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DTA OF POLYACRYLONITRILE FIBERS IN AIR

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ABSTRACT

The effect of experimental conditions on the results of DTA of polyacrylonitrile fiber in air and in helium over the temperature range from 200 to 400 °C has been investigated. It is shown that such DTA factors as the heating rate, the sample weight, the crucible size and the location of the thermocouple are of primary importance when the thermal analysis of the PAN fiber is carried out in air. The character of the effect of these factors suggests that the thermal transformation of PAN and its oxidation are interrelated. However, when the access of air is limited and the heating rate is high, these processes are separated, which is shown by two maxima on the DTA curve.

INTRODUCTION

In our previous paper[1] it has been reported that when the DTA of powdered polyacrylonitrile (PAN) was carried out in air, a characteristic dependence of thermal effects on some parameters of the instrument and the procedure of analysis was found. The most important factors were (a) the geometry of the sample holder and the location of the thermocouple; (b) the mass, volume and dispersity of the sample and (c) the rate of the temperature rise.

The data obtained permitted some suggestions to be made on the peculiarities of thermo-oxidative processes under various conditions of thermal treatment. The thermal treatment of the PAN fibers in air in the range 150 to 350 °C is known to be an important stage in the processes of the industrial manufacture of carbon fibers[2, 3]. The mechanical and physico-chemical properties of the fiber exhibit some specific features and therefore it was of interest to study the effect of the above factors on the DTA of the PAN fiber and to compare this effect with that found previously for the PAN powder.

EXPERIMENTAL

The PAN fiber was obtained by wet spinning from the solution of an acrylonitrile homopolymer in dimethylformamide. The filament yarn contained 300 filaments and had a linear density of 30 tex.

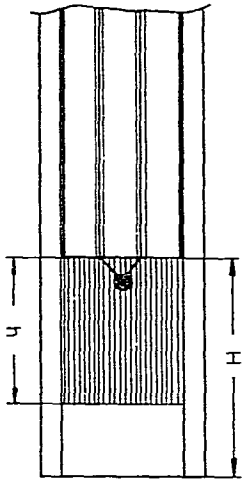


Fig. 1. Crucible with a sample of the PAN fiber (in section).

DTA was carried out in an assembly comprising the heating arrangement and the programming system of the derivatograph (MOM, Hungary). Thermal effects were registered by using a Pt–Pt/Rd differential thermocouple and an EZ 10 potentiometric recorder (Czechoslovakia) with the sensitivity of 0.5 mV for the whole scale. The temperature was measured with a chromel–copel thermocouple and a KVP potentiometer. A glass tube with inner diameter of ca. 3 mm was used as crucible. It was tightly fixed on the ceramic rod of the thermocouple (Fig. 1) and its height (H) was regulated by moving the rod inside the tube.

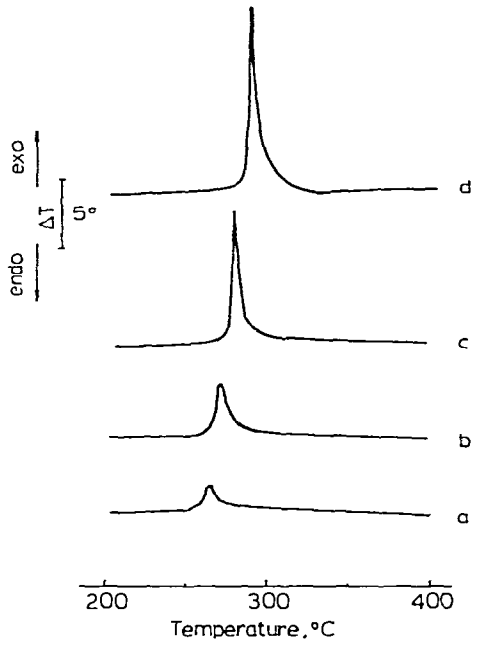
As a rule, the thermocouple junction was placed at a height of ca. 1 mm from the center of the crucible bottom. The sample was a bundle of parallel threads of the PAN fiber occupying the whole volume of the crucible or its part. The sample weight depended on the length (h) of threads and their number. For comparison in some experiments the crucible was filled with the yarn cut into small pieces (<0.3 mm) or as entangled filaments. It was found that the way the sample is packed in the crucible is of no importance if the sample weight and the packing density remain constant.

