Effect of Rare Earth (Ho, Tb and Dy) Laurates on the Thermal Degradation of Poly (Vinyl Chloride)

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Summary: Non-oxidative thermal degradation of PVC and the effect of (Ho, Tb and Dy) laurates on it was studied using thermogravimetric technique in the temperature range of 150 to 1000°C. It is observed that these metal laurates effectively reduce the dehydrochlorination of PVC. The synergistic effect of combination of these salts was also studied and discussed. Kinetic parameters such as activation energy, order of reaction and Arrhenius factor have been also calculated by the Coats and Horowitz methods. Results show that above mentioned metal laurates increase the activation energy required for the dehydrochlorination of PVC.

Introduction

Poly vinyl chloride (PVC) is one of the most frequently used plastic with many applications in various industrial sections. The wide applicability of PVC is due to its mode of modification by various additives, chemical resistance and low production costs. PVC and its various formations do not burn readily but decompose to give toxic and corrosive products, which constitutes a crucial problem in considering their use. The process of degradation has been studied by various workers and three different mechanisms based on different active centers mainly radical, ionic and molecular have been suggested [1-4]. Stabilizers are used to terminate the unzipping of the chain and to reduce the auto catalytic effect of HCl produced as a result of degradation. Metal carboxylates are extensively used not only as the stabilizers but also as lubricants [5-7]. Metal carboxylates inhibit the evolution of HCl and color formation during the processing of PVC.

The aim of this paper is to study the stabilization effect of various rare earth metal laurates on the dehydrochlorination of PVC in an inert atomosphere.

Results and Discussion

TG curves for PVC and PVC mixed with different metal laurates are reproduced in figure 1. It is evident from the TG curves that the degradation of PVC occurs in two distinct steps. The first weight loss in the temperature region of 180 to 380°C is because of dehydrochlorination of PVC. The second weight loss above the temperature of 380°C is due to the evolution of volatile products which are formed by the cyclization of short polyene linkages [8-11]. The comparison of TG curves for pure PVC and PVC samples containing different metal laurates show that all metal laurates partially reduce the dehydrochlorination of PVC in the temperatu e range of 180 to 270°C. It is also observed that the temperature at which dehydrochlorination starts is also increased. It means that these rare earth metal laurates reduce the catalytic effect of hydrogen chloride on PVC degradation which is due to the interaction of hydrogen chloride with double bond of dehydrochlorinated chain [12-16]. These metals laurates effectively quench hydrogen chloride thus decreasing its availability in the polymer matrix to interact with double bond of dehydrochlorinated polymer chain. Due to this, long polyene linkages self stabilize and the formation of short destabilized polyene linkages decrease. Dehydrochlorination which occurs due to reduced number of destabilized polyene linkages is also decreased.

The kinetic parameters for the dehydrochlorination process were calculated using Horowitz [20] method from the slopes of the plots between $\ln\ln W_o/W$ vs θ using the relationship:-

$$\ln\ln W_o/W = \theta E /RTs^2$$

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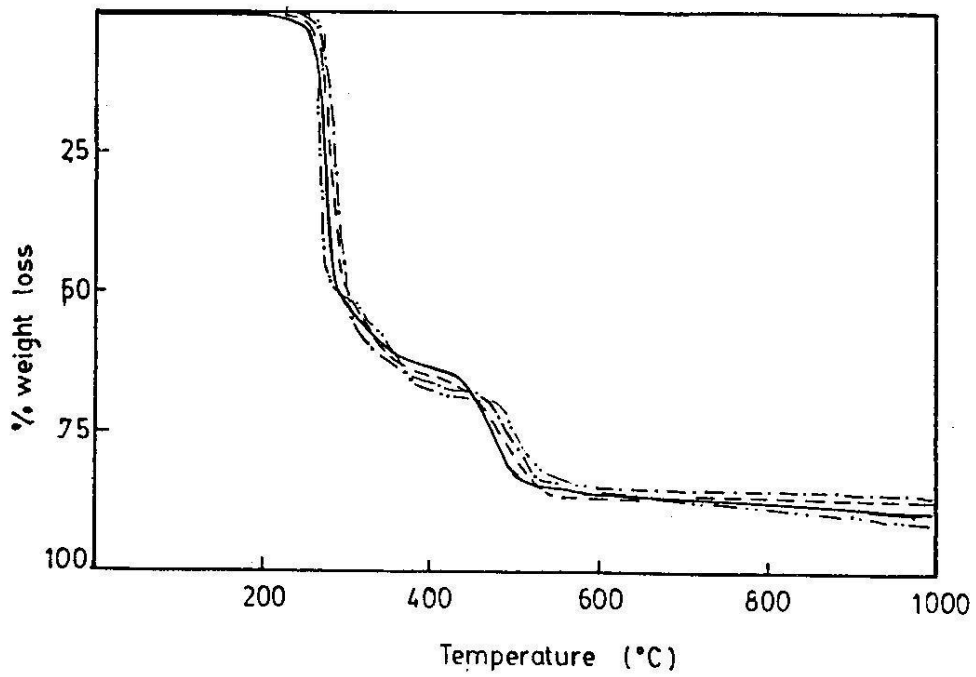

Fig. 1: TG curves for PVC ( ); PVC + Tb- laurate (- - -) PVC + Ho-laurate (-,-,-,); PVC + Dy-laurate (-,,-,,-).

