Catalytic initiation of polyacrylonitrile stabilization

A. Shiedlin and G. Marom
Casali Institute of Applied Chemistry, School of Applied Science and Technology, The Hebrew University of Jerusalem, 91904 Israel

and A. Zilkha
Department of Organic Chemistry, The Hebrew University of Jerusalem, 91904 Israel

(*Received 15 June 1984*)

A catalytic surface treatment of polyacrylonitrile fibres by dibutyltin dimethoxide is investigated as to its capacity to facilitate the stabilization of the fibres to produce a satisfactory carbon fibre precursor. The stabilization is based on a combination of the catalytic treatment step and of the usual thermal oxidation step which follows. The effectiveness of the surface treatment is determined through comparing physical, thermal and mechanical properties of stabilized fibres with and without catalytic pre-treatment. The results show that a 1 minute catalytic treatment shortens the usual 220°C thermal oxidation process by at least 2 hours, and that the process is applicable in particular to polyacrylonitrile fibres which are 'slow oxidizers' in general due to their chemical composition.

(Keywords: polyacrylonitrile fibres; catalytic stabilization; thermal oxidation; dibutyltin dimethoxide; density; thermal behaviour; mechanical properties; carbon fibres)

INTRODUCTION

The stabilization process of the precursor fibre is crucial to the quality of the final carbon fibre. Hence, one of the most significant steps in the preparation of carbon fibres from acrylic precursor fibres is the oligomerization of the nitrile groups. Despite the fact that the stabilization process has been commercially practiced for over fifteen years now, and that it has been thoroughly investigated, it still attracts a great deal of scientific attention resulting in important new data. For example, a review paper by Goodhew, Clarke and Bailey[1] published in 1975 states that 'the strong intermolecular forces due to the nitrile groups do not allow the reorganization necessary for the development of crystallinity, so that the material is virtually amorphous. ... It is a result of the amorphous nature of the acrylic fibres that they are attractive commercially....' However, a more recent review by Henrici-Olivé and Olivé[2] published in 1983 states categorically that 'PAN homopolymer melts at approximately 320°C, whereby 'melting' refers to the endothermic breaking up of the highly ordered crystalline regions' and that 'introduction of a comonomer into the polymer chain depresses the melting point'.

An important aspect of the stabilization process is the role of comonomers such as vinyl acetate, methyl acrylate and sodium itaconate usually present in the acrylic precursor. Their effect, on the one hand, is to facilitate the stabilization reaction by reducing the nitrile dipole interactions and increasing chain segment mobility. As a result, the oxygen permeation through the fibre is increased, the time interval required for nitrile oligomerization is enlarged, thus helping to dissipate the large reaction heat, and also, by radical breaking of the weakest bonds some of those comonomers provide sufficient initiation radicals. On the other hand, the presence of a comonomer brings about a melting point depression thus limiting the treatment temperature which may be employed without causing fibre fusion. The reduction of the upper temperature limit has a concomitant effect on the initiation mechanism since the temperature should not be dropped below a point where sufficient initiation radicals are still produced.

The initiation mechanism is indeed the focal point of the present study. It proposes a new method to accelerate the initiation step, thereby shortening the time interval required for achieving stabilization. The method is based on a previous study of the treatment of PAN fibres with organotin compounds[3]. In that study the idea was to eliminate completely stabilization by thermal oxidation and to replace it by catalytic polymerization of the nitriles of partially swollen fibres. Although the process employed relatively low temperatures and was rapid (in the order of a few minutes) it exhibited a number of disadvantages, such as the difficulty to wash out the tin impurities which remain in the fibre and affect the ultimate properties of the graphite products, and the absence of oxidation of the main carbon backbone which is an essential part of the stabilization. It was therefore conceived that those disadvantages may be removed if the catalyst is applied to the fibre surface only, where during a very short period of time nitrile oligomerization is initiated, followed by washing away the catalyst before transferring the fibre to the oxidation oven.

An appropriate fibre precursor for testing that idea would be Acrilan, which contains ~7% vinyl acetate. This fibre is a 'slow oxidizer' due to insufficient supply of initiating radicals. This problem, usually overcome by

0032-3861/85/030447-05$03.00

raising the treatment temperature, cannot be solved easily with Acrilan. The presence of vinyl acetate depresses the melting point by some 50°C compared to PAN[1]. Since even a slight superficial fusion may prevent the fibre from becoming fully stabilized, the thermal treatment of such fibres has to start at a relatively low temperature ($\sim 220°C$). As a result Acrilan fibres are not considered an appropriate precursor but would be ideal in a study of the effect of catalytic initiation.

The selection of the specific catalyst employed in the present study emerged from an explorative effort to screen organometallic compounds such as lead naphthenate, and specifically organotin compounds such as polydibutyltin oxide and α, ω-dichloro oligostanoxane[4]. Dibutyltin dimethoxide was chosen in view of its highest reactivity.

EXPERIMENTAL

Materials and catalytic system

The initiator, dibutyltin dimethoxide was prepared from dibutyltin dichloride by a procedure generally based on ref. 5. Acrilan fibres of 3 denier were supplied by Israel Chemical Fibres.

The catalytic treatment was carried out in a DMF/-xylene mixture of a 1:1 molar ratio containing $0.13\ g\ cm^{-3}$ of the initiator.

Stabilization procedure

In standard stabilization experiments the fibres were mounted on $