A Comparison of the Stabilities of Some Rare Earth Metal Soap Stabilizers

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Summary: Rare earth (Dy, Nd, Pr and Tb) metal soaps that can be used as stabilizers for PVC, were synthesized from lauric acid. The thermal stability studies of these samples were conducted by employing differential thermal analysis in dynamic nitrogen atmosphere. The results reveal that these metal laurates start to degrade at temperatures higher than those required for lauric acid. Dysprosium laurate is the most stable having a melting point of 145°C.

Introduction

It is an established fact that polymers degrade when subjected to heat and light [1]. The ease and rate of degradation is a function of the composition, exposure and conditions of treatment of the polymer. Hence the use of stabilizers in commercially available polymer products is essential. The incorporation of stabilizers in polymers increase the time of onset of appreciable degradation during the processing or service of these materials [2]. The ideal stabilizer does not exist. While using a stabilizer the health hazard point should always be kept in mind besides monetary considerations.

Metal soaps constitute an important class of stabilizers. These are typically commercial laurates and stearates [2]. The metal soap systems impart significant lubricant action besides acting as stabilizers. Various metal (Ba, Ca, Al and Pb) stearates have been used for poly (vinyl chloride) - PVC- stabilization [3-5]. Rizwan and Fazal [6] have studied the thermal degradation of PVC samples stabilized by rare earth laurates. In this paper the thermal stabilities of some rare earth metal soaps have been studied by employing differential thermal analysis (DTA).

Results and Discussion

Two exothermic peaks at 50°C and 217°C appear in the DTA curve of lauric acid reproduced in Figure 1. The first peak resulted from the melting of the sample, whereas the second peak was consequence of the commencement of the decomposition. Carboxylic acids upon initial

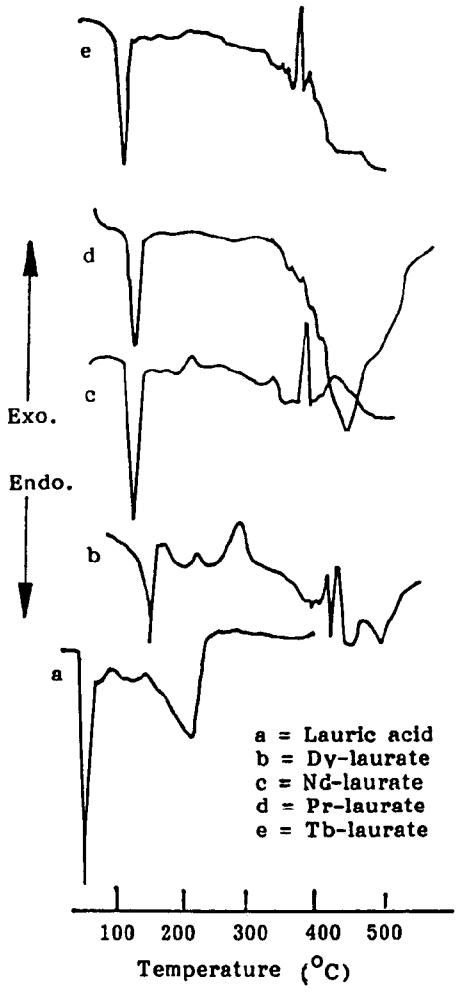

Figure 1.

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thermal break down are known to produce carbon dioxide and hydrocarbon [7]. Minor exothermic changes are evident in between these endotherms.

Dysprosium laurate melted at 145°C followed by exothermic heat effects with maxima at 212°C and 275°C. A sharp endotherm appears at 420°C. Neodymium laurate DTA curve has a melting peak at 110°C. It is followed by exotherms at 195°C (small), 365°C (sharp) and 410°C (broad). In DTA curve of praseodymium laurate melting peak appears at 110°C. A large endotherm is visible at 430°C preceded by rapid evolution of volatiles between 350°C to 400°C. The DTA curve of terbium laurate has a melting endotherm at 95°C followed by exotherm at 360°C. In all these samples peaks proceeding the melting endotherms represent various stages of thermal degradation of metal soaps as the decomposition of compounds may lead to either exothermic or endothermic changes depending upon the energies involved and number of bond making and breaking incidents during heating [8]. Sharp endotherms for fusion obviate the crystalline nature of these samples.

It is evident from Figure 1 that the thermal stabilities of metal laurates are greater than that of lauric acid. In order to support this, the heats of fusion were calculated from the DTA curves using the expression [9]:-

$$\Delta H = Ax/As \cdot ms/mx \ \Delta Hs$$

where, A = area of the peak; m = mass of sample; ΔH = heat of reaction; s = reference material and x = sample.

Hodany's method was used to determined the areas of melting peaks [10]. It is evident from the results presented in Table-1 that the heats of fusion for metal laurates are higher than that of lauric acid. 187.0 J/g required for the melting of lauric acid is in good agreement with the literature cited value of 182.9 J/g [11]. Dysprosium laurate is the most stable as it melts at comparatively higher temperature requiring greater energy of melting.

Table-1: Heats of fusion of rare earth metal soaps

Sample	Melting point (C)	Heat of fusion (J/g)
Lauric acid	50	187.0
Dy-laurate	145	278.2
Nd-laurate	110	237.0
Pr-laurate	110	225.8
Tb-laurate	95	211.5

Experimental

Chemicals and reagents

Lauric acid (Sigma, Item No. 14250). Nitrates of Dysprosium, Neodymium, Praseodymium and Terbium (99.99% purity, M/S Rare Earth Products).

Synthesis of metal laurates

5.7g lauric acid was dissolved in 200ml of distilled water containing 1.12g potassium hydroxide to obtain potassium laurate. 0.1M aqueous solution of praseodymium (III) nitrate was added in constantly stirred potassium laurate solution to initiate the precipitation of praseodymium laurate. Similarly other metal laurates were synthesized. The precipitates were filtered, washed copiously with deionized water and dried in a vacuum oven at room temperature till constant weight.

Characterization of metal laurates

The infra red spectrum of lauric acid showed characteristic carbonyl peak at 1730 cm^{-1}. However in the metal laurate this peak appeared at lower wave numbers thus point towards the complexation of lauric acid ligand with the respective rare earth metal ion. In addition to this the respective metal content in these samples was determined by X-ray fluorescence spectrometry. The metal concentrations were 20.8%, (21.3%), 19.0%, (19.4%), 18.8% (19%) and 21.6% (21/.9%) in Dy, Nd, Pr and Tb laurates respectively. The figures in the brackets represent the calculated values for these metals considering that three lauric acids are complexed with a singlet trivalent rare earth metal ion.

Differential thermal analysis

The DTA curves were recorded on a Shimdazu (Japan) DT30 thermal analyzer in dynamic nitrogen atmosphere with a gas flow rate of 50 ml/min. 5 to 10 mg of the samples were heated from ambient temperatures to 500°C at a heating rate of 10°C/min.

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