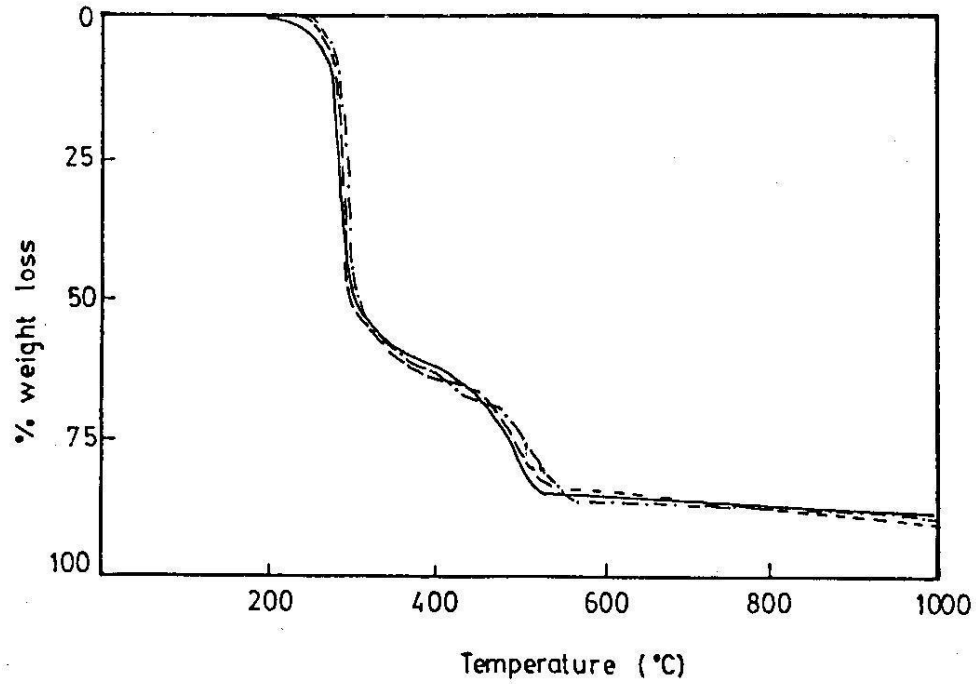

Fig. 2: TG curves for (Tb + Ho)-laurates ( ); PVC + (Dy + Ho) - laurates (- - -); PVC + (Tb + Dy)-laurates (-,-,-).

where: W_o = initial weight: W = weight at temperature T; R = Gas constant: Ts^2 = reference temperature (when ln W/W_o = 1/e = 0.368); θ= Theta (i.e. T-Ts) and E = activation energy.

and Coats's method [21] from the expression:-

$$\log ([1-(1-\alpha)^{1-n}/T^2(1-n)] = \log AR/aE\ [1-2RT/E] = E/2.3RT$$

where : T = temperature (°K); R = Gas constant; A = Arrhenius factor ; a = linear heating rate; n = order of reaction; E = Activation energy of reaction.

The plot of log $(1-(1-\alpha)^{1-n}/T^2(1-n)$ vs 1/T results in a straight line of slope -E/2.3R for the correct value of n.

The values obtained for order of reaction, arrhenius factor and energy of activation are given in Table 1. For pure PVC, the order of reaction for dehydrochlorination was found to be one. Whereas, the activation energy observed are found to be quite close to the value obtained by other workers [22,23]. The small difference in the energy of activation may be due to various factors including particle size of the sample and experimental conditions. This is confirmed by Danforth [24] who studied various PVC samples with different weights and found that the activation energy changes with the size of the sample. The values of order of reaction for PVC samples containing different stabilizers was also found to be in the range of one (Table 1). This suggests that the mechanism of dehydrochlorination is not greatly affected with the addition of these rare earth metal laurates. It may be because of the fact that these metal laurates only quench hydrogen chloride and stop further auto acceleration of dehydrochlorina- tion.

The synergic effect of mixed metal stearates was also studied in the ratio of 1:1. The combinations of metal laurates also stabilize PVC but the effect is not so pronounced. The values of order of reaction for PVC samples containing lead and alkaline metal stearate are also nearly one as observed for all other samples. The values of activation energy for PVC samples containing different stabilizer are found to be higher as compared to pure PVC. The high values of activation energies indicate that the presence of metal laurates in the PVC matrix hinder its degradation.

