

Studies in the Thermal Degradation of Poly(vinyl chloride)

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SYNOPSIS

Thermal degradation of poly(vinyl chloride) (PVC) was studied in nitrogen atmosphere in the presence of rubber seed oil and epoxidized rubber seed oil, barium and lead soaps of rubber seed oil, and epoxidized seed oil at various temperatures. The rate of dehydrochlorination at 1% degradation and the time required to attain 1% degradation were used to assess the effect of the additives on the thermal susceptibility of PVC to dehydrochlorination. It was found that epoxidized rubber seed oil, the metal soaps of rubber seed oil, and epoxidized rubber seed oil markedly enhance the thermal stability of PVC. The order of increasing stabilizing influence was metal soaps of epoxidized rubber seed oil > metal soaps of rubber seed oil > epoxidized rubber seed oil > rubber seed oil. © 1993 John Wiley & Sons, Inc.

INTRODUCTION

Poly(vinyl chloride) (PVC) is an important technical polymer. One of the problems associated with the manufacture and use of PVC is its low thermal stability. At elevated temperatures, well below its melting point, PVC loses HCl and becomes discolored, leading to the deterioration of properties. The thermal degradation of PVC is now understood to be initiated at unstable sites in the structure of the polymer. The poor thermal stability of PVC requires the use of heat stabilizers in the processing of the polymer. Several workers have reported on the degradation and stabilization of PVC.¹⁻¹⁰ It is generally understood that heat stabilizers function by replacing labile atoms in PVC, modifying chain reaction, and thus inhibiting the elimination of HCl and interrupting conjugated polyene sequences. Additives that have found practical application as thermal stabilizers for PVC include metal salts of inorganic and organic acids, organometallic compounds, and inhibitors of radical chain reactions. More recently, interest has been shown in the use of epoxides (including epoxides of vegetable oils) in the thermal stabilization of PVC.^{11,12}

Rubber seed oil (RSO) is obtained from the seeds of the plant *Hevea brasiliensis*. Chemical analysis

shows that RSO has the following characteristics:¹³ specific gravity 0.9185, refractive index 1.4, and iodine value 145.8, and contains oleic acid (23%), linoleic acid (33%), linolenic acid (23%), and saturated acids (20%). At present, rubber seed has no commercial value in Nigeria. This paper is part of a continuing materials sourcing study and examines the effect of RSO and some of its derivatives on the susceptibility of PVC to thermal dehydrochlorination.

EXPERIMENTAL

Materials

Poly(vinyl chloride) (PVC) (BDH) (\bar{M}_n 1.0×10^5), particle size of 100% passes B.S 60 mesh and 74% passes B.S 200 mesh, was purified by solution in THF/acetone and precipitated, with constant stirring, in a large excess of methanol. The precipitated polymer was filtered after 24 h, washed with methanol, and air-dried. Rubber seed oil (RSO) was obtained from the Rubber Research Institute of Nigeria, Iyanomon, Benin City.

Epoxidation of Rubber Seed Oil

Epoxidation of RSO was carried out at 29°C using peracetic acid prepared *in situ* by reacting various amounts of hydrogen peroxide (30% v/v) with ex-

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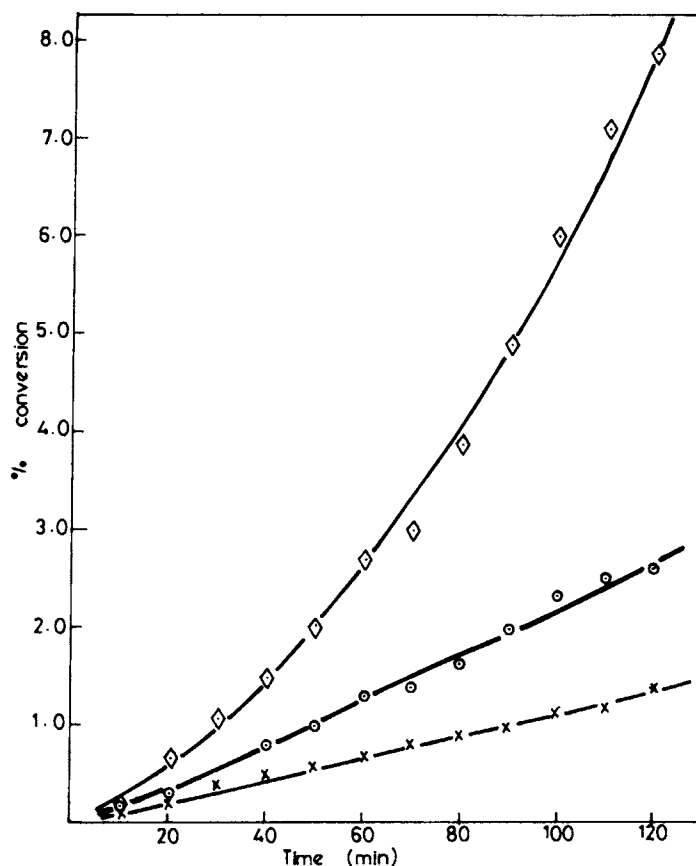


