The Pyrolysis of Acrylic Fiber in Inert Atmosphere.
I.   Reactions up to 400°C

W. N. TURNER and F. C. JOHNSON, *Rolls-Royce Ltd., Composite Materials Department, Littleover, Derby, England*

Synopsis

The pyrolysis of acrylic fiber up to 400°C in an inert atmosphere at 1° and 6°C/min was studied by means of thermogravimetric and differential thermal analysis.   The exothermic reaction occurring at 180–300°C was shown to be due to the reaction of nitrile groups by comparing the extent of exotherm with the number of nitrile groups present, determined by infrared spectroscopy.   In addition, results of single-fiber tensile measurements, density, and elemental analysis of the pyrolyzed fibers are interpreted in terms of possible molecular structures.   The gases evolved on pyrolysis were analyzed for both ammonia and hydrogen cyanide and the liberation of ammonia was attributed to a termination reaction of the polymerization of nitrile groups.   The critical conditions necessary for the production of high strength and modulus carbon fiber are discussed briefly in relation to the chemical changes occurring on pyrolysis.

INTRODUCTION

In 1961 Shindo[1] demonstrated that carbon fibers having moderate tensile strength and modulus could be prepared from an acrylic precursor fiber by pyrolyzing in an inert atmosphere with or without a prior oxidative treatment.   Independent research at both Rolls-Royce[2] and RAE[3] has shown that suitable selection of the starting acrylic composition and optimization of the pyrolysis conditions will lead to vast improvements in fiber properties.   The most important pyrolysis parameters are the tensioning of the fiber and the rate of temperature rise.

In the present commercial production of carbon fibers from acrylics a prior treatment of the precursor fiber in air is favored.   This enables the subsequent pyrolysis to be completed more quickly.   However, carbon fibers of similar physical properties may be produced by a slow pyrolysis solely in an inert atmosphere.[4]

In contrast to carbon fibers produced from cellulose derivatives,[5] acrylics yield fibers having high orientation without the necessity of a stretching treatment at temperatures above 1700°C.   It seems, therefore, that the desirable physical properties are related to the unusual chemical structures obtained during the pyrolysis of acrylic fibers.   This paper deals solely with the reactions occurring below 400°C in an inert atmosphere; the higher temperature reactions and oxidative pretreatment will be reported later.

Processing in this temperature range has a critical effect on both the retention of the fiber morphology and on the subsequent development of physical properties on carbonization and graphitization.

The thermal degradation of polyacrylonitrile has been studied over a wide range of pyrolysis conditions.[6-9] However, the nature and sequence of reactions occurring during a programmed pyrolysis are still uncertain. Grassie and Hay[8] postulated the formation of a hydrogenated naphthyridine structure and Takata et al.[10] gave additional supporting evidence from a
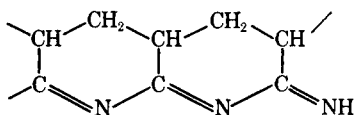
study of the relevant model compounds. Kennedy and Fontana[11] disclosed a sudden exothermic reaction under vacuum at 265°C which they attributed to naphthyridine ring formation in combination with chain scission. More recently, however, Hay[12] has related the exotherm to the production of ammonia.

The present paper deals with the reactions occurring in fibers when pyrolyzed according to a linear temperature program. In consequence, the techniques of thermogravimetric and differential thermal analysis were particularly appropriate, especially when combined with quantitative analysis of both the residue and the evolved gases.

EXPERIMENTAL

Materials and Sample Preparation

Courtelle fiber, $1^1/_2$ denier, was supplied by Courtaulds Ltd. in the form of a continuous filament tow. This commercial acrylic composition had methyl acrylate as the main comonomer unit and had the following elemental analysis: C, 66.6; N, 24.3; H, 5.7; O, 3.4. Samples for pyrolysis were prepared by winding the fiber tow onto a nimonic steel frame and knotting the loose ends. This assembly was then heated at 1°C/min to the required temperature in an argon flow.

Analytical Techniques

Differential Thermal Analysis (DTA). The apparatus was similar to the design described by Lodding and Hammel[13] and was capable of analysis up to 1000°C. The purge gas passed through the sample cell during analysis and continuously removed any degradation products. "Dead burned" alumina was a suitable reference material and the sample comprised a 10% w/w mixture of finely chopped fiber in this alumina. Diluted sample mixtures gave sharper and more reproducible peaks for acrylic materials by reducing the effects of packing and thermal capacity changes on the exotherm.

