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Physical changes during thermal oxidation of PAN fibres and effects of γ-radiation pre-treatment

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Abstract

Oxidation experiments have been carried out at 250 °C on PAN terpolymer fibres under both constrained and free recovery conditions. The effects of pretreating the fibres with γ-radiation prior to oxidation were also studied. Constraining the fibres in the stabilisation process produces a more open structure which can account for the more pronounced hygroscopic nature of oxidised fibres. Treating the fibres with γ-radiation reduces weight losses occuring in the stabilisation process and accelerates the overall oxidation reactions. These conclusions were reached from a series of evaluations including solubility tests, DSC analysis, scanning electron microscopy (SEM) examination, and dynamic mechanical and load/extension curves.

INTRODUCTION

The production of carbon fibres involves three heating processes: thermal oxidation, carbonisation and graphitisation [1]. The purpose of the thermal oxidation process is to induce dimension stability prior to the carbonisation stage by producing an infusible structure. Hence the term stabilisation is often used to describe this process.

Stabilised PAN fibres, however, are also used as fibres in their own right for high temperature applications and for fire-retardant textiles. Dimension stability is achieved through the formation of ladder molecular structures, generated by a combination of cyclisation, dehydrogenation and oxidation reactions. These reactions are predominantly intramolecular and consequently only a few cross-links are produced during the thermal oxidation process [2]. The cross-links are often referred to as step ladders and arise from strong intermolecular attractions between those CN groups from neighbouring chains which are out-of-step with the helical configuration along the backbone chains [3,4]. Watt et al. [5] proposed that the step ladder structure is oxidised further and, through loss of water and subsequent tautomeric rearrangement, gives rise to the formation of pyridone units in the chains.

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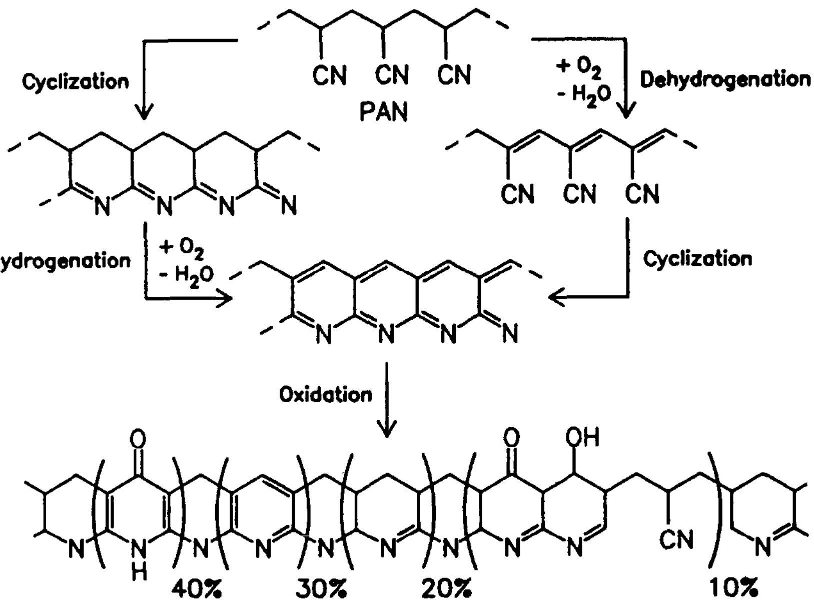

Fig. 1. Reactions involved in the stabilisation of PAN fibres (after Fitzer et al. [1]).

The steps involved in the formation of stabilised PAN fibres have been confirmed by several authors [6–8] and are shown in Fig. 1. The aromatisation index is often used to characterise the overall structure of oxidation stabilised PAN fibres [4,9–11].

The cyclisation process for homopolymer PAN fibres occurs by a free radical initiation stage followed by oxidative reactions. These two consecutive processes are evidenced by an initial endothermic reaction followed by a series of cumulative oxidation reactions giving rise to ladder structures oriented along the fibre axis [3,12].

Copolymers

The presence of polar groups C=O, OH and COOH in the chains facilitates the initiation of the cyclisation process through nucleophilic attack and accelerates the subsequent oxidative ring closure reactions. For this reason copolymers containing carboxylate esters and carboxylic acid groups are preferred to homopolymers for the production of PAN fibre precursors. The incorporation of co-monomers in the main chains reduces the nitrile dipole interactions, increases chain segment mobility and increases the free volume of the system. As a result of the above events the oxygen permeation through the fibre is increased and the overall reaction time for the stabilisation process is reduced, affording considerable savings in manufacturing costs.

Pretreatments

PAN fibres can also be pretreated to reduce the stabilisation time through more rapid oxidation reactions. It has been found, for instance, that immersing the fibres in warm potassium permanganate solution can reduce the activation energy for the cyclisation reactions, and also lower the temperature for onset of the initiation reactions [13]. Considerable reduction in stabilisation time has also been obtained by treating the fibres with warm dibutyltin dimethoxide solution [14]. In general, chemical treatments are more widely carried out on the final carbon fibres than on the PAN precursor, primarily as a means of introducing polar groups on the surface in order to enhance interfacial adhesion with resins in the production of composites.

A major objective of this work is to examine the effects of pretreating PAN fibres with γ-radiation on the chemical and physical changes taking place in the fibre stabilisation process. Fibre treatment with γ-irradiation has been proposed for the stabilisation of polycarbosilane for the production of SiC fibres [15], but there appears to be very little information on such treatments for the production of carbon fibres.

Physical factors

It has been suggested that by restricting length shrinkage, or even stretching the fibres during the stabilisation process, the orientation of laddered structures can be locked into the fibres, thereby eliminating the need for further drawing of the fibres in any subsequent operations [2,10,16].