RESULTS AND DISCUSSION

It was established in preliminary experiments that in the range from 200 to 400 °C for the PAN fibre (as well as for powdered samples) the shape of the DTA curve in air depends on experimental conditions. The effects of the most important experimental factors were investigated.

(1) *Rate of temperature rise*

Figures 2 and 3 show the results of two series of experiments at different heating rates of the PAN fiber in helium and in air, respectively. The increase in the heating rate leads to a great increase in the exothermic peak and to its displacement toward



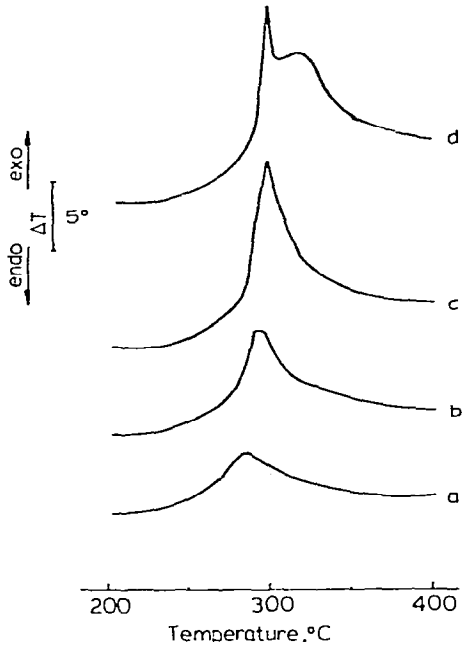


Fig. 2. DTA curves in helium. Heating rate (°C min^{-1}): (a) 2.5; (b) 5; (c) 10; (d) 20. $H = h = 6$ mm. Sample weight: 15 mg.
Fig. 3. DTA curves in air. Heating rate (°C min^{-1}): (a) 2.5; (b) 5; (c) 10; (d) 20. $H = h = 6$ mm. Sample weight: 15 mg.

TABLE 1

CHARACTERISTICS OF THE EXOTHERM AT DIFFERENT HEATING RATES

Heating rate (°C min^{-1})	*Peak height (arbitrary units)*		*Height ratio*	*Temp. of the maximum (°C)*		*Temp. difference* (°C)
	In air	*In helium*		*In air*	*In helium*	
2.5	21	9	2.3	288	264	24
5	36	19	1.9	295	270	25
10	64	46	1.4	300	280	20
20	66[a]	62	1.1	302[a]	290	12

[a] For the first maximum.

higher temperatures. A comparison of the values of the exotherm in helium and in air at the same heating rate suggests that in the latter case oxidative reactions provide great contribution. As the heating rate increases, the relative value of this contribution decreases in the low temperature part of the DTA curve and increases at higher temperatures. In particular, this trend is shown by the appearance of the second maximum on the DTA curve at these temperatures at a fairly high heating rate (20 °C min^{-1}).

Table 1 shows numerical data characterizing the DTA peaks at a maximum (Figs. 2 and 3). When PAN is heated in air, the exothermic process always begins earlier than in helium but attains a maximum at higher temperatures. Table 1 shows

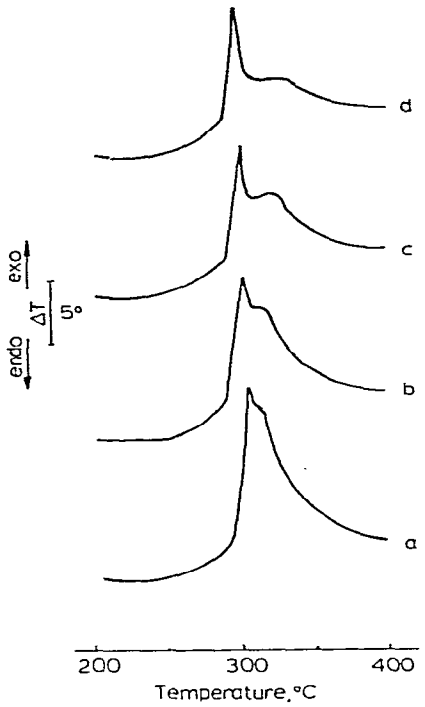


Fig. 4. DTA curves in air. Heating rate: 20°C min^{-1}. Crucible height (H, mm): (a) 4; (b) 6; (c) 8; (d) 10. Sample weight: 10 mg (h = 4 mm).

that the differences in the heights and temperatures of the peaks for helium and for air decrease when the heating rate increases.

