Comparative Studies on the Thermal Stability of Commercial Poly(Vinyl Chloride)

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SYNOPSIS

The thermal stability of a polymer is a characteristic function of its structure. In this study molecular weight measurements, differential thermal analysis, dehydrochlorination, and IR are the methods used to determine the thermal stability of commercial PVC products. The study was performed on Saudi Basic Industries Corporation (SABIC) products as well as established products for comparative purposes. The study showed comparable results for both types of products.

INTRODUCTION

A lot of work has been performed to study the thermal stability of PVC. One of these studies points out the use of IR to determine the PVC double-bond content.[1] Others have used different chemical methods.[2,3] The branching characteristic has also been the subject of study by different researchers.[4-8] The dehydrochlorination and the thermal behavior of this polymer were also determined.[9-11] All these studies were performed to discover the reasons behind the thermal unstability of this polymer.

Saudi Basic Industries Corporation (SABIC) has been a competitive resource in the production of different types of polymers. Among these products is poly(vinyl choloride) (PVC). This product has roughly met the quality standards for international products. It is available in the local market and abroad for many different applications. However, these applications are limited since this polymer has a characteristic of weak thermal stability.

It is the aim of this study to investigate the thermal stability differences between Saudi products and other established products. The Saudi products are identified as LADENE PVC 57S, 70S, 67SG, and 62S, and the other products are Shell PVC 57S, and Goodrich PVC 70S. All these products are in their risen state.

EXPERIMENTAL

The techniques of investigation involved spectroscopic methods, mainly Fourier transform infrared (FT IR), differential thermal analysis (DTA), gel permeation chromatography (GPC), and chemical analysis to determine the dehydrochlorination process. FT IR: A Perkin-Elmer model 1500 spectrometer was used. Solvent-free film of PVC resin was prepared using tetrahydrofuran (THF) as a solvent. Less than 1 mg PVC sample was placed on KBr window, and the solvent was added dropwise until it completely dissolved the resin. The solution was allowed to spread over the face of the crystal and evaporated completely using a hot plate at moderate temperature. When the film appeared to be free of solvent the window was placed on a demountable cell.

GPC: Waters 150 GPC interfaced with 730 data module was used. The instrument was calibrated with several narrow molecular weight polystyrene standards ranging from peak average molecular weight of 1800 to 1,850,000. Solution with a concentration of 0.15% mass/volume (m/v) for each polystyrene standard in THF was injected 2–3 times using the data module 730 in the LC mode. The retention time (elution volume) for each polystyrene standard was fed into the data module in order to calibrate the GPC system for the analysis of the PVC resins. The samples were prepared in GPC-grade THF solutions as 0.15% (m/v) concentration

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Table I   Characteristics of Commercial PVC Samples

PVC Sample	M_n	M_w	Red-Blue (s)	Δ pH	Relative Int. of $\dfrac{C-Cl}{C-H}$ Band	T_g (°C)
LADENE						
57S	67559	101982	139.4	2.4	0.38	85
67SG	96013	142477	145.1	2.2	0.43	85
70S	103457	154079	136.5	1.9	0.43	87
62S	89441	129006	122.5	2.4	0.42	86
Shell						
57S	73218	106474	163.6	2.2	0.43	82
Goodrich						
70S	109629	166042	130.55	1.9	0.45	83

and were filtered through 0.5-μm stainless steel filters prior to injection. All the samples were analyzed using an ultrastyragel column with exclusion limits of 500, 10^3, 10^5, and 10^6 Å. The flow rate used was 2 ml/min and the sample size was 80 μL at an operating temperature of 35°C. These conditions were always met during the analysis of each sample.

DTA: Differential scanning calorimetry DSC-4 from Perkin-Elmer was used for thermally analyzing the samples. Argon was used as an inert atmosphere, and the temperature range selected was from 50 to 120°C. The heating rate and sample size were 10°C/min and 10 mg, respectively.

Dehydrochlorination: The dehydrochlorination test was performed using Congo-Red test method according to ISO/R182-1970(E) at 190°C and also the pH method at the same temperature, the nitrogen flow rate was 6 L/h.

RESULTS AND DISCUSSION

The real composition of all the PVC samples studied is not known since these samples contain additives such as stabilizers, antioxidants, UV absorbers, etc. These data were not available to help analyzing the IR spectrum obtained. However, the relative intensity of C–Cl to C–H stretching band in each sample was determined as shown in Table I. This relative intensity of C–Cl to C–H is an indication of how much chlorine each sample contains in its structure. The study showed that Goodrich 70S contained the most chlorine and LADENE 57S the least; the rest of the samples contained almost the same amount of chlorine. The liberation of the chlorine in a form of hydrogen chloride is a measure of how stable the polymer is. This is known as dehydrochlorination,

which was measured as a function of the time of color change using Cong-Red test and pH methods at 190°C in 10 min time. The results showed that the Shell 57S sample was the most stable followed by LADENE 67SG and then LADENE 70S. This may indicate that these samples contain less labile chlorine atoms than the others. The molecular weight measurement values are not absolute and have been obtained using polystyrene standard calibration. The polydispersity is different for each sample and that is due to the conditions of polymerization applied in each case.

The increase in T_g values of these samples compared to the values obtained for pure PVC is due to the modification of these samples with additives.[12–15] The DTA results also showed an endothermic process at $\simeq$ 290°C accompanied by an increase in weight loss for all samples except LADENE 57S, which might be due to crosslinking.

The results showed different thermal behavior for these samples, and this apparently is due to their different composition. Also it may be related to the different conditions of polymerization.

In conclusion, it can be said that the Saudi domestic products are comparable to the established products, and their thermal stability falls within the acceptable boundaries.

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