According to Fitzer et al. [17] the overall shrinkage is made up of a physical component, called entropy shrinkage, which is associated with partial relaxation of the orientation of the PAN chains, and a chemical component, called reaction shrinkage, which is obviously associated with the cyclisation and overall oxidation reactions. Entropy shrinkage takes place above the T_g of the polymer and is completed at temperatures below 200 °C, while the chemical reaction shrinkage starts above 200 °C and is completed at ca. 300 °C, using a 5 °C min^{-1} heating rate. Both entropic and reaction shrinkage is much less for homopolymer fibres and they increase on increasing the amount of carboxylate comonomer, normally methyl acrylate. The additional presence of small amounts of a carboxylic acid (normally itaconic or acrylic acid) helps in maintaining a relatively low shrinkage during the stabilisation process.

It is generally accepted that both precursor and stabilised PAN fibres have a disordered, amorphous, phase and an ordered phase. The atactic nature of PAN means that the ordered phase cannot be regarded as truly crystalline, but it is thought that the molecular chains have a regular helical configuration owing to strong intramolecular dipole–dipole interactions between nitrile group pairs. This helical organisation of nitrile groups fits into a cylindrical sheath ca. 6 Å in diameter. Bound nitrile group pairs are formed between neighbouring cylinders as a result of intermolecular attractions. It is thought that the amorphous phase is composed of irregular helical configurations having less intermolecular nitrile group pairings.

Changes in molecular structure have been followed using wide angle X-ray diffraction [9], showing that the formation of ladder polymer from the linear PAN molecules is initiated in the amorphous phase and then forms the boundaries of the ordered phase. Incomplete stabilisation produces fibres which show both zones and cores, a phenomenon that is related to oxygen diffusion during the stabilisation process. Polished cross-sections of fibres examined by reflected light microscopy show cores with outer zones, whose dimensions are directly related to oxidation time [2,18].

PAN fibres show an overall increase in density with stabilisation depending on a number of factors as shown in Fig. 2. The change in density has been related to oxygen up-take and fibres with density in the range of 1.34–1.39 g cm^{-3} have been shown to have an oxygen content of 5–9% by weight [19].

Excessive stabilisation giving higher densities appears to produce undesirable microvoids as they reduce fibre strength. Very little is known to date, however, of the changes in dimensions, morphology, chemical state and mechanical properties of PAN fibres at different stages of the stabilisation process. It is, therefore, another objective of this work to illustrate and quantify these phenomena with the view of providing a more complete picture of the stabilisation process.

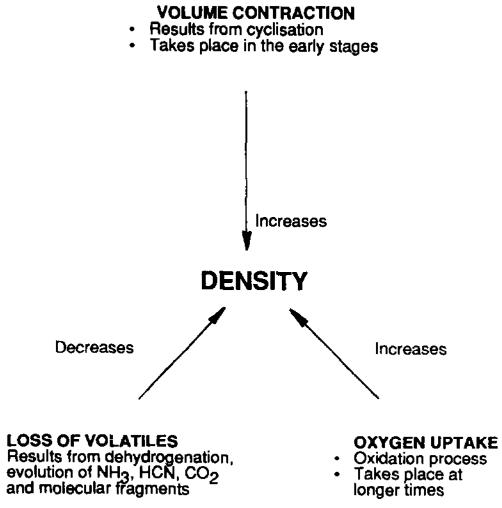

Fig. 2. Factors affecting the density of stabilised PAN fibres.

EXPERIMENTAL

The investigation was carried out using two commercial samples of PAN fibre precursors for the production of carbon fibres, respectively manufactured by Courtaulds Plc (known as Courtelle) and by Enichem SpA (designated as Terpolymer). Both fibres are believed to be based on interpolymers containing more than 90% acrylonitrile with the remainder consisting of methyl acrylate and a carboxylic acid.

Characterisation of PAN precursors

The two commercial fibres were subjected to several analytical tests to find out whether any major differences existed with respect to structure and thermal oxidation characteristics. These include an elemental analysis carried out by CHN Analysis Ltd., DSC analysis using the DuPont 910 instrument and IR spectra on films cast from dimethylformamide (DMF) solutions, both immediately after drying and after 1 h oxidation in air at 250 °C.

Simulation of the fibre stabilisation process

Thermal oxidation of the fibres was carried out in a forced-air circulation oven at 250 °C by tightly winding the fibres around a steel frame, 50 cm high and 30 cm wide, for various periods of time up to 200 min. Similar experiments were carried out on unconstrained fibres of similar length. Two minutes were allowed for conditioning the fibres to the set temperature of the oven between each oxidation treatment. The same experiments were also carried out on samples previously treated in an unconstrained state by γ-radiation at a dose rate of 25 kGy h^{-1} to a total dose of 150 kGy (15 MRad).

Bulk and dimensional changes

During the course of the stabilisation process the weight loss and the change in diameter and length of the fibres were measured for both constrained and unconstrained experiments. The changes in microstructure were monitored by SEM examinations..

In order to assess the entropic contribution to the overall dimensional changes shrinkage tests were carried out at 150 and 180 °C by freely suspending the fibres, 50 cm long, in an oven for 10 min and subsequently measuring the length with an accurate steel rule and the diameter with the aid of an optical microscope.

Chemical and physical changes

The extent of combined oxidation and cyclisation reactions was assessed by measuring the solubility and swelling of the fibres in DMF and by DSC analysis at a heating rate of 20 °C min^{-1}. Swelling was monitored by measuring the change in fibre diameter. The physical state of the fibres during the course of the stabilisation process was monitored by means of dynamic mechanical spectra measurements at 5 Hz from room temperature to 200 °C, using the Polymer Laboratories DMTA apparatus, with a pretension load of 1 N. The change in length of the fibres with increasing temperature was also recorded during the dynamic mechanical tests to obtain additional information on the physical state of the fibres.

Load/extension curves were obtained on fibre 'tows' from tensile tests at room temperature using a 4301 Instron machine.