Figure 1 Dehydrochlorination of PVC in the presence of 10% (w/w) RSO at (X) 170°C, (O) 180°C, and (◇) 190°C.

cess glacial acetic acid. The level of epoxidation of RSO was determined by the method described by Durbetaki.¹⁴ The epoxidized rubber seed oil (ERSO) was stored under nitrogen at 7°C until required.

Preparation of Metal Soaps of RSO and ERSO¹⁵

The oil sample (9.2 g) was dissolved in 50 mL of hot ethanol and treated with 20 mL of 20% (w/v) sodium hydroxide solution. To this mixture, 100 mL of 30% (w/v) solution of the metal salt was added slowly with continuous stirring. The precipitated metal soap was washed with hot water and air-dried. Soaps of RSO and ERSO were prepared using $\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$ and $\text{Pb}(\text{NO}_3)_2$.

Dehydrochlorination

Dehydrochlorination studies were carried out using PVC in the presence of 10% (w/w) RSO and ERSO at 170, 180, and 190°C and in the presence of 3% (w/w) metal soaps of RSO and ERSO. The polymer (1.5 g) was mixed thoroughly with the additive in a

mortar and transferred into a degradation tube. The tube was connected to a source of nitrogen maintained at a flow rate of $60 \text{ cm}^3 \text{ min}^{-1}$ and immersed in a thermostated oil heater. The evolved HCl was passed into standard sodium hydroxide solution. The residual concentration of the sodium hydroxide solution determined at regular intervals of time by titration with standard HCl solution provided a measure of the amount of HCl evolved. The amount of HCl evolved was converted to percent conversion of the HCl in the given polymer sample.

RESULTS AND DISCUSSION

The rates of degradation of PVC in the presence of RSO at 170, 180, and 190°C are shown in Figure 1. The rates of dehydrochlorination at 1% degradation were found to be of the same order of magnitude ($10^{-2} \% \text{ min}^{-1}$) but was highest at 190°C ($R_{\text{DH}} 4.29 \% \text{ min}^{-1}$). The time required for degradation to reach 1% conversion varied from 30 min at 190°C to 90 min at 170°C. It can be seen from the results in

