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Note

Characterization of blends and copolymers of ethylene and methyl methacrylate by combined thermogravimetric analysis–infrared spectroscopy

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Distinguishing blends of two homopolymers from their copolymers presents a problem to the analytical chemist. While a variety of techniques have been tried, no one tool is universally applicable. Hence, new techniques are constantly being sought to supplement existing ones. Chiu[1] has reported a coupled thermogravimetric analyzer–gas chromatograph system with which he was able to distinguish styrene–methyl methacrylate homopolymer blends from copolymer on the basis of a comparison of their thermal degradation products at different stages in the decomposition.

If the only interest is the analysis of *major* volatile thermal degradation products, then a less expensive, less sophisticated technique, thermogravimetric analysis coupled with infrared spectrophotometry, may prove useful in the characterization of polymer blends and copolymers. The coupling of infrared spectrophotometers to thermogravimetric analyzers has been previously applied to the analysis of organic mixtures[2] and to monitoring the release of NH_3 and H_2O from hydrated ammonium salts[3]. The purpose here is to report the use of TG–IR in distinguishing polyethylene–polymethyl methacrylate blends from an ethylene/methyl methacrylate copolymer.

EXPERIMENTAL

Nine to 12 mg of sample were loaded in a DuPont 950 thermogravimetric analyzer (TG) and heated in a 15 ml min^{-1} stream of nitrogen at 10°C min^{-1} to 300°C and at 3°C min^{-1} from 300 to 485°C. The weight loss was followed on a DuPont 900 thermal analysis system recorder. The volatile effluents were drawn by vacuum ($<$0.5 mm Hg pressure drop) via 2 ft. of 0.05 in. ID stainless steel hypodermic tubing through a Grubb Parsons 1-m, 45-ml volume infrared cell mounted in the beam of a Pye Unicam SP 1000 infrared spectrophotometer. The stainless steel tubing was connected through silicone rubber septa to the IR cell and to a glass ball joint connected to the open end of the TG's quartz furnace tube. The Grubb Parsons cell was used because it offered the best compromise between long pathlength for sensiti-

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vity and small volume for rapid throughput. Scans from 3800 to 625 cm^{-1} were made every 5½ min in order to identify the volatile degradation products as they began to appear. From these scans and calibrations for the components of interest, one can determine the amount of a given component present at any time. This, together with the flow-rate, can be used to calculate the evolution rate in mg min^{-1}. Integration of this rate then yields the total number of milligrams of that component evolved.

RESULTS AND DISCUSSION

The samples treated in the manner just described included: (1) methyl methacrylate homopolymer containing no additives; (2) a 76.5:23.5 ethylene/methyl methacrylate copolymer; (3) a dry blend composed of 80.6% polyethylene and 19.4% polymethyl methacrylate prepared in a Spex Industries Inc. freezer/mill; and (4) a melt blend composed of 81.8% polyethylene and 18.2% polymethyl methacrylate prepared on a 3-in roll mill at 180 °C. In all four cases the major thermal degradation product sufficiently volatile to reach the IR cell was methyl methacrylate (MMA). Table 1 summarizes the TG and IR data.

TABLE 1

RESULTS OF TG-IR ANALYSIS OF ETHYLENE-METHYL METHACRYLATE SAMPLES

Sample	*TG data*	*Infrared spectral data*		
	Temperature for 1% weight loss (°C)	*Temperature of initial evolution of MMA (°C)*	*Percent conversion of sample to MMA monomer*	*Percent conversion of PMMA to monomer*
MMA (99.7%) homopolymer	280	182	91.7	92
PE/PMMA (80.6%, 19.4%) dry blend	300	225	21.0±1.7[a]	108
PE/PMMA (81.2%, 18.2%) melt blend	300	303	12.4±0.9[a]	68
E/MMA (76.5%, 23.5%) copolymer	335	370	2.9±0.6[a]	12

[a] The number given first represents the average of two independent experimental results. The second number represents the average deviation.

The thermogravimetric analyzer provides precise control of the thermal degradation of the sample. The copolymer shows a 35 °C higher temperature for the same weight loss than either blend. The IR data provide further evidence for a significant difference in the behavior of a copolymer versus a blend. The temperature of initial evolution of MMA is higher for the copolymer, but the most significant difference in behavior is the percent conversion of PMMA to monomer. The last column in the table shows that for homopolymer and dry blends essentially 100% of the polymer is converted and recovered as monomer, whereas for the copolymer only 12% was converted to monomer. The melt blend yielded 68% of its PMMA as monomer, instead of the expected 100%. This may be due to partial grafting of the polymethyl methacrylate to the polyethylene in the high temperature oxidative atmosphere of the mill.

It then appears that an E/MMA sample can be identified as a copolymer or a blend from a knowledge of its composition (easily obtained from IR data on a pressed film) and TG–IR data. If 60–100% of the PMMA appears as monomer, the sample is a blend. If less than 20% is recovered as monomer, it is a copolymer.

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