RESULTS AND DISCUSSION

The IR spectra for the two polymers are shown in Fig. 3, while the data from both DSC and elemental analysis are given in Table 1. These show that

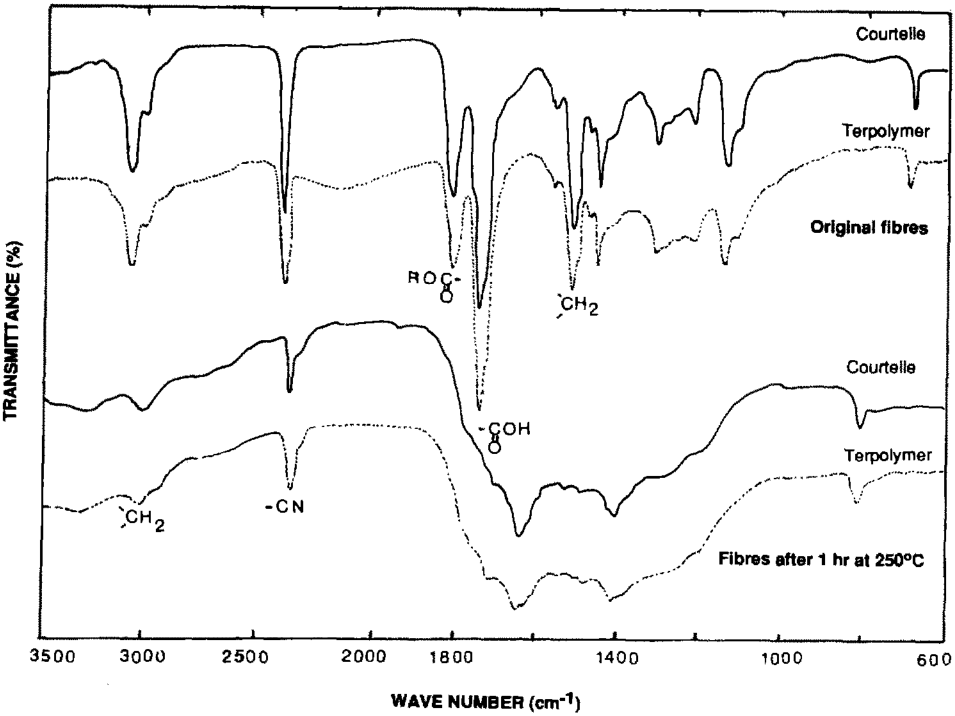

Fig. 3. IR spectra of PAN fibres.

TABLE 1

Thermal analysis data and elemental constitution of PAN fibres

	Courtelle fibres	Terpolymer fibres
DSC data (20 °C min^{-1})		
Exotherm initiation temperature (°C)	284	281
Exotherm peak temperature (°C)	309	306
Elemental Analysis		
Carbon (%)	65.73	65.93
Hydrogen (%)	5.74	5.79
Nitrogen (%)	24.02	24.10
Oxygen (%)	4.51	4.18

the two fibres have a similar chemical constitution and exhibit similar thermal oxidation behaviour, apart from the higher heat of reaction exhibited by the Courtelle fibres.

The progress of the oxidation process for fibres stabilised under both free-shrinkage conditions and constrained length conditions, including the effects of fibre pretreatment by γ-radiation, is shown in Fig. 4 by comparing the respective DSC traces for different oxidation times varying from 1 to 201 min. In all cases one notes a shift to higher temperatures for both the incipient point and the peak temperature of the exothermic reactions, which is accompanied by a decrease in the height of the peak as a result of the reduction in residual reactivity. While no major differences can immediately be detected in the chemical state of the fibres for treatments under free-shrinkage and constrained conditions, the samples that were pre-treated with γ-radiation display a reduction in the time for the onset of the exothermic reactions.

Plots of the incipient exotherm temperature as a function of the oxidation time are shown in Fig. 5. While no definite conclusion can be made regarding the shallow endotherm preceding the strong endotherm at high temperatures, interesting changes in the DSC traces are observed with respect to the small endotherms at lower temperatures. The endotherm peaks at 95 °C for the original fibres, in fact, disappear after 1 minute of oxidation in all cases, but it reappears again with greater predominance at higher temperatures with increasing oxidation time. When the heating rate was decreased from 20 °C min^{-1} to 10 °C min^{-1} the endothermic peak was no longer observed (Fig. 6).

An experiment carried out on a cycling heating programme also caused the endothermic peak to vanish, suggesting that this phenomenon is associated with the evaporation of moisture from the sample (Fig. 7). Such a conclusion was subsequently reaffirmed by performing experiments first on samples pre-dried in a vacuum oven at 80 °C and subsequently on similar

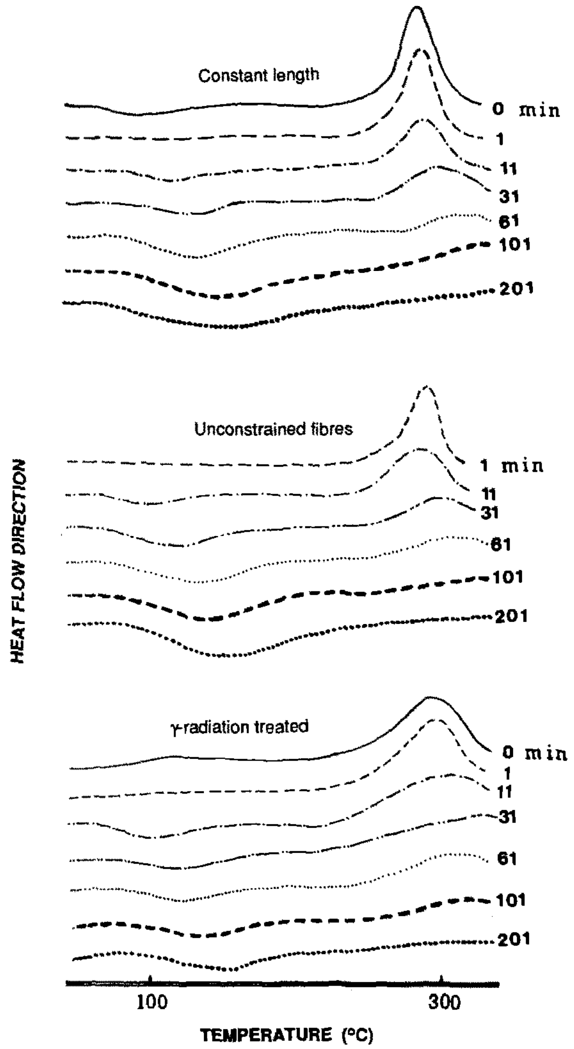

Fig. 4. DSC curves for Courtelle fibres at various stages of the stabilisation process at 250 ° C.

samples exposed to moisture. From these observations it is clear, therefore, that the thermal oxidative stabilisation process increases the level of water absorption of the fibres.

