

NOTES

Determination of Melting of PAN-MMA Copolymer Fibers by Differential Thermal Analysis

INTRODUCTION

When acrylic fibers are exposed to a flame, they will melt and burn. If heated sufficiently slowly, however, coloration and crosslinking reactions occur which alter the structure of the polymer so as to completely eliminate the melting point. The extent to which these reactions proceed during heating is a function of the heating rate; so, in a sense, for acrylics the melting behavior depends upon the heating rate.

Although there have been a number of studies of polyacrylonitrile (PAN) by differential thermal analysis,¹⁻³ until recently melting had not been observed using this technique. In a recent publication, Dunn and Ennis,⁴ using fast heating rates with DTA, have assigned a small endotherm that occurred before the strong 300°C exotherm to the melting point. They also referred to a personal communication from P. E. Slade who made similar observations for acrylonitrile-vinyl acetate copolymers. The melting point of PAN determined from DTA by Dunn and Ennis was 326°C. They also reported a small heat effect at 240°C which "could be attributed to a previously unreported second-order transition for PAN with a relatively high degree of crystallinity." In earlier work, Chiang⁵ studied crystallization and melting behavior of PAN by x-ray diffraction and noted that in the temperature region 250°-270°C, characteristic order gradually deteriorated and disappeared. Since this temperature region is just below that at which PAN undergoes a major exothermic reaction (see, for example, Thompson²), Chiang was uncertain whether the observed destruction of order was due to "melting" or slow chemical reaction. Krigbaum and Tokita⁶ reported a melting point for PAN homopolymer of 317°C by extrapolating the melting point depression curves determined by dilatometric methods of PAN-dimethyl formamide and PAN-butyrolactone solutions.

In the course of studies concerned with the graphitization of acrylic fibers, it was observed by DTA that an energy absorption occurred in methyl methacrylate-PAN copolymers which also appeared to correlate with the physical appearance of melting.

EXPERIMENTAL PROCEDURE AND RESULTS

A number of experimental PAN yarns containing varying amounts of methyl methacrylate (MMA) comonomer were generously supplied by the American Cyanamid Central Research Laboratories. Samples of each yarn were weighed to 0.01 g and rolled into wads which were compressed in a 1/8-in.-diameter steel mold so as to form cylindrical pellets. Some spring-back occurred when the pellets were removed from the mold, but they remained well consolidated. DTA traces were obtained at high gain (0.001 mv/div using platinum thermocouples) in an atmosphere of flowing nitrogen at a heating rate of 10°C/min using a Stone Tracor DTA apparatus. Sintered aluminum oxide powder was used as the inert reference substance. Portions of the DTA traces obtained for the different yarns are reproduced in Figure 1. For clarity, the vertical scale has been displaced an arbitrary amount for successive traces. In each instance an endothermic reaction precedes, and is later overwhelmed by, the extremely strong exothermic reaction centered around 340°C. The endotherm begins at a lower temperature the higher the MMA concentration.

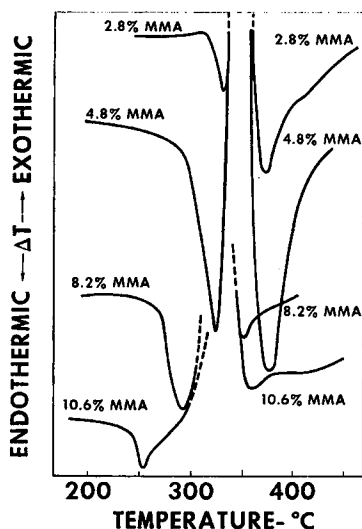


Fig. 1. Differential thermal analysis traces obtained from acrylic fibers having various concentrations of methyl methacrylate (MMA). The endotherms preceding the strong exotherms are attributed to melting.

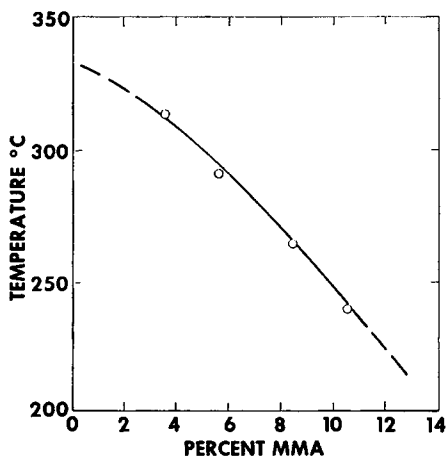


Fig. 2. Temperature of initial melting of acrylic fibers as a function of the MMA concentration.

The physical appearance of the samples was observed after different conditions of heating in the DTA apparatus. A sample heated to a temperature below the start of the endothermic reaction and then cooled back down to room temperature was discolored a dark brown but still displayed a fibrous habit, i.e., it had not flowed. A sample heated to above the endotherm but quickly cooled before undergoing the exothermic reaction had flowed and wetted the platinum container. Samples heated through the exothermic reaction had foamed.

The fact that the samples behaved like liquids at temperatures above the endotherm and like solids at temperatures below it is sufficient to identify the endotherm with melting. The inception of melting of copolymers as a function of MMA concentration

(i.e., the solidus curve) as determined from DTA traces is presented as Figure 2. The melting temperature of PAN homopolymer determined by extrapolation of the data presented in Figure 2 is about 330°C. This is somewhat above the values determined by Krigbaum and Tokita and by Dunn and Ennis.

Considering the importance of heating rate on the observation of melting, the agreement with these previous authors is satisfactory. The heat effect observed at 240°C by Dunn and Ennis was not observed for the MMA-PAN copolymers. In general, copolymers are considered less crystalline than the homopolymer, and the absence of the 240°C heat effect for the copolymers may be related to this fact.

References

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