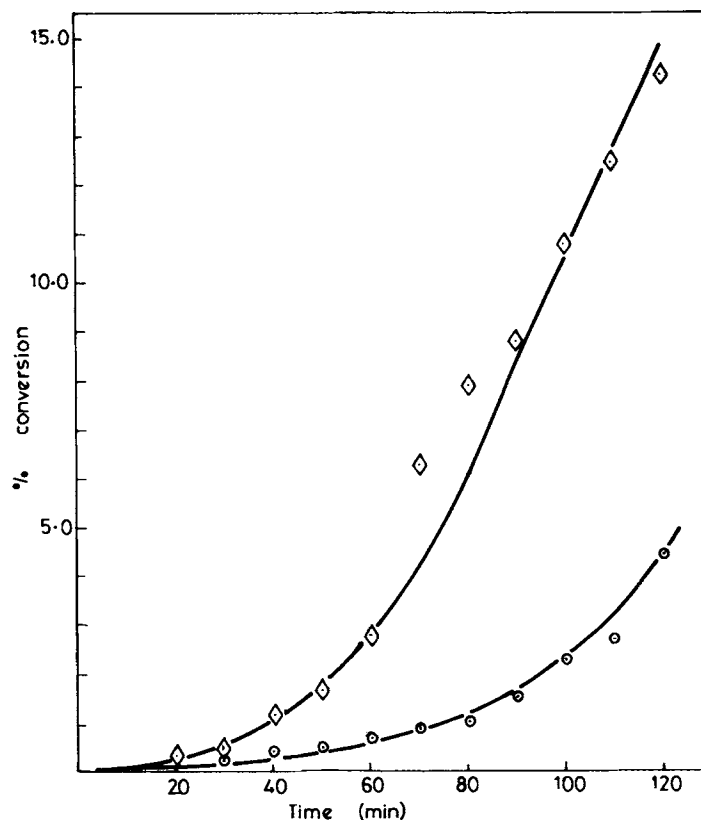


Figure 2 Dehydrochlorination of PVC in the presence of 10% (w/w) of ERSO: (4.8 mol % epoxidized) at (○) 180°C and (◇) 190°C.

Figure 1 that at 190°C the rate of degradation can be divided into two segments: an initial low rate of evolution of HCl (occurring up to about 40 min of degradation) followed by a relatively higher rate of steady evolution of HCl. It is thought that a breakdown in some of the components of RSO at 190°C may lead to products that could accentuate dehydrochlorination. A similar trend was reported for the degradation of PVC in cashew nut shell (CNS) oil.¹⁶

The rates of dehydrochlorination of PVC in the presence of epoxidized rubber oil are shown in Figures 2 and 3. Figure 2 shows the rates of degradation of PVC in the presence of 4.8 mol % ERSO at 180 and 190°C. The rates of dehydrochlorination of PVC at 1% conversion were found to be $3.60 \times 10^{-2}\%$ min^{-1} and 5.83% min^{-1} for degradation of 180 and 190°C, respectively. The time required for degradation to attain 1% conversion was 75 min at 180°C and 40 min at 190°C. Figure 3 shows the results of degradation of PVC in the presence of 10.6 mol % ERSO at 180 and 190°C. The rates of dehydrochlorination of PVC at 1% conversion were $1.35 \times 10^{-2}\%$ min^{-1} at 180°C and $6.13 \times 10^{-2}\%$ min^{-1} at 190°C,

and the time required to dehydrochlorination to reach 1% degradation was 92 min at 180°C and 40 min at 190°C. These results indicate that ERSO exhibits some stabilizing influence on the thermal degradation of PVC and that this influence is exhibited at the early stages of degradation (below 1% conversion). The stabilizing effect of ERSO on the thermal degradation of PVC is considered to result from the facile reaction of HCl with epoxy group to form chlorohydrin, which is thought to reduce the autocatalytic effect of the HCl evolved at the initial stages of dehydrochlorination on the degradation process.

At 1% degradation, the rates of dehydrochlorination of PVC in the presence of ERSO are higher than the rates in the presence of RSO. If ERSO stabilizes PVC against thermal degradation by reacting with the HCl evolved at the initial stages of dehydrochlorination, its effectiveness will depend on the stability of heat of the chlorohydrin formed by the reaction. That the rates of dehydrochlorination at 1% degradation in the presence of ERSO are higher than the rates in RSO indicates that chlorohydrin may not be heat-stable. It can be seen from