Plots of the peak endotherm temperature against oxidation time are shown in Fig. 8. These show that fibres stabilised under fixed length conditions develop hygroscopic characteristics at a faster rate than those oxidised with free recovery.

Solubility and swelling tests carried out in DMF have subsequently revealed that even after only 1 minute of oxidation the fibres form a loose gel, while after 11 min oxidation the fibres did not lose their identity even after prolonged boiling. For oxidation times greater than 31 min the fibres

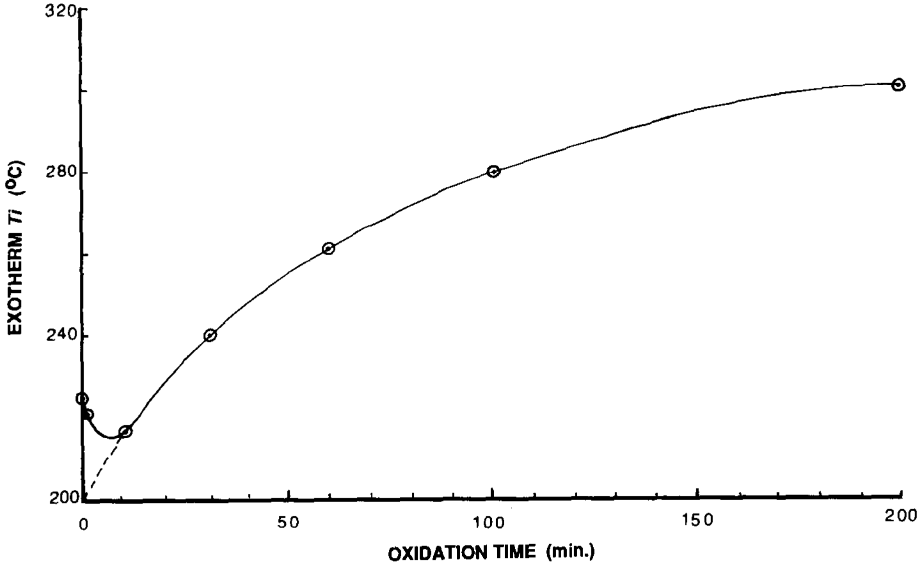

Fig. 5. Effects of stabilisation time at 250 °C on the initiation of the exothermic reactions.

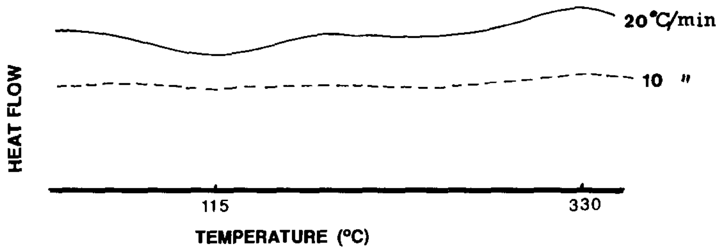

Fig. 6. Effect of heating rate in the DSC analysis on the low temperature endotherm of PAN fibres (Courtelle fibres after 61 min oxidation at 250 °C).

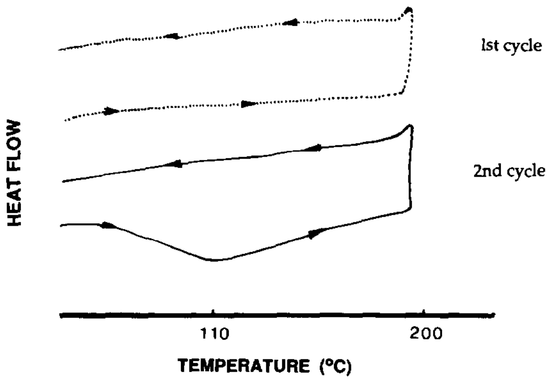

Fig. 7. Effects of cycling heating in the DSC analysis on the low temperature endotherm of PAN fibres (Courtelle fibres after 61 min oxidation at 250 °C).

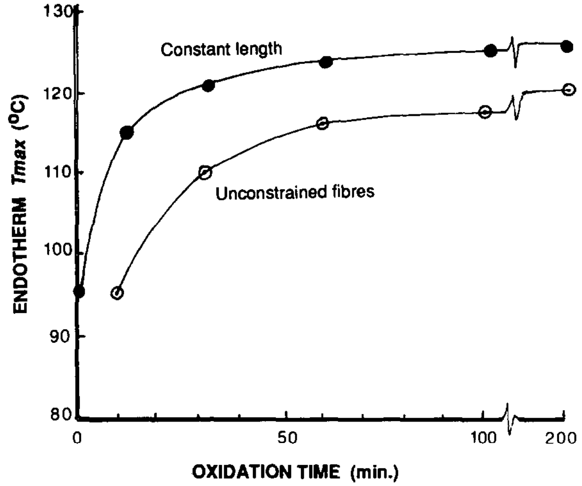

Fig. 8. Effect of oxidation time at 250 °C for Courtelle fibres on the peak endotherm temperature using heating of 20 °C $\min^{-1}$ in the DSC analysis.

remain completely undissolved and only a small amount of swelling takes place, as shown in Fig. 9. No detectable differences were noted for fibres treated with γ-rays, including the total solubility of non-oxidised fibres.