Thermogravimetric Analysis (TGA).   Fiber, 10 mg, in the form of a loosely tied knot was suspended from a modified electrobalance beam via a hooked silica suspension thread.   The sample was positioned in the hot zone of a furnace through which argon was passed at a constant rate to exclude any atmospheric air.

Infrared Analysis.   The pyrolyzed fibers were studied using the KBr disc method and spectra obtained on a Perkin Elmer 257 grating spectrophotometer.

Elemental Analysis.   The residues were examined by a microcombustion technique using an F. and M. 185 elemental analyzer.   For these thermally stable materials it was found that comparison of areas rather than heights of the chromatographic peaks gave more accurate results.

Analysis of Gaseous Volatiles.   The ammonia evolved was determined by mass spectrometry.   The volatiles produced from a small-scale pyrolysis were swept by means of an argon flow through a cold trap at $-35°C$ to remove the less volatile fraction.   This gas was then sampled, via a heated capillary line and porous leak, directly into the analyzer chamber of a standard AEI MS. 10 mass spectrometer.   At the end of each pyrolysis, the cold trap was warmed to confirm that no appreciable vapor absorption had occurred.

The hydrogen cyanide content of the argon purge gas was determined directly by a colorimetric method.[14]   A heated exhaust line was used to prevent absorption of HCN on the metal surfaces and the cyanide was fixed by bubbling through an excess of NaOH solution.

Tensile Properties.   Single fibers from the pyrolysis were tested in tension to failure.   Tension was applied by means of a lead screw driven at constant speed and was measured on a 10-g dynamometer.   An extensometer provided the appropriate extension data for the calculation of tensile modulus.

Density Measurement.   The "density bottle" technique was used with boiled distilled water as the immersion liquid.

RESULTS

The traces obtained from both differential thermal and thermogravimetric analysis at $1°C/min$ are reproduced in Figure 1.   This shows an exotherm occurring between 190 and 285°C which reaches a maximum at 262°C. The apparent exothermic drift on the baseline is identical to that observed on a blank run at this sensitivity and is therefore of no direct significance. Prior calibration of the apparatus, using the heat of fusion of benzoic acid, showed that the exotherm represented 8–11 kcals/mole of monomer unit. The weight loss curve shows a minor weight change in the region of 75–115°C which is due to the loss of absorbed water.   True degradative weight loss begins at 190°C and shows an inflection from 290–340°C.   This indicates that, after a weight loss of 11% during the exotherm, a more thermally stable structure is formed which degrades further beyond 340°C. However, the weight loss pattern in the exothermic region does not reflect
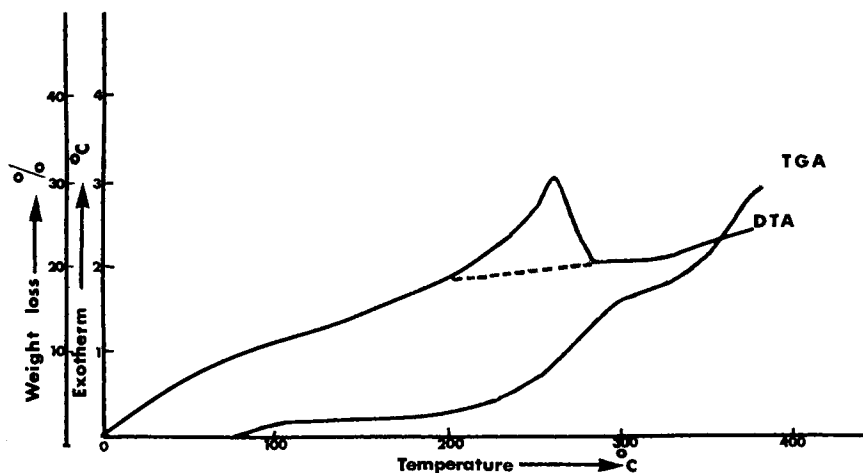
Fig. 1. DTA and TGA traces of fiber heated at 1°C/min in argon.

the general shape of the exotherm. This is shown more clearly by the results of analysis of 6°C/min (Fig. 2). At this heating rate the exotherm begins at a substantially lower temperature than that for the onset of weight loss.