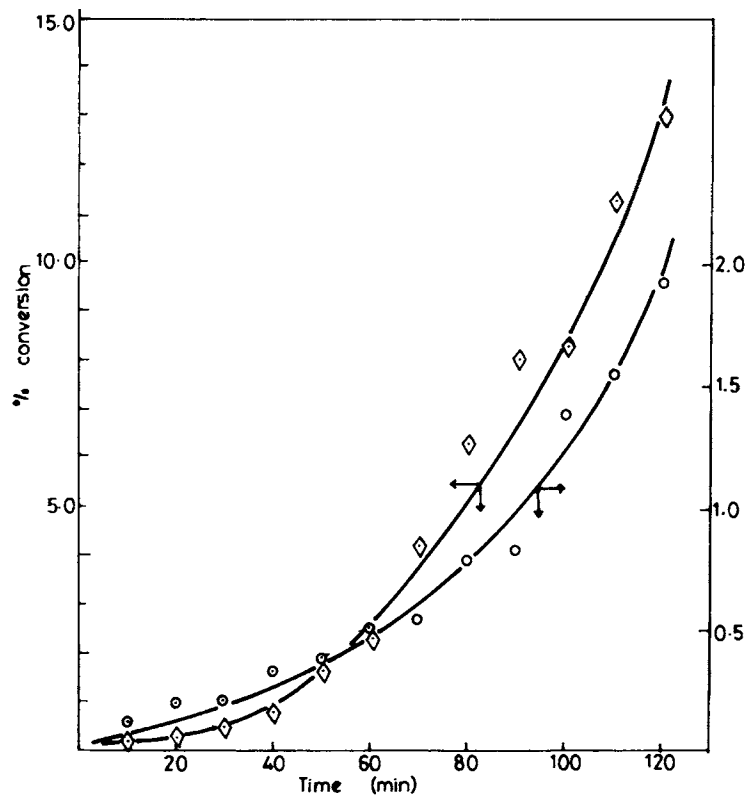


Figure 3 Dehydrochlorination of PVC in the presence of 10% (w/w) of ERSO (10.6 mol % epoxidized) at (○) 180°C and (◇) 190°C.

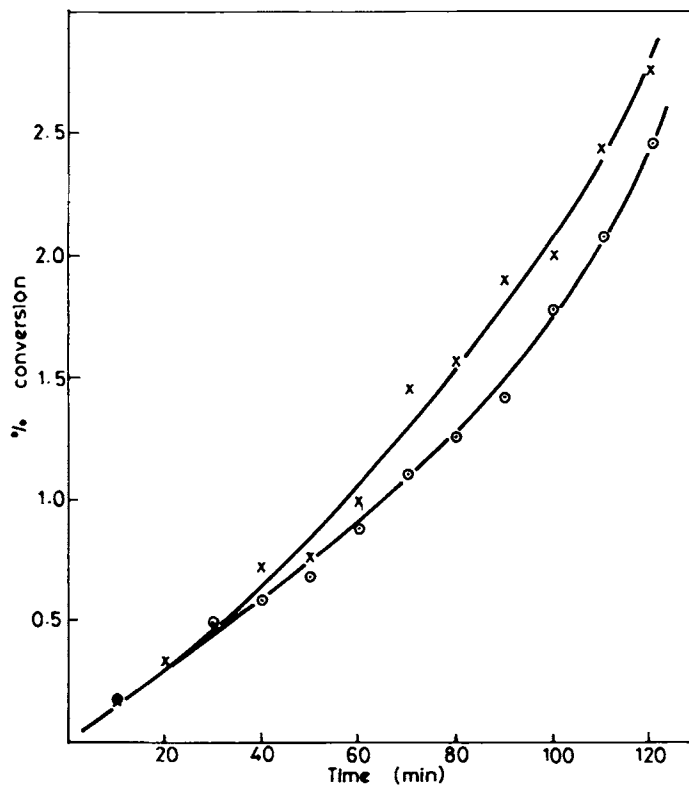


Figure 4 Dehydrochlorination of PVC at 190°C in the presence of 3% (w/w) metal soaps of RSO: (X) barium soap; (○) lead soap.