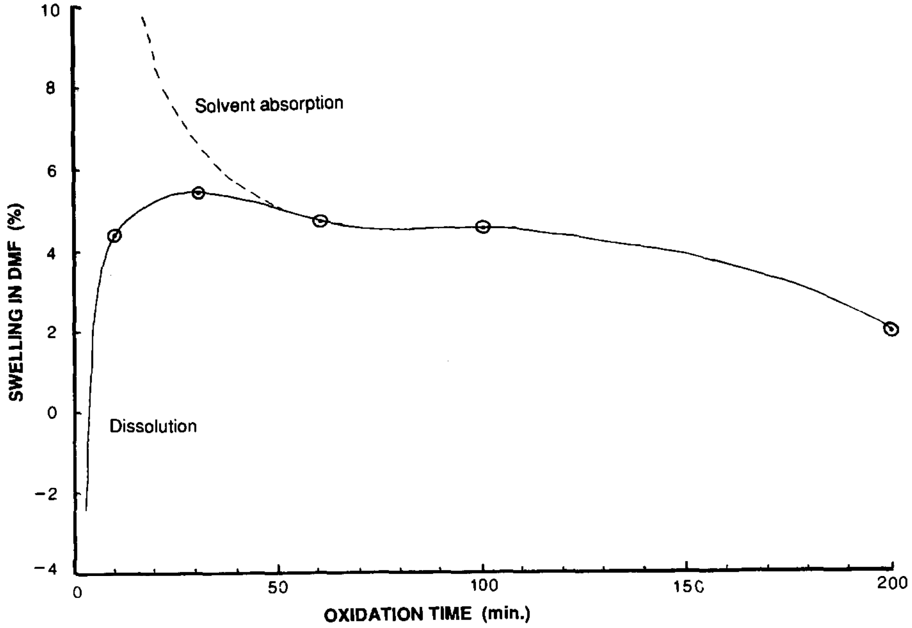

Fig. 9. Solubility characteristics of partially oxidised PAN fibres (Courtelle fibres) after 34 min at 250 °C.

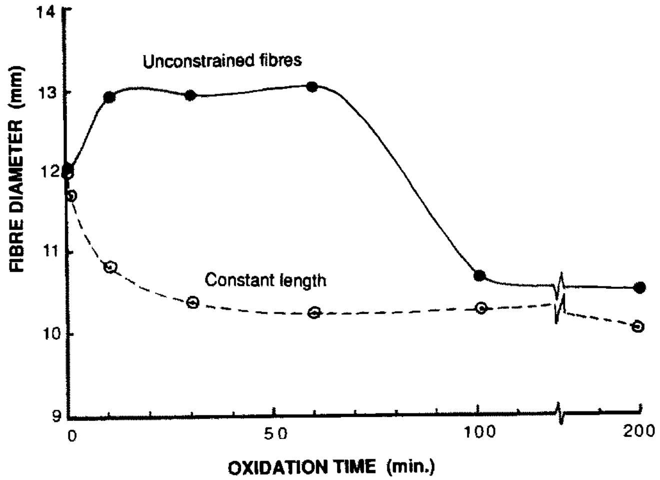

Fig. 10. Changes in fibre diameter during stabilisation of PAN fibres (Courtelle fibres at 250 °C).

Combining the latter observation with the increased oxidation rate discussed earlier leads to the conclusion that the γ-radiation treatment produces chain scission reactions without affecting the oxidative cyclisation mechanism.

The dimensional stability tests on fibres at 150 and 180 °C revealed an overall constant entropic shrinkage of 6.3% with a slight increase for fibres treated with γ-rays. The results for untreated fibres are in good agreement with the data reported by Fitzer et al. on fibres heated with a constant temperature rise of 5 °C min^{-1} [17]. Furthermore the above dimension stability tests have shown that entropic shrinkage is almost completely eliminated even after only 1 min of oxidation at 250 °C.

The longitudinal shrinkage of unconstrained fibres due to chemical reactions was found to occur more rapidly for fibres pre-treated with γ-radiation reaching an equilibrium value of 38% at 250 °C, compared with a total shrinkage of 33% for untreated fibres.

The change in diameter of the fibres as a function of the oxidation time is shown in Fig. 10 for both constrained and unconstrained stabilisation. The measurements were not sufficiently accurate, however, to detect any difference for fibres treated by γ-radiation.

It is interesting to note that while the length of the fibres increases monotomically with oxidation time, the diameter of the fibres stabilised in the unconstrained state goes through a plateau for oxidation time between 11 and 61 min and then decreases very rapidly to approximately the same value as for the fibres stabilised under fixed length conditions. This suggests that stabilisation of PAN fibres by oxidation at 250 °C is achieved after about 100 min.

TABLE 2

Calculated density variation of PAN fibres during thermal oxidation at 250 °C

Oxidation	Density ratio [ρ (final)/ρ (initial)]			
	Unconstrained fibres		Constrained fibres	
	Natural	γ-ray treated	Natural	γ-ray treated
11 min (peak)	0.99	1.19	1.075	1.18
100 min (stable)	1.82	1.89	1.30	1.35

The weight loss for both untreated and γ-ray treated fibres taking place during the course of the oxidation process is shown in Fig. 11. A maximum is observed in both cases at 11 min heating time, with a small increase occurring after 31 min. The reduction in weight loss achieved by fibres treated with γ-rays is very striking. The fact that the same trend is shown for both treated and untreated fibres confirms that the same chemical reactions are taking place but to a different extent.

Combining the data in Fig. 10 with those in Fig. 11 the variation in density can be calculated, as shown in Table 1. These data confirm that while the γ-radiation treatment causes only a small increase in density, much higher densities are obtained when fibres are oxidised under unconstrained conditions.