The elemental analysis of the residues was used to calculate the atomic ratios of nitrogen, hydrogen, and oxygen to carbon during the pyrolysis and the ratios are plotted in Figure 3. The oxygen contents were not measured directly but were calculated by difference and therefore contain the errors of the carbon, hydrogen, and nitrogen determinations. While the oxygen/carbon ratio remained fairly constant up to 1000°C, the hydrogen content decreased linearly from about 200–600°C and was almost zero at 1000°C. The nitrogen, however, was removed in two separate regions, namely between 300–400°C and above 600°C. It is interesting to note that even at 1000°C the residue retains a high proportion of nitrogen.

The infrared absorbances of the 2240 cm^{-1} nitrile peaks were measured at various stages in the pyrolysis. It was found that a close correlation existed between the loss of nitrile and the extent of exotherm at heating rates of both 1° and 6°C/min, as shown in Figure 4. The progress of the exotherms was estimated by integration of the DTA peaks and the super-imposed points represent the amount of nitrile reacted within the residue. To obtain this figure, correction was made for any nitrile which was lost from the residue by evolution of nitrogen-containing compounds. This was done by combining the appropriate elemental analysis and weight loss data. No attempt was made to correct the DTA results for this relatively minor evolution of volatiles.

As the nitrile absorbance at 2240 cm^{-1} decreased, a sharp peak at 2190 cm^{-1} of low intensity appeared. This peak was assigned to a conjugated C=N system[15] rather than to the conjugation of unreacted nitrile groups with unsaturation in the polymer backbone. From published data,[16]
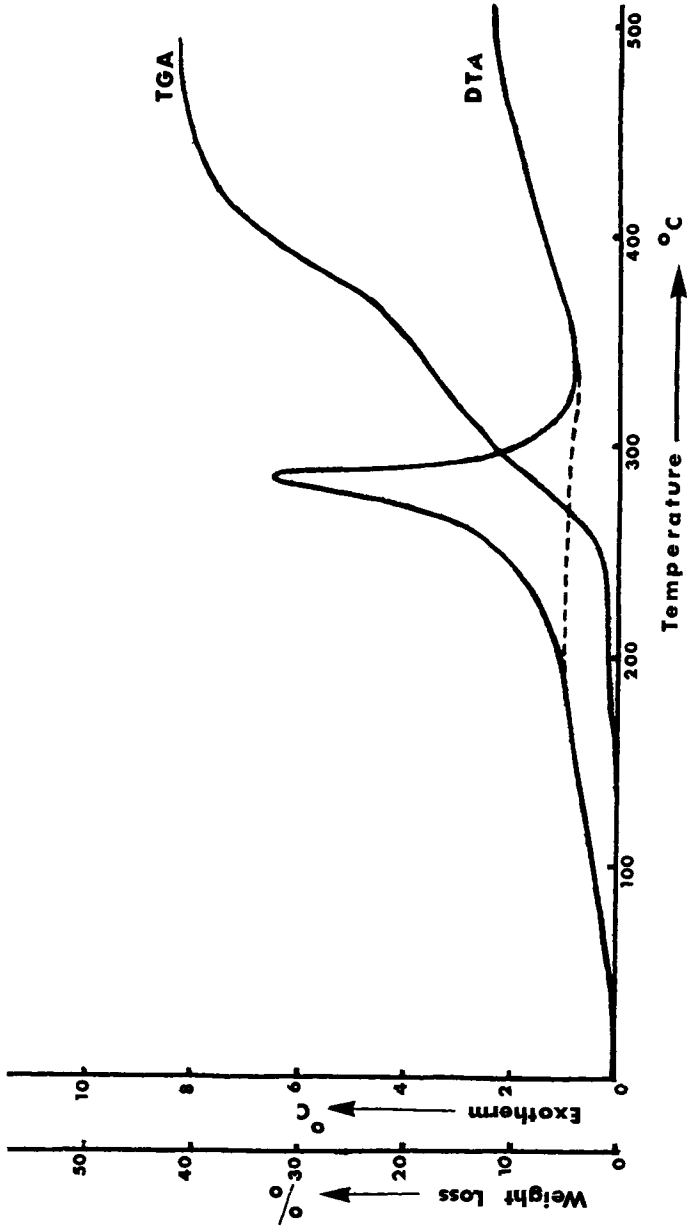
Fig. 2. DTA and TGA traces of fiber heated at 6°C/min in argon.