In accordance with the data in the literature[4], these observations can be explained as follows: the oxidative reactions beginning during DTA in air at lower temperatures than the thermal transformation of PAN in an inert atmosphere, are capable both of initiating this transformation and of retarding it. When the temperature increases (at an increased heating rate), the rate of the thermal transformation of PAN greatly increases (Fig. 2) and the inhibiting effect of oxygen should decrease. The appearance of two maxima on the DTA curve (Fig. 3d) at a high heating rate in air is probably due to the fact that under these conditions the thermal transformation accompanied by the evolution of great amounts of gaseous products[5] proceeds faster than the oxidative reactions, the rate of which depends on the dynamics of the gaseous exchange in the crucible.

(2) *Crucible height*

The effect of the height of the cylindrical crucible on the shape of the DTA curves of the PAN fiber in air, other geometric parameters (the crucible diameter, the location of the thermojunction and the shape and size of the sample) being constant, is shown in Fig. 4, which gives the results of experiments at a heating rate of 20°C min^{-1}. The increase in the height (depth) of the crucible leads to a decreasing exothermic effect. Doubtless this is related to the lower contribution of oxidative reactions.

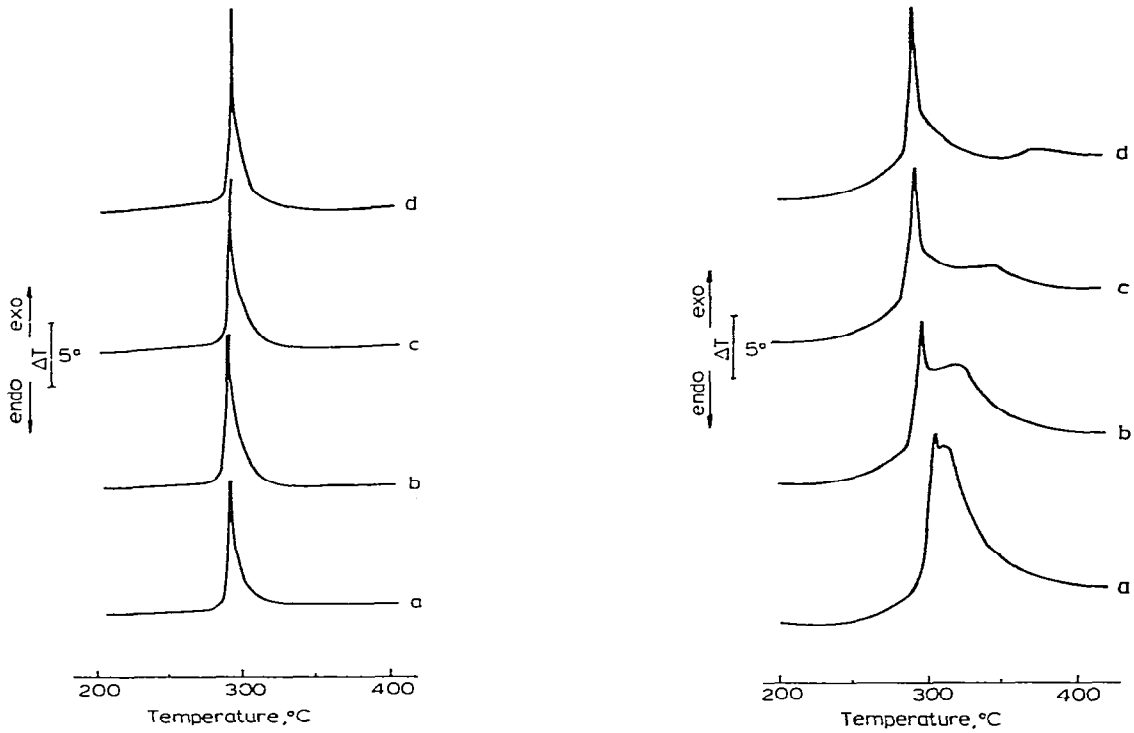


Fig. 5. DTA curves in helium. Heating rate: 20°C min^{-1}. $H = h$. Sample weight: (a) 10 mg (h = 4 mm); (b) 15 mg (h = 6 mm); (c) 20 mg (h = 8 mm); (d) 25 mg (h = 10 mm).

Fig. 6. DTA curves in air. Heating rate: 20°C min^{-1}. $H = h$. Sample weight: (a) 10 mg (h = 4 mm); (b) 15 mg (h = 6 mm); (c) 20 mg (h = 8 mm); (d) 25 mg (h = 10 mm).

The character of the DTA curves (Fig. 4) indicates that two exothermic processes exist and the degree of their superposition depends on the height of the crucible. When it increases, the maximum of the first (low-temperature) exotherm slightly shifts toward lower temperatures (from 307 to 303°C). At the same time the second exotherm can undergo a great displacement in the opposite direction and the greater this displacement, the greater is the decrease in the intensity of the exotherm*. These data confirm the conclusion that the first exotherm is related to the thermal transformation (although oxidative reactions also provide some contribution) and the second exotherm is related to the oxidation of the product of thermal transformation. Since oxidation depends on the rate of the gaseous exchange in the crucible, the higher the crucible, the slower it proceeds.