The more open structure predicted for fibres oxidised under free recovery conditions can probably account for their more pronounced hygroscopic characteristics.

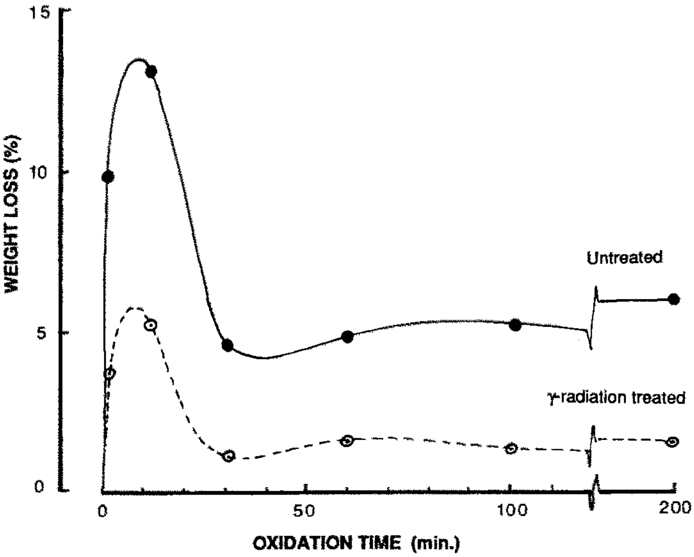

Fig. 11. Weight loss of PAN fibres during stabilisation at 250 °C (Courtelle fibres).

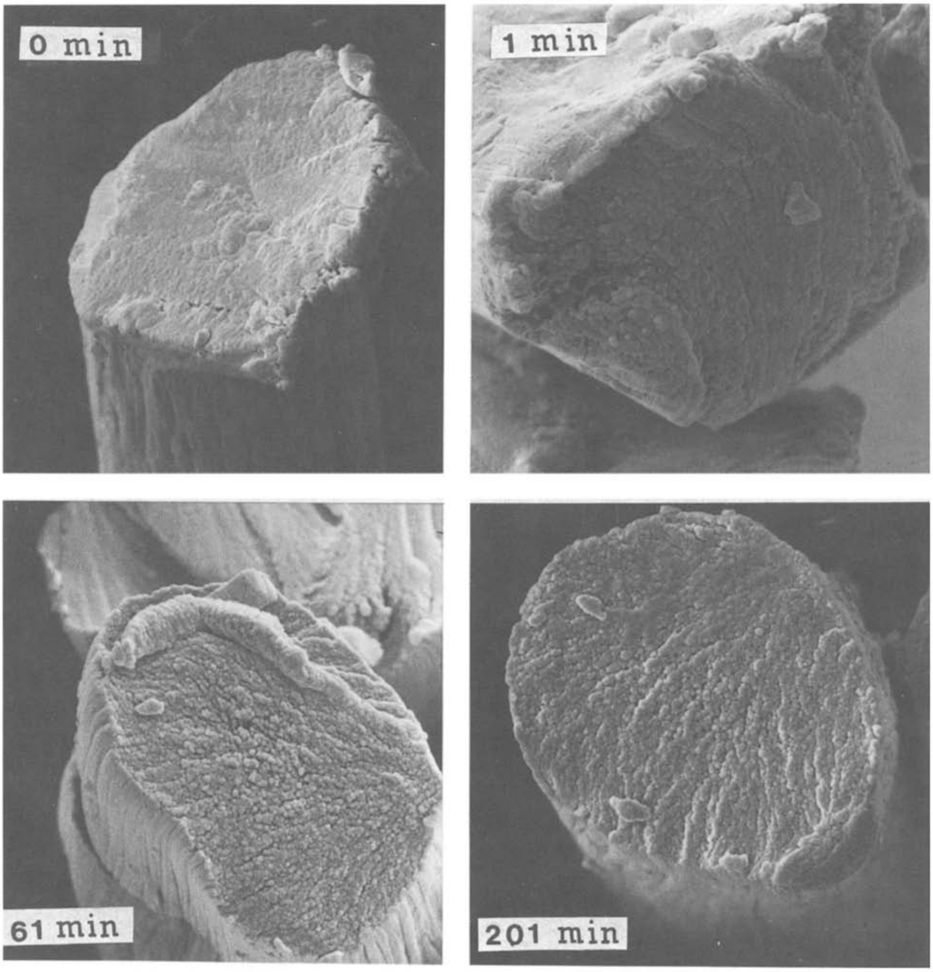

Fig. 12. Changes in microstructure of PAN fibres during thermal oxidation at 250°C (Courtelle fibres).

The changes in microstructure taking place during thermal oxidation are shown in Fig. 12. In all cases the formation of a fibrillar structure takes place at fairly short time, possibly coinciding with the maximum weight loss. Samples oxidised under free recovery conditions, however, appear to exhibit a coarser microstructure.

The traces in Fig. 13, depicting the dynamic modulus as a function of the temperature, show that the main transition broadens and shifts to higher temperatures with increasing oxidation time.

The overall decrease in modulus at high temperatures becomes smaller with increasing oxidation time. However, while the modulus remains constant only when approaching 200 min oxidation time, no stretching of the fibres under the dynamic test takes place even after 11 min. The tan δ traces

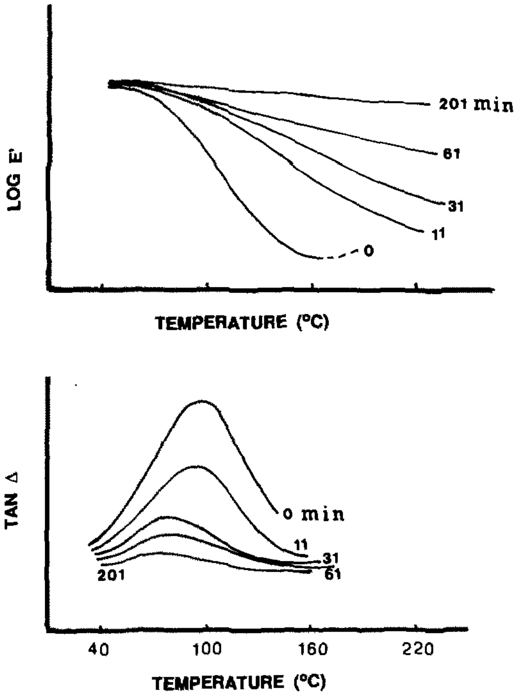

Fig. 13. Dynamic mechanical spectra of PAN fibres (Terpolymer) at different stages of the stabilisation process at 250 ° C.