the latter system would be expected to absorb in the region 2215–2235 cm^{-1}. In consequence this peak was not included in the determination of residual nitrile content. Spectral changes in other wavelength regions agreed with other published data[7,8] and were consistent with the formation
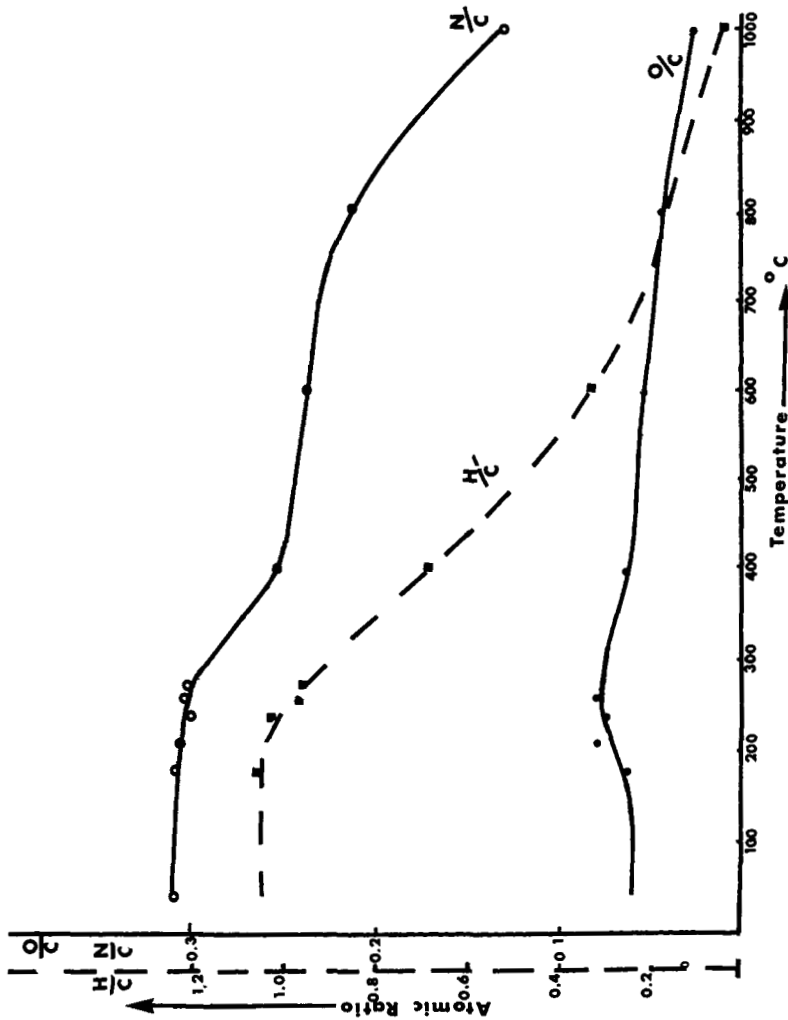

Fig. 3. Atomic ratios of elements present in the residue at various stages in the pyrolysis at 1°C/min. O) N/C atomic ratio; ■) H/C atomic ratio; ●) O/C atomic ratio.

of a highly conjugated C≡N system (1600 cm^{-1} absorbance) and free amino groups up to about 300–350°C. On heating beyond this temperature, broad electronic absorption progressively obscured the spectra.