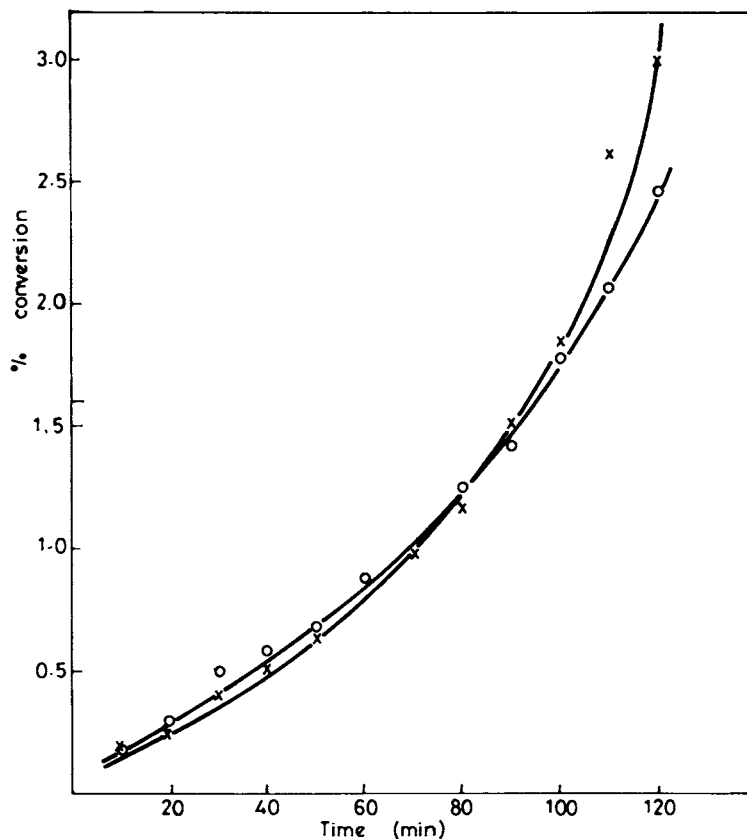


Figure 5 Dehydrochlorination of PVC at 190°C in the presence of 3% (w/w) of metal soaps of epoxidized (10.6% epoxidized) RSO: (X) barium soap; (O) lead soap.

the results in Figures 2 and 3 that the rates of steady evolution of HCl are much higher than those observed for degradation in the presence of RSO.

Figure 4 shows the rates of dehydrochlorination of PVC at 190°C in the presence of 3% (w/w) barium and lead soaps of RSO. The rates of degradation at 1% conversion were found to be $2.14 \times 10^{-2}\% \text{ min}^{-1}$ and $1.80 \times 10^{-2}\% \text{ min}^{-1}$ for the barium soap and lead soap, respectively. The time required for dehydrochlorination to reach 1% degradation was 56 min for the barium soap of RSO and 75 min for the lead soap of RSO. These results clearly indicate that the metal soaps of RSO are more effective in stabilizing PVC against thermal degradation than are ERSO and RSO. The mechanism proposed for the thermal stabilization of PVC by metal soaps is similar to that for ERSO. The observed difference in the effectiveness of the additives (ERSO and metal soaps of RSO) as stabilizers of PVC is thought to be due to the higher stability of the chlorides of the metals to heat than that of chlorohydrin. It can be seen from the results that the lead soap of RSO is more effective than is the barium soap in the sta-

bilization of PVC to thermal degradation. The rates of steady evolution of HCl are much lower in the metal soaps than in ERSO.

The rates of dehydrochlorination of PVC at 190°C in the presence of metal soaps of ERSO are shown in Figure 5. The time required for dehydrochlorination to attain 1% conversion was about 70 min for the barium and lead soaps of ERSO, and the rate of dehydrochlorination at 1% degradation was $1.80 \times 10^{-2}\% \text{ min}^{-1}$ for the barium and lead soaps of ERSO. It was thought that metal soaps of ERSO would show the combined effects of the epoxy group and the metal soap in stabilizing PVC against thermal deterioration. The results from this study show that the metal soaps of ERSO are more effective thermal stabilizers for PVC than is ERSO; they are about as effective as the metal soaps of RSO.

Table I summarizes the dehydrochlorination data obtained from this study. It can be seen from these results that RSO derivatives exert a stabilizing effect on the thermal degradation of PVC and that the lead soap of RSO was the most effective thermal stabilizing additive.

Table I Thermal Degradation of PVC in the Presence of RSO and Some of Its Derivatives

| Additive | Temp (°C) | Time Required for Degradation to Attain 1% Conversion t_{DH} (min) | Rate of Degradation at 1% Conversion R_{DH} (% min ⁻¹) |
|--|--------------|--|--|
| (i) RSO (10% w/w) | 170 | 90 | 2.16×10^{-2} |
| | 180 | 50 | 2.67×10^{-2} |
| | 190 | 30 | 4.29×10^{-2} |
| (ii) ERSO (10% w/w) 4.8 mol % epoxidized | 180 | 75 | 3.60×10^{-2} |
| | 190 | 40 | 5.83×10^{-2} |
| (iii) ERSO (10% w/w) 10.6 mol % epoxidized | 180 | 92 | 1.35×10^{-2} |
| | 190 | 40 | 6.13×10^{-2} |
| (iv) Metal soap of RSO (3% w/w) | | | |
| | | | |
| Barium soap | 190 | 56 | 2.14×10^{-2} |
| Lead soap | 190 | 75 | 1.80×10^{-2} |
| (v) Metal soap of ERSO (3% w/w) | | | |
| | | | |
| Barium soap | 190 | 70 | 1.80×10^{-2} |
| Lead soap | 190 | 70 | 1.80×10^{-2} |

The authors are grateful to the University of Benin for the grant URPC 60/489 to F. E. O.

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Received January 6, 1992

Accepted July 28, 1992