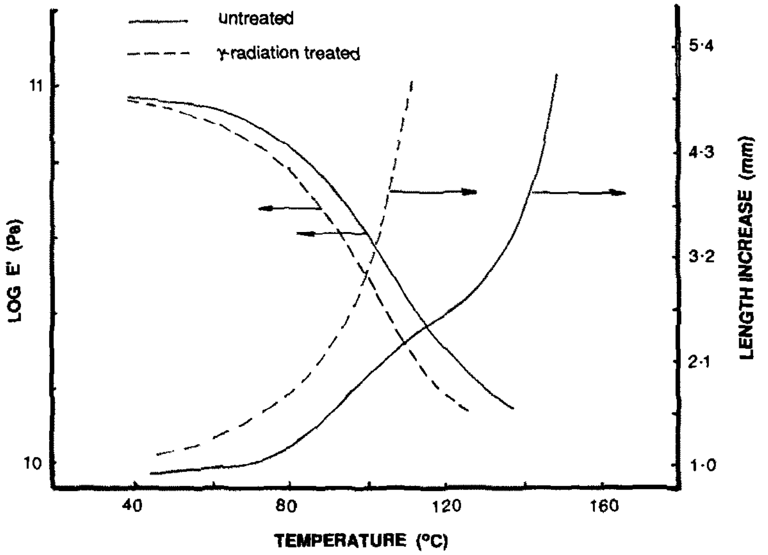

Fig. 14. Effect of γ-radiation treatment of dynamic modulus and fibre extension (Terpolymer fibres).

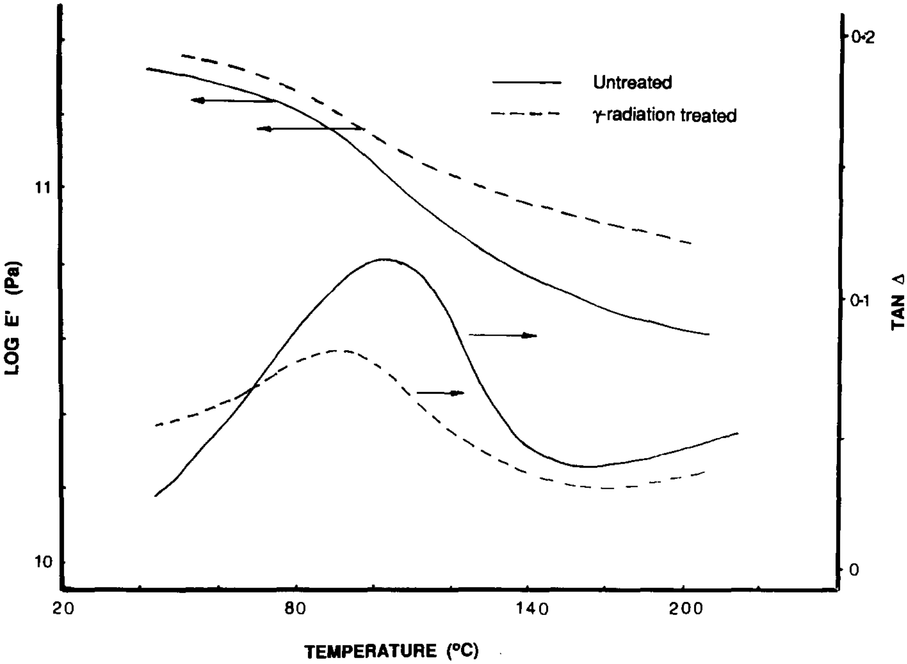

Fig. 15. Effect of pretreating fibres with γ-radiation on the dynamic mechanical spectra of PAN fibres at an intermediate stage of the stabilisation process (Terpolymer fibres after 11 mins. at 250 ° C).

in Fig. 13 show, on the other hand, that the α-dispersions are gradually depressed but the peak moves to lower temperatures with a small peak remaining at 50 ° C even after 200 min oxidation time. This can be attributed to a plasticisation effect resulting from molecular fragments from the oxidation process, possibility enhanced by absorbed water.

In Figs. 14 and 15 the curves for tan δ and fibre extension for untreated fibres are compared with those for fibres irradiated with γ-rays prior to the oxidation process. These reveal a broadening of the tan δ curve for the irradiated fibres with a concomitant reduction in the temperature at which the fibres undergo a rapid extension.

Coupled with the lowering of the modulus at high strains shown in Fig. 16, the conclusion about chain scission and plasticisation by molecular fragments, resulting from the γ-radiation treatment, is confirmed again. The acceleration effect that this has on the oxidation process, suggested by the earlier examination of the DSC traces, is also confirmed by the dynamic mechanical spectra in Fig. 15, where it is shown that for an oxidation time of 11 min the tan δ peak is displaced at a lower temperature, while the modulus at elevated temperatures is higher for fibres that were pre-treated with γ-rays.