The changes in tensile behavior and density of the pyrolyzed fiber are shown in Figures 5 and 6, respectively. During the exothermic reaction
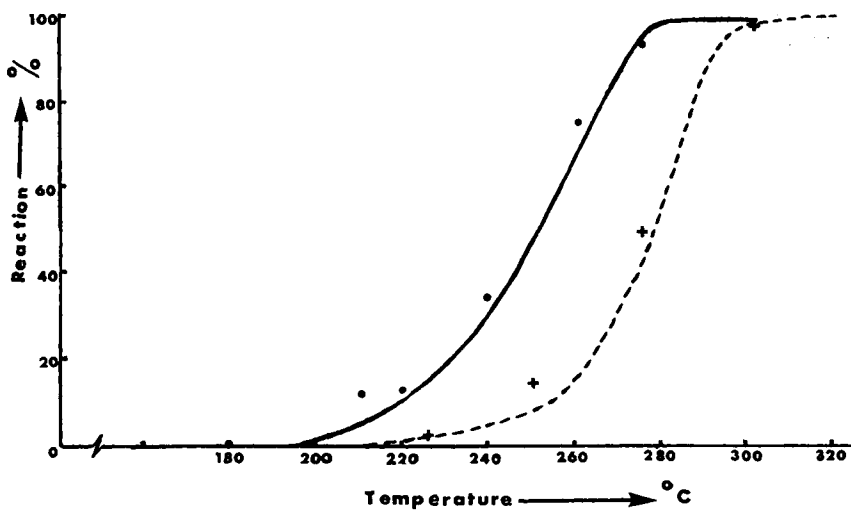
Fig. 4. Relation between the exothermic reaction and the nitrile conversion in the fiber. Integrated exotherms: ———) at 1°C min⁻¹; ————) at 6°C min⁻¹. Nitrile reaction: ●) at 1°C min⁻¹; +) at 6°C min⁻¹.
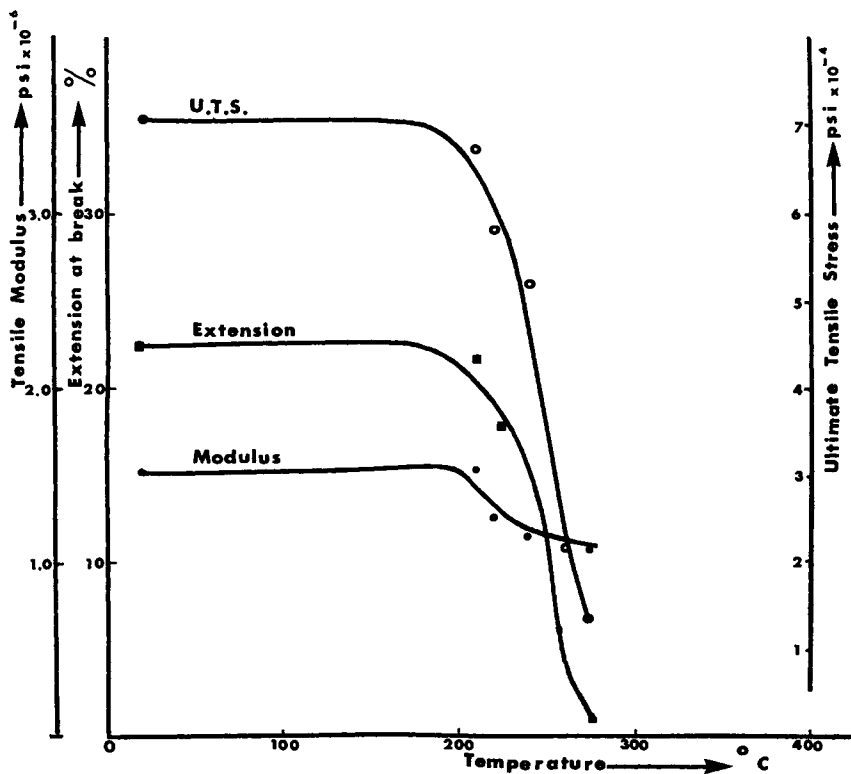

Fig. 5. Mechanical properties of partially pyrolyzed fibers.

both the ultimate tensile strength and the elongation at break decrease rapidly while the tensile modulus falls slightly. These changes are accompanied by a densification of the fiber.

Figure 7 shows the evolution of ammonia and hydrogen cyanide determined by mass spectrometry and colorimetry, respectively, on pyrolysis at 1°C/min. The amounts of ammonia determined were small and represented a total loss of 4% of the original nitrogen as ammonia up to 300°C. The relation of the ammonia evolution to the exotherm is shown in Figure 8. A heating rate of 6°C/min was used so that larger peaks were obtained and therefore enabled a more detailed comparison of the two traces. It
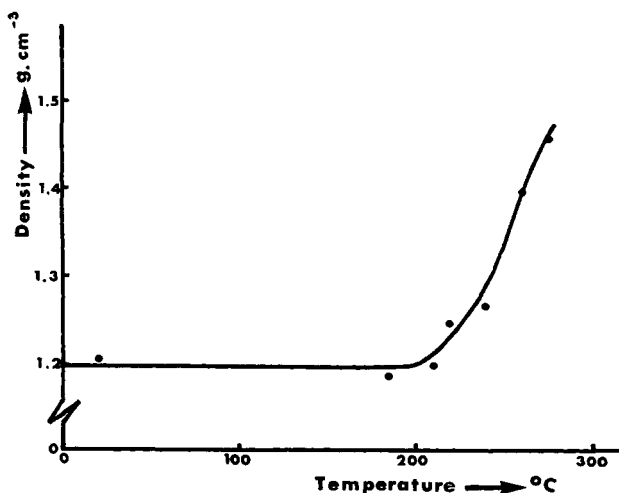

Fig. 6. Densities of fibers pyrolyzed to various temperatures at 1°C/min.

can be seen that the appearance patterns have different characteristics, despite the similarity in temperature at which they reach a maximum. This observation also applies to the results from the pyrolysis at 1°C/min.

