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# COMBINED THERMOGRAVIMETRIC AND INFRARED ANALYSIS OF POLYMERS

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## ABSTRACT

The techniques of thermogravimetry and infrared spectroscopy have been combined in a unique method to provide quantitative and qualitative analyses of polymers. The amounts of additives, polymers, carbon black, and inorganic fillers are determined by thermogravimetry, and the additives and polymers are identified by infrared spectroscopy, all in one set of experiments.

The method involves condensing the effluent from the thermogravimetric analyzer in replaceable glass tubes for transport to the infrared spectrometer. The method is illustrated with thermogravimetric and infrared analysis data for a Hypalon fuel hose and for a fluorosilicone fuel gasket. The main advantage of the method is the ability to collect as many separate fractions of the thermogravimetric effluent as required to identify the minor and major components of a polymer.

## INTRODUCTION

The analysis of polymers often requires both quantitative and qualitative data. The quantitative data can be obtained by thermogravimetry (TG), which yields the percentage composition of such components as plasticizers, polymers, and fillers [1]. The qualitative identification can be obtained by infrared spectroscopy, but in practice many polymer formulations are difficult to analyze directly by this method due to the presence of carbon black, which strongly absorbs infrared radiation, or due to the intractable nature of the polymer. To circumvent these limitations, a number of workers have pyrolyzed polymers in a test tube [2,3] or in an infrared cell with a hot wire [4] and examined the resulting pyrolysate by infrared spectroscopy. Although this method is fast and sometimes useful, the resulting pyrolysate is usually a complex mixture, and its IR spectrum is difficult to interpret.

This report describes the simple coupling of thermogravimetric and infrared techniques so that both quantitative and qualitative information can be obtained on polymer formulations from one set of experiments. This coupling is accomplished by using replaceable glass collection tubes as room temperature traps for collecting the condensed volatiles and decomposition products from the thermogravimetric (TG) analyzer for subsequent infrared (IR) analysis. This method has the advantage that the TG effluent can be divided into as many fractions as required, and an infrared spectrum can be obtained of each fraction. Other workers [5,6] have examined the gaseous products from TG by IR, but to our knowledge the combined TG data of polymers and IR spectra of the condensable effluent have not been reported.

The purpose of this report is to describe the TG/IR method and to illustrate its usefulness with examples of the analysis of polymer formulations that are used in the automobile industry.

## EXPERIMENTAL

### *Thermogravimetry*

A DuPont (model 951) thermogravimetric analyzer (TGA) was used in conjunction with a DuPont (model 990) thermal analysis system. The thermocouple (chromel/alumel) was placed just outside the sample pan to prevent its being spattered by the sample during decomposition. The TGA furnace tube was shortened so as to be contained entirely within the TGA furnace. The neck of the furnace tube was narrowed to 7 mm to hold a removable glass tube 100 mm long, 6.5 mm OD and 4 mm ID, which extends outside the furnace and acts as an air condenser to collect the pyrolysates for infrared analysis.

### *Infrared spectrophotometry*

A Digilab (model FTS 20C) Fourier transform infrared spectrometer (FTIR) was used. Most pyrolysate samples were run by multiple internal reflectance, for which a 50 × 5 × 2 mm 45° KRS-5 crystal was used in a Harrick 4X-TBC-VA accessory. Some of the pyrolysates from chloro-polymers etched the KRS-5 crystal, so they were run by transmittance with a 25-mm diameter potassium bromide crystal.

The air in the FTIR was purged through molecular sieves to remove water vapor and carbon dioxide. However, small amounts of the latter remained, giving extraneous IR bands in the pyrolysate spectra at 2350 and 667 $\text{cm}^{-1}$, which should be ignored.

### *Procedure*

The TGA was purged with nitrogen after loading a 20–30-mg sample of the polymer. During the TG analysis, the integral and derivative signals of the TGA were noted so that a glass tube could be installed into the neck of the furnace tube at the proper temperature to collect the pyrolysate. The nitrogen purge was switched to air at about 600°C to burn off any carbon black and char.

To remove the condensed pyrolysate for IR analysis, the glass tube was held horizontally while a drop of chloroform was added at the clean end. The tube was rocked slightly to allow the chloroform to dissolve the pyrolysate. The tube was then tipped upright against a KRS-5 crystal, and the chloroform solution was spread evenly on the crystal. An IR spectrum was obtained after the chloroform had evaporated. Methanol was used to transfer the fluorine-containing pyrolysates that were insoluble in chloroform.