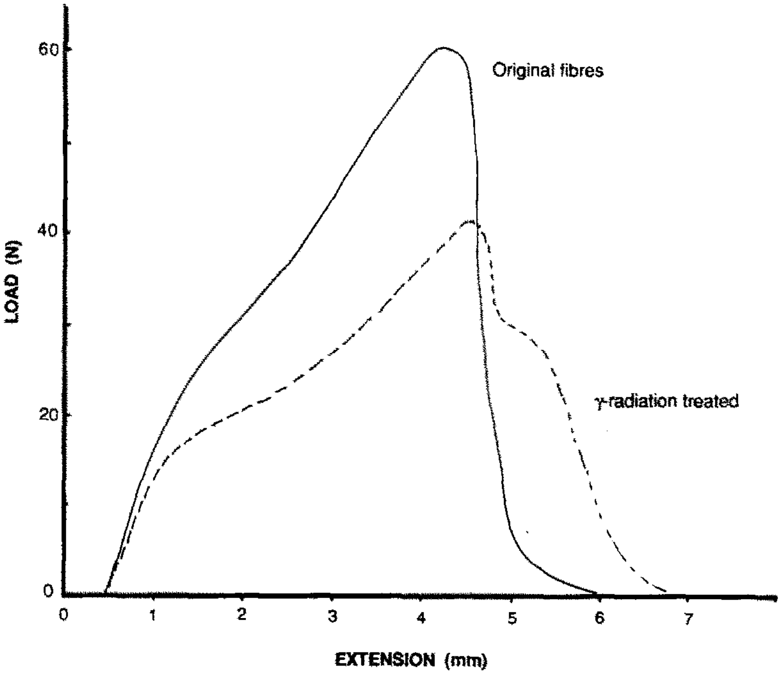

Fig. 16. Effect of γ-radiation treatment on the load/extension characteristics of PAN fibres (Courtelle).

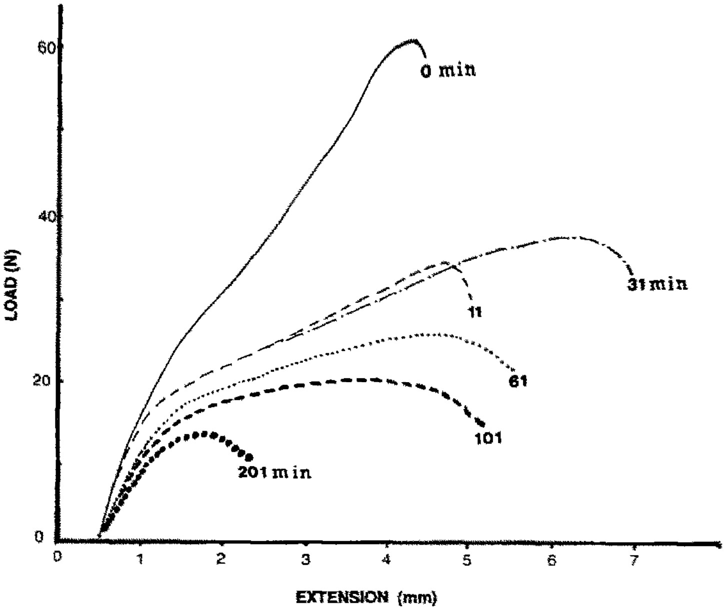

Fig. 17. Changes in load/extension characteristics of PAN fibres (Courtelle) in the course of the stabilisation process at 250 °C.

Finally, in Fig. 17 the load/extension curves are shown for fibres at different oxidation times. These reveal a gradual reduction in strength of the fibres with increasing oxidation time and a very large drop in ductility for oxidation times between 100 and 200 min, confirming that the optimum oxidation time at 250 °C is around 100 min.

CONCLUSIONS

The main conclusions to be derived from this study are:

(i) Thermal oxidation of PAN fibres under unconstrained conditions produces a substantially more dense structure than at constant length.

(ii) Pre-treatment of PAN fibres by γ-radiation can accelerate appreciably the oxidation process as well as reducing the weight loss.

(iii) Greater molecular fragmentation takes place during oxidation when PAN fibres are pre-treated with γ-rays but the overall weight loss is reduced.

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REFERENCES

1 E. Fitzer, W. Frohs and M. Heine, Carbon, 24 (1986) 387–395.
2 W. Watt, Proc. R. Soc. London, Ser. A, 319 (1970) 17–32.
3 G. Henrici-Olive and S. Olive, Adv. Polym. Sci., 51 (1983) 3–60.
4 G. Henrici-Olive and S. Olive, Polym. Bull., 5 (1981) 457–461.
5 W. Watt, D. Johnson and E. Parker, Proc. Int. Carbon Fibres Conf., Plastics Institute, London, 1974, pp. 3–11.
6 T. Takahagi et al. J. Polym. Sci. A, Polym. Chem. Ed., 24 (1986) 3101–3107.
7 T. Uchida, I. Phionoya, Y. Ho and K. Nucada, 10th U.S. Carbon Conf., (1971) pp. 31–32.
8 M. Coleman and R. Petcavich, J. Polym. Sci., Polym. Phys. Ed., 16 (1978) 821–832.
9 T. Ko, C. Lin and H. Ting, J. Appl. Polym. Sci., 37 (1989) 541–552.
10 A. Takaku and J. Shimizu, J. Appl. Polym. Sci., 29 (1984) 1319–1323.
11 T. Ko, C. Lin and H. Ting, J. Appl. Polym. Sci., 37 (1989) 553–566.
12 H. Balard and J. Meybeck, Eur. Polym. J., 14 (1978) 225–231.
13 T. Ko and C. Liu, J. Mater. Sci. Lett., 7 (1988) 628–630.
14 A. Sheidlin, G. Marom and A. Zilkha, Polymer, 26 (1985) pp. 447–451.
15 K. Okamura, T. Matsuzawa and Y. Hasegawa, J. Mater. Sci. Lett., 4 (1985) 55–59.
16 G. Henrici-Olive and S. Olive, Macromol. Chem., 187 (1986) 1801–1806.
17 W. Watt, Handbook of Composites, 1 (1985) 327–387.
18 A. Takaku, T. Hashimoto and T, Miyoshi, J. Appl. Polym. Sci., 30 (1985) 1565–1571.