
<td>60</td>
<td>0.40</td>
<td>42.25</td>
<td>0.36</td>
</tr>
<tr>
<td>ERSO (10 wt per cent)</td>
<td>48 per cent epoxidation</td>
<td>0.72</td>
<td>14.42</td>
<td>0.65</td>
</tr>
<tr>
<td></td>
<td>10.6 per cent epoxidation</td>
<td>0.81</td>
<td>12.35</td>
<td>0.74</td>
</tr>
<tr>
<td>Metal soaps of RSO (3 wt per cent)</td>
<td></td>
<td>0.68</td>
<td>14.78</td>
<td>0.62</td>
</tr>
<tr>
<td>Barium soap</td>
<td>30</td>
<td>0.80</td>
<td>12.59</td>
<td>0.73</td>
</tr>
<tr>
<td>Cadmium soap</td>
<td>60</td>
<td>0.64</td>
<td>16.88</td>
<td>0.58</td>
</tr>
<tr>
<td>Lead soap</td>
<td>30</td>
<td>0.57</td>
<td>21.88</td>
<td>0.52</td>
</tr>
<tr>
<td></td>
<td>60</td>
<td>0.81</td>
<td>6.88</td>
<td>0.91</td>
</tr>
<tr>
<td>Metal soaps of ERSO (3 wt per cent)</td>
<td></td>
<td>0.64</td>
<td>16.88</td>
<td>0.58</td>
</tr>
<tr>
<td>Barium soap</td>
<td>30</td>
<td>0.90</td>
<td>8.11</td>
<td>0.82</td>
</tr>
<tr>
<td>Cadmium soap</td>
<td>60</td>
<td>0.90</td>
<td>8.11</td>
<td>0.82</td>
</tr>
<tr>
<td>Lead soap</td>
<td>30</td>
<td>0.59</td>
<td>21.63</td>
<td>0.54</td>
</tr>
<tr>
<td></td>
<td>60</td>
<td>0.99</td>
<td>7.02</td>
<td>0.90</td>
</tr>
</tbody>
</table>

$[\eta]_0 = \text{Intrinsic viscosity of undegraded PVC} = 1.10$

dehydrochlorination of the PVC samples. Table 2 shows that the values of relative intrinsic viscosity are highest for PVC degraded in the presence of metal soaps of epoxidised rubber seed oil and lowest for the sample degraded in the absence of the additives which indicates a stabilising effect. Results reveal (Table 2) that the stabilising ability of the metal soaps of epoxidised rubber seed oil is higher than that for the soaps of the unepoxidised oil. The metal soaps of the epoxidised rubber seed oil are thought to exhibit combined effects of the epoxy group (HCl scavenger) and of the metal soap (substitution of labile chlorine atoms within PVC additive moieties) in stabilising PVC against thermal degradation.

The levels of unsaturation in PVC samples degraded at 180°C for 30 min in the presence of the rubber seed oil derivatives are shown in Table 3. The iodine values for PVC samples degraded in the presence of rubber seed oil derivatives varied from 58.17 for PVC stabilised with epoxidised rubber seed oil (with 4.6 per cent epoxide content) to 29.08 for PVC stabilised with lead soap of rubber seed oil. These results represent a decrease of between 5.83 per cent and 52.91 per cent in iodine value relative to the value obtained for unstabilised PVC. The elimination of HCl during thermal degradation of PVC leads to the formation of olefinic double bonds in the polymer molecule. Therefore, provided that the extent of degradation is low, and dehydrochlorination is not accompanied by secondary reactions involving the double bonds, measurement of the level of unsaturation in the degraded polymer sample should provide satisfactory estimate of the relative stabilising ability of additives. The ratio of the iodine value of degraded PVC sample to the value of undegraded sample, $IV/IV_0$, can, therefore, be used to assess the relative
effect of the rubber seed oil derivatives on the thermal degradation of PVC: the smaller the IV/IV₀ value the greater the relative stabilising ability of the additive. The results in Table 3 show that the addition of metal soaps of rubber seed oil to PVC reduced the level of unsaturation in the degraded polymer sample.