## RESULTS AND DISCUSSION

The first example of the application of this TG/IR method is the analysis of the rubber used in fuel hoses. Because of its good ozone and heat resistance, chlorosulfonated polyethylene (DuPont Hypalon) is often used in the outer layer of fuel hoses.

To obtain reference TG and IR data for Hypalon (Fig. 1), a sample of unused Hypalon rubber formulated in this laboratory [7] was heated in the TGA. The first fraction from the TGA was collected at 200–325°C, and its IR spectrum (Fig. 1A) primarily represents dioctyl sebacate. Only 2.5 wt% dioctyl sebacate was added to the Hypalon, so Fig. 1A represents about 0.5 mg of dioctyl sebacate. This illustrates the sensitivity and selectivity of the method by being able to isolate minor components and obtain well-defined IR spectra, free from interfering bands of the bulk polymer.

The sharp change in the TG curve at 320°C represents the evolution of hydrogen chloride from the Hypalon, and the magnitude of the change indicates the approximate amount of chlorination of the polyethylene.

A second fraction was collected from the TGA at 330–425°C, and its spectrum (Fig. 1B) possibly represents some additives and the initial pyrolysis products of the Hypalon polymer. A third fraction was collected from 430 to 550°C, and its spectrum (Fig. 1C) represents the main pyrolysis products of Hypalon.

Hypalon and other chlorinated polyethylenes (e.g., Dow 236 and 342) give very similar pyrolysate spectra, as shown in Fig. 1C, and, therefore, cannot be distinguished from one another by spectra comparison. The spectra are sufficiently characteristic, however, to distinguish chlorinated polyethylenes from other chlorinated polymers, particularly by comparing the intensity and shape of the IR bands in the region 700–1000 $cm^{-1}$. For example, we have found that the pyrolysate spectra of neoprene and polyvinyl chloride are somewhat similar to Fig. 1C, except that the 990 and 910 $cm^{-1}$ bands

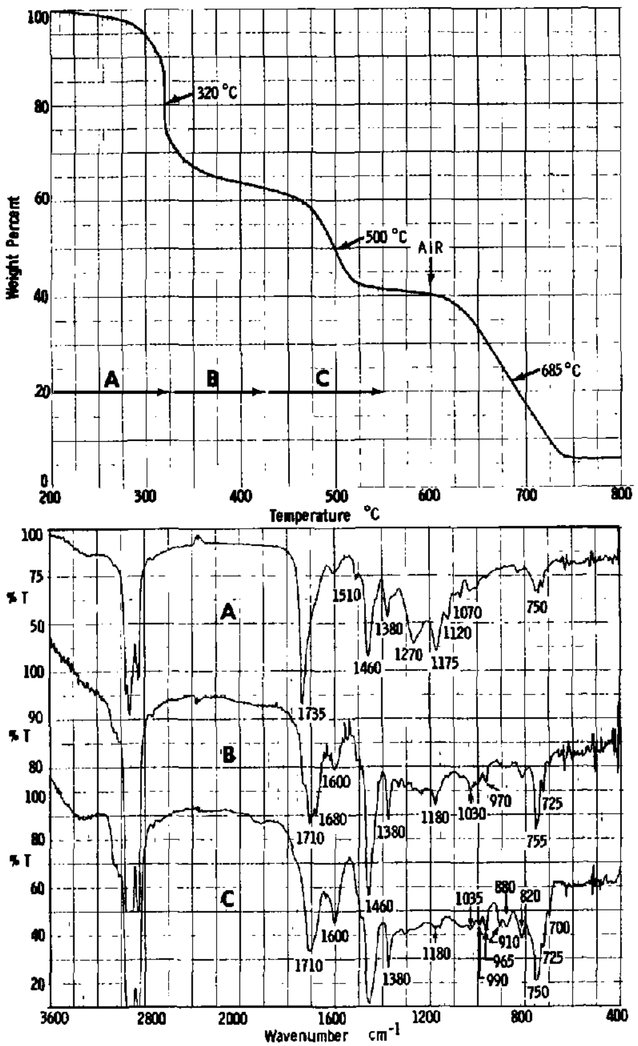

Fig. 1. TG curve and IR spectra of the TG effluent for a formulated [7] Hypalon, a chlorosulfonated polyethylene. The upper figure is the integral curve of the thermogram. The first derivative curve is not shown, but the temperatures for the first derivative maxima are numbered beside the integral curve. The horizontal arrows indicate the temperature ranges where the TG effluent was condensed in glass tubes. The lower figure shows the IR spectra of the corresponding condensed fractions of the TG effluent.

are much smaller relative to the other bands in this region.