The hydrogen cyanide evolved up to 400°C accounted for 16% of the nitrogen present in the starting material. Elemental analysis combined with the weight loss values from 300°C to 400°C showed that HCN was the major product containing nitrogen in the temperature range. This explains the observed drop in N/C atomic ratio in the same region.

During the exotherm a pale yellow liquid was condensed in the cold trap; it polymerized slowly on standing at room temperature and had an appreciable infrared absorption at 2240 cm^{-1} and an elemental analysis (C, 67.3; H, 6.8; N, 20.7; O, 5.2%) similar to that of the starting polymer. The yield of this product was approximately 7% and accounted for much of the weight lost up to 300°C.
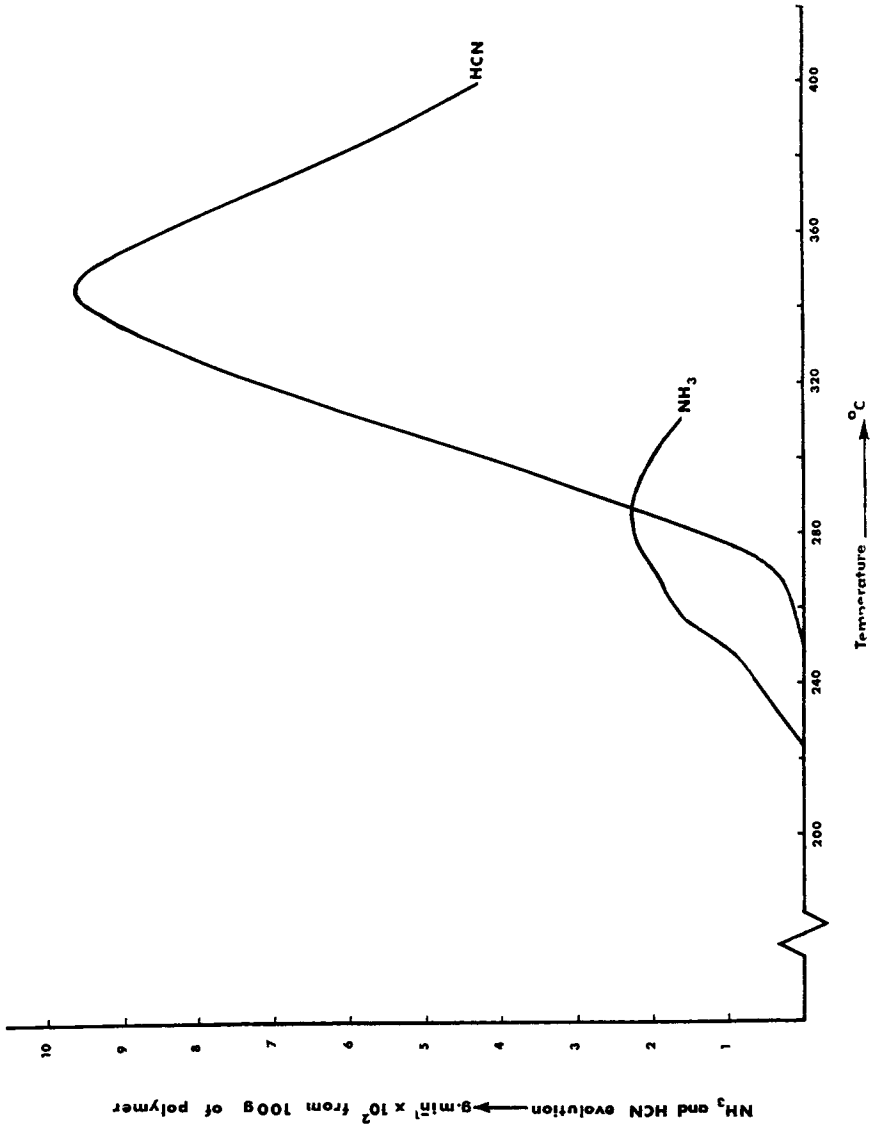
Fig. 7. Rates of evolution of NH₃ and HCN from 100 g of polymer on pyrolysis at 1 °C/min.