Table 1: Values of activation energy, order of reaction and arrhenious factor for PVC and PVC mixed with different rare earth metal laurates.

Sample	range of studied	Coat's method order of reaction	Coat's method Act. energy (kJ/mol)	Horowitz's method Value of arrhenius factor	Horowitz's method Act. energy (kJ/mol)
PVC	0.5 - 2.5	1.0	135.8 ± 5.8	4.5×10^9	115.8 ±4.2
PVC + Tb-laurate	0.4 - 2.0	1.0	149.6 ± 6.5	5.6×10^6	136.5±6.7
PVC + Ho-laurate	0.4 - 3.0	1.0	149.6 ± 6.5	5.6×10^7	168.9 ±7.2
PVC + Dy-laurate	0.5 - 3.0	1.0	162.2 ± 8.1	4.5×10^6	148.4 ±5.9
PVC + (Tb + Ho)-laurate	0.5 - 3.0	1.0	169.9 ± 6.8	9.6×10^7	152.9 ±.6
PVC + (Tb + Dy)-laurate	0.5 - 3.0	1.0	193.6 ±8.7	7.8×10^8	182.1 ±8.2
PVC + (Dy + Ho)-laurate	0.5 - 3.0	1.0	187.4 ±6.9	9.1×10^7	177.3 5. ±4

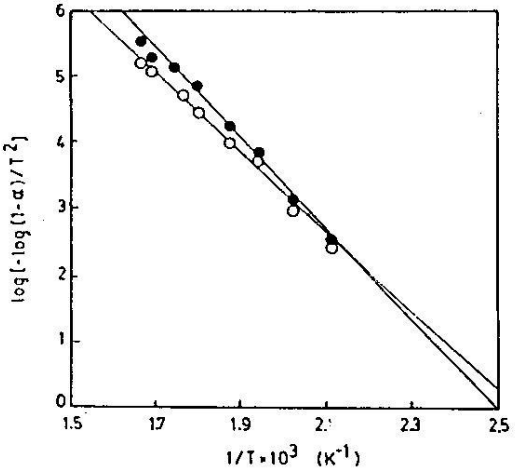

Fig. 3: Plots of log [-log (1-)/T^2] against for PVC (O); PVC + Tb-laurate ()O).

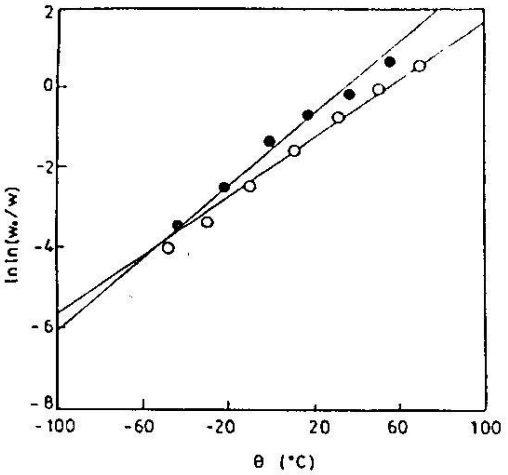

Fig. 4: Plots of ln ln (w_o/w) against for PVC (O); PVC + Tb- laurate (O).

Experimental

Chemicals and reagents

Chemicals and reagents used are: Lauric acid (Sigma. item No. L4250); Potassium hydroxide (Merck, item No. 5021); Nitrates of Holomium (+3), Terbium (+3) and Dysprosium (+3) of 99.999% purity, (M/S Rare Earth Products) and Poly (vinyl chloride) cat. No. F-622, Formosa Plastics Corp. USA, Molecular weight 10000 ± 200, viscosity No. 150/R to 1961 (E), 87, particle size 100% passes to B.S. 60 mesh 74% passes 200 mesh).

Preparation of metal stearates

Potassium salt of lauric acid was obtained by dissolving 5.689 g of lauric acid in 200 ml. of alkalined water containing 1.122 g of potassium hydroxide 200 ml. of the solution of metal chloride (0.1 M) prepared in distilled water was added to the solution of potassium salt and precipitation occurred. Precipitates of metal laurates were filtered, washed with water and dried under vacuum till constant weight was obtained.

Preparation of samples

5% w/w samples of metal laurates with PVC were prepared by grinding the required amount in an agate mortar for 10-15 minutes. In order to study the synergistic effect of these metal laurates 0.25 g each of two metal laurates were mixed with 10 g of PVC.

The TG curves were recorded on the NETZCH simultaneous thermal analyzer STA 429. The heating rate of 10°C/min was employed. The TG curves were recorded for 40 mg samples in a dynamic nitrogen atmosphere with a gas flow rate of 50ml/min.

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