We have also found that chlorinated polymers generally give pyrolysate spectra that are considerably different than their corresponding polymer spectra, because they pyrolyze after evolving hydrogen chloride when heated. For this reason pyrolysate spectra such as Fig. 1C that are relatively free of bands for other components in the polymer formulation are important as reference spectra for identifying chloro-polymers. On the other hand, we have found that many polymers, such as esters, urethanes and fluorocarbons, generally give pyrolysate spectra that are similar to their corresponding polymer spectra, so that literature spectra of the polymer can often be used to identify the pyrolysate spectra.

The ability to separate closely eluting fractions from the TGA is another advantage of this method. A fluorosilicone used as a fuel-system gasket pyrolyzed into two fractions eluting around 480 and 520°C (Fig. 2). The IR spectrum (Fig. 2A) of the first fraction closely matched a reference spectrum for poly(trifluoropropyl siloxane) [8]. The spectrum (Fig. 2B) of the second fraction closely matched the pyrolysate spectrum that we obtained for Viton

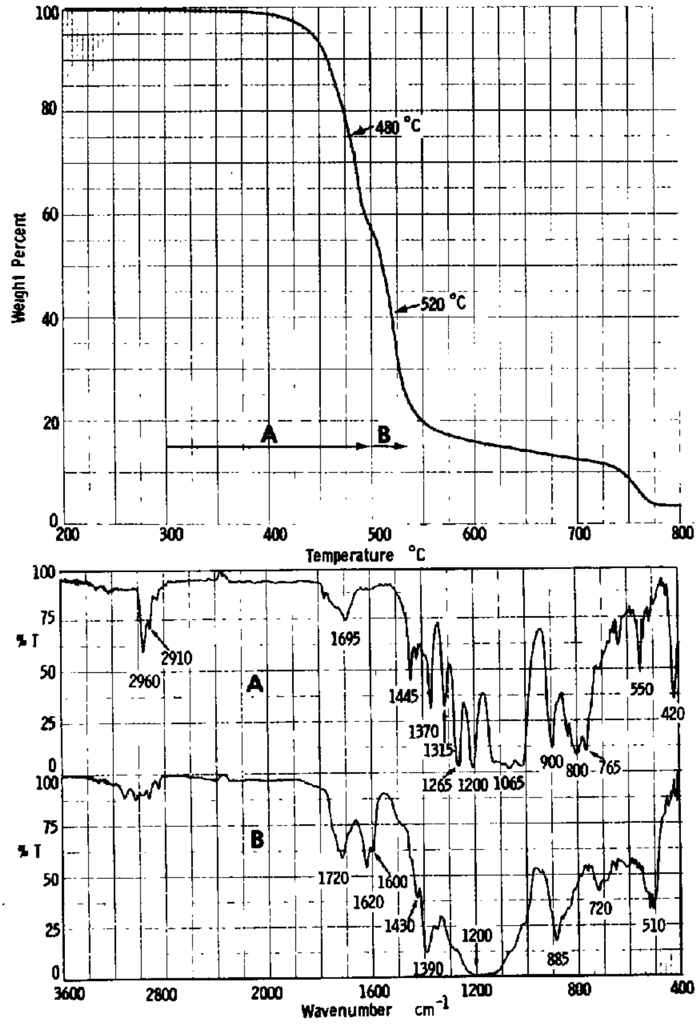

Fig. 2. TG curve and IR spectra of the TG effluent for a gasket that contained polymers of a fluorosiloxane and a fluorocarbon.

A-HV, a polyfluorocarbon. Thus, we were able to determine that the gasket contained polymers of a fluorosiloxane and a fluorocarbon.

We have catalogued the TG curves and pyrolysate spectra of about 30 polymers, including hydrocarbons and those containing nitrogen, oxygen, fluorine or chlorine. Some simple polymers required the collection of only a single fraction and IR spectrum for identification, while others required the collection of as many as four fractions to identify the additives and polymers. Further separations of the condensed components can be made by using more than one solvent to transfer the condensate from the glass tube to the IR crystal. For example, hexane can be used to remove condensed hydrocarbons before using chloroform or a stronger solvent to transfer the condensed pyrolysate. Thus, most polymers can be analyzed by the combination of the TG and IR techniques described.

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