(3) *Sample Weight*

The sample weight of the PAN fiber affects differently the results of DTA in helium (Fig. 5) and in air (Fig. 6). In the first case only the intensity of the single sharp exothermic peak varies whereas in the second case great changes in the shape of the DTA curve are observed similar to those which depend on the crucible height

* By the intensity of the exotherm we mean the maximum deviation of the DTA curve from the base line in the range of this thermal effect.

(Fig. 4). In the series of experiments shown in Figs. 5 and 6 both the crucible height and the sample weight (the length of the bundle of threads) were changed at the same time so that the crucible remained full. If we compare the DTA curves in air for different sample weights in the same crucible (Figs. 4 and 6), it becomes clear that the increase in weight leads to increasing intensity of the first exotherm and decreasing intensity of the second exotherm, both of them shifting in opposite directions on the temperature scale. When the sample weight greatly increases, the DTA curve in air (Fig. 6d) becomes similar to that in an inert atmosphere.

A natural interpretation of these phenomena is that not only the amount of heat evolved as a result of the thermal transformation of PAN but also the volume of gaseous products of degradation preventing oxidative reactions, depend on the mass of the polymer. To separate the mass effect from the volume effect, a series of experiments was carried out under conditions similar to those shown in Fig. 4, but the free volume of the crucible was filled with a bundle of inert (thermally treated) fiber. The DTA curves in this series of experiments and those in Fig. 4 were in fairly good agreement, which suggests that the results of DTA are much more affected by the sample mass than by its volume.

The influence of the sample weight is somewhat different when it is changed by varying the number of threads in the bundle, its length remaining constant and equal to the crucible height (Fig. 7). A comparison of Figs. 4, 6 and 7 shows that the in-