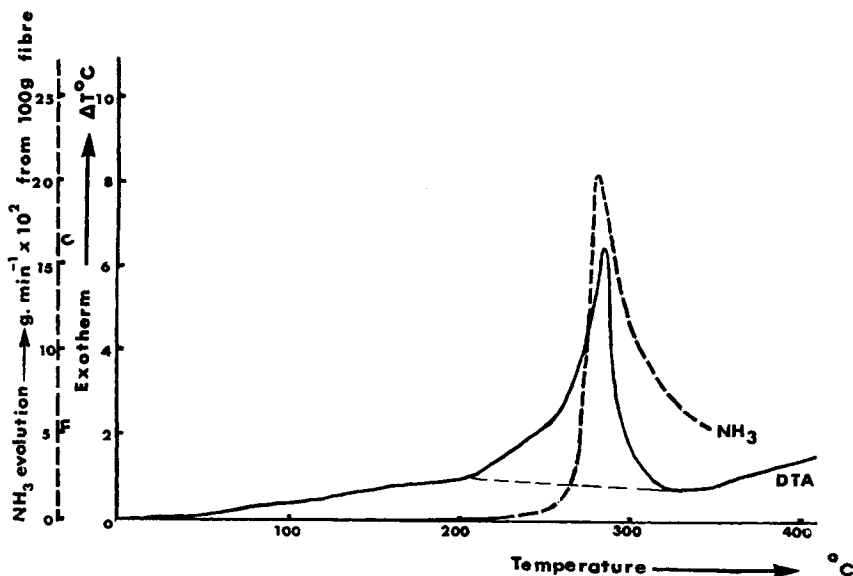Fig. 8. Comparison between the evolution of NH_3 and the exothermic energy at 6°C/min.

DISCUSSION

In a recent paper Hay[12] related the exotherm to the liberation of ammonia. From previous studies on the discoloration of acrylics he inferred that the nitrile reaction occurred before the exotherm. In contrast, our infrared results showed that the exotherm is coincident with nitrile reaction at heating rates of both 1° and 6°C/min even though the position of the exotherm on the temperature scale was dependent upon the rate of heating. No similar direct correlation was found with the ammonia evolution under our pyrolysis conditions. In addition, the amounts of ammonia formed were considered to be insufficient to cause an exotherm of 8–11 kcal/mole. Calculation showed that only one in approximately 25 monomer units reacted to give ammonia. However, the heat of polymerization of nitrile groups can be calculated approximately from published C—N bond energies[17] and was found to be exothermic to the extent of 5–10 kcal/mole. The lack of an observed exotherm on the DTA of polymethacrylonitrile (PMAN) may be due to the masking of this effect by the endotherm occurring on depolymerization of this polymer. For this reason it is difficult to correlate the results of pyrolyses of PMAN and polyacrylonitrile.

The spectral changes were consistent with the formation of a hydrogenated naphthyridine structure by the polymerization of the pendant nitrile groups in the acrylic fiber up to 300°C.

From the tensile behavior and density measurements, it appeared that chain scission had occurred but crosslinking did not contribute significantly to the mechanical properties of the fiber. This also explains the reported[18] solubility in formic acid of fibers pyrolyzed between 250°C and 400°C.
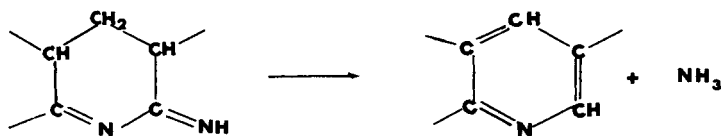
Mechanism 1
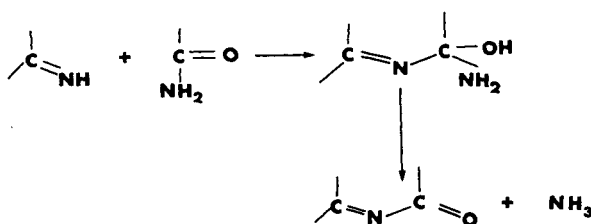
Mechanism 2

Fig. 9. Possible mechanisms for ammonia formation.

The appearance pattern of ammonia in relation to the exotherm suggested that it might be formed on termination of the nitrile polymerization. In addition to the mechanism of Hay, ammonia may also be produced via a reaction involving amide groups in the polymer (Fig. 9). These might originate from the starting polymer or form during the early stages of the pyrolysis by reaction with water vapor. Future work will test this mechanism by examination of the ammonia evolution from acrylamide copolymers with acrylonitrile. The hydrogen cyanide must arise through decomposition of the structure formed by the polymerization of the pendant nitrile groups. The change in the N/C ratio from 300°C to 400°C suggests that at least a proportion of the HCN lost is not accompanied by the simultaneous loss of the polyene fragment from the polymer carbon backbone. The resulting structure should be capable of crosslinking by analogy with dehydrochlorinated polyvinylidene chloride. This reaction, in combination with the progressive dehydrogenation, will lead to a more thermally stable residue and explains the substantial reduction in weight loss above 400°C.

The condensed liquid produced during the exotherm was thought to be caused by distillation of comparatively low molecular weight fragments formed by chain scission of the precursor polymer.

From this accumulated chemical evidence, some of the necessary pyrolysis conditions for the production of high physical property carbon from acrylics may be explained.

The severity of the exotherm necessitates a slow pyrolysis between 180°C

and 300°C to retain the fiber morphology and prevent thermal runaway. During the exotherm, chain scission and cyclization produce an essentially linear hydrogenated naphthyridine polymer of lower molecular weight. These changes cause a collapse in the molecular packing of the acrylic polymer as indicated by the increase in density. Therefore, it is necessary to retain tension on the fiber in this temperature range to maintain the orientation of the polymer structure parallel to the fiber axis. Similarly, tension is also required from 300°C to 500°C when the main weight loss and dehydrogenation cause further collapse in the fiber structure.

CONCLUSION

The exotherm, occurring on a temperature-programmed pyrolysis in inert atmosphere, was related to the reaction of nitrile groups in the fiber. The evolution of ammonia was attributed to a termination reaction of the nitrile polymerization. However, further work is required to substantiate this mechanism. The chemical changes occurring up to 400°C have been interpreted in terms of molecular structures present in the residue. More definite structural evidence is difficult to obtain on account of the insolubility of the pyrolyzed fibers. Future publications will deal with the reactions above 400°C and also on low temperature oxidation.

References

1. A. Shindo, Rep. Gov. Ind. Res. Inst., Osaka, Japan, No. 317, Dec. 1961.
2. A. E. Standage and R. Prescott, *Nature*, **211**, 169 (1966).
3. W. Watt, L. N. Phillips, and W. Johnson, *The Engineer*, **221** (1966).
4. A. E. Standage and R. Prescott, Brit. Pat. No. 1,128,043, April 1965.
5. R. Bacon and W. A. Schalamon, 8th Biannual Conf. on Carbon, Buffalo, N. Y., June 1967.
6. R. Houtz, *J. Textile Res.*, **20**, 786 (1950).
7. W. J. Burlant and J. L. Parsons, *J. Polym. Sci.*, **22**, 156 (1956).
8. N. Grassie and J. N. Hay, *J. Polym. Sci.*, **56**, 189 (1962).
9. A. R. Monahan, *J. Polym. Sci. A-1*, **4**, 2391 (1966).
10. T. Takata, I. Hiroi, and M. Taniyama, *J. Polym. Sci. A-2*, 1567 (1964).
11. J. P. Kennedy and C. M. Fontana, *J. Polym. Sci.*, **39**, 506 (1959).
12. J. N. Hay, *J. Polym. Sci. A-1*, **6**, 2127 (1968).
13. W. Lodding and L. Hammel, *Rev. Sci. Instrum.*, **30**, 885 (1959).
14. W. N. Aldridge, *Analyst, Lond.*, **69**, 262 (1944); *ibid.*, **70**, 474 (1945).
15. R. Liepins, D. Campbell, and C. Walker, *J. Polym. Sci. A-1*, **6**, 3059 (1968).
16. R. E. Kitson and N. E. Griffith, *Anal. Chem.*, **24**, 334 (1952).
17. G. E. Coates and L. E. Sutton, *J. Chem. Soc.*, 1187 (1948).
18. K. Miyamishi, M. Okamoto, O. Ishizuka, and M. Katayama, *J. Soc. Text. Cellul. Ind. Japan*, **23** (7), 342 (1967).