Thermoxidative Degradation

The viscosity parameters and levels of unsaturation of PVC samples degraded in air at 190°C in the presence of metal soaps of rubber seed oil are shown in Table 4. The results show that the values of intrinsic viscosity of the degraded PVC samples are lower than the value for the undegraded sample. It can be seen from Table 4 that whereas the value of intrinsic viscosity of the PVC sample degraded without the additives is only about 30 per cent of the value of the undegraded sample, the values of intrinsic viscosity of PVC samples degraded in the presence of metal soaps of rubber seed oil are much higher with values of between 60 and 90 per cent of the value of the undegraded sample. These results indicate that the metal soaps of rubber seed oil exert stabilising effect on the oxidative thermal degradation of PVC. The Huggins' constant is generally used as a measure of polymer-solvent and polymer-polymer interaction. In conjunction with intrinsic viscosity values the Huggins' constant, being a parameter indicative of variations in intermolecular forces, provides an overall view of macromolecular conformation and behaviour in solution.

Table 3 — Levels of unsaturation in PVC samples degraded at 180°C in the presence of rubber seed oil derivatives for 30 min.

<table>
<thead>
<tr>
<th>Additives</th>
<th>Iodine value (IV) (g/l/100g)</th>
<th>Relative iodine value (IV)/IV₀</th>
</tr>
</thead>
<tbody>
<tr>
<td>None</td>
<td>61.76</td>
<td>6.50</td>
</tr>
<tr>
<td>RSO (10 wt per cent)</td>
<td>55.24</td>
<td>5.81</td>
</tr>
<tr>
<td>ERSO (10 wt per cent)</td>
<td>58.17</td>
<td>6.12</td>
</tr>
<tr>
<td>4.8 per cent epoxide content</td>
<td>48.47</td>
<td>5.10</td>
</tr>
<tr>
<td>10.6 per cent epoxide content</td>
<td>38.77</td>
<td>4.08</td>
</tr>
<tr>
<td>Metal soaps of RSO (3 wt per cent)</td>
<td>35.55</td>
<td>3.74</td>
</tr>
<tr>
<td>Barium soap</td>
<td>29.08</td>
<td>3.06</td>
</tr>
<tr>
<td>Cadmium soap</td>
<td>10.6</td>
<td>9.08</td>
</tr>
</tbody>
</table>

The iodine value obtained for PVC samples degraded in the presence of rubber seed oil derivatives are markedly lower, by as much as 85 iodine value units, that the corresponding value for the PVC sample degraded in the absence of the additives. It can be seen that relative iodine value, IV/IV₀, varied from about 18.0 for PVC sample degraded in the absence of rubber seed oil additives to about 9.0 for PVC sample degraded in the presence of cadmium soap of rubber seed oil. These results indicate that the rubber seed oil derivatives stabilise PVC against oxidative thermal degradation.

Table 5 shows the viscosity parameter for PVC samples degraded in the presence of metal soaps of...
epoxidised rubber seed oil (ERSO), and epoxidise Jatropha seed oil (EJISO). It can be seen that at comparable levels of epoxidation and in the presence of similar metal soaps of the epoxidised oils the values of \([\eta]/[\eta]_0\) obtained with PVC samples degraded with Jatropha seed oil derivatives are higher than the values obtained for PVC degraded with rubber seed oil derivatives. These results indicate that the derivatives of Jatropha seed oil are relatively more effective in stabilising PVC against thermal degradation than derivatives of rubber seed oil. It has been suggested that the nature of the hydrocarbon portion of the fatty acid component of vegetable oils may influence PVC stability by altering the polymer-matrix polarity\(^\text{12}\) although the exact nature of the effect is not fully understood. In a previous study\(^\text{27}\) it was reported that metal soaps of rubber seed oil were more effective than the corresponding soaps of unsaturated fatty acids (oleic and linoleic acids) in stabilising PVC against thermal degradation and explanations in terms of the contribution of the chemical identity of the hydrocarbon moiety of the soaps, to the overall stabilisation process were proffered. The relatively high level of C\(_{18}\) unsaturated fatty acid content of rubber seed oil (64.23 per cent) may account for the observed lower stabilising ability of derivatives of
rubber seed oil. The unsaturated fatty content of Jatropha seed oil is 41.71 per cent \(^{28}\) while that of rubber seed oil is about 80 per cent.

**Conclusion**

This study shows the relative effectiveness of rubber seed oil derivatives as thermal stabiliser for PVC. The results indicate a potential for the application of epoxidised rubber seed oil and its metal soaps as thermal stabilisers in PVC formulations.

**References**