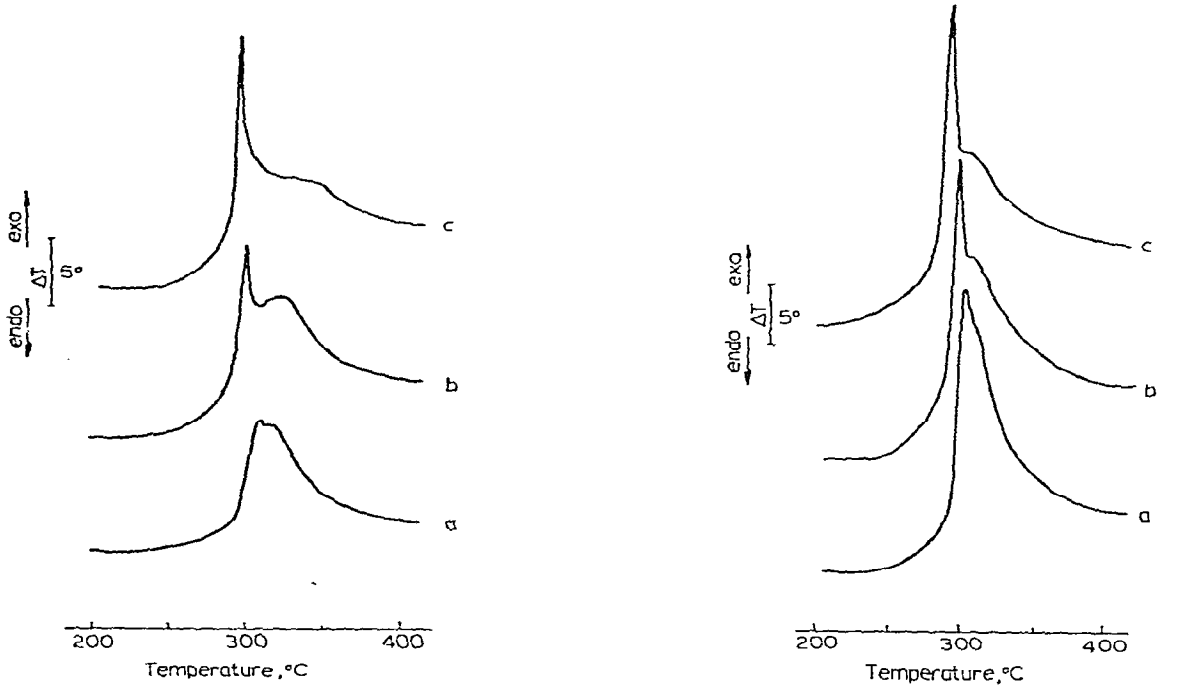


Fig. 7. DTA curves in air. Heating rate: 20 °C min^{-1}. $H = h = 6$ mm. Sample weight: (a) 10 mg (50 threads); (b) 15 mg (75 threads); (c) 20 mg (100 threads).

Fig. 8. DTA curves in air. Heating rate: 20 °C min^{-1}. $H = h$. Sample weight: (a) 10 mg ($h = 4$ mm); (b) 15 mg ($h = 6$ mm); (c) 20 mg ($h = 8$ mm). The thermojunction is placed in the center of the crucible.

crease in the packing density leads to an increase in both exotherms. It might be assumed that this is due to more favorable conditions of heat transfer to the thermocouple. The ratio of intensities of the first and second exotherms (compare Figs. 4b and 7a) changes in favor of the latter when the sample density decreases because this facilitates the access of air to the polymer.

The effect of the sample weight on the shape of the DTA curve of the PAN fibers in air can be great or small depending on the experimental conditions. The location of the thermojunction is of great importance. Thus, Fig. 8 shows the results of a series of experiments similar to that in Fig. 6 but the thermocouple junction was in the center of the sample mass (and of the crucible). In other experiments, when the thermojunction was located at the upper edge of the crucible, the sample weight affected only the intensity of the single exothermic peak.

CONCLUSIONS

The results of DTA of the PAN fiber obtained in this work show the general character of the dependences found previously in experiments on the PAN powders but there are some specific features. The bimodality of the DTA curves in air in the range from 200 to 400 °C is observed for the PAN powders over a wide range of heating rates starting from ca. 5 °C min^{-1}, whereas the PAN fibers are characterized by this phenomenon only at the highest heating rate (20 °C min^{-1}). When the heating rate increases, the height of the exothermic peak on the DTA curve of the fiber (in helium and in air) also greatly increases, which is not observed for powder.

Data in this work also confirm the conclusion that under conditions of limited access of air and fast heating, the DTA curve of the PAN sample is bimodal; the first maximum is mainly related to the thermal transformation of PAN and the second maximum is due to the oxidation of the product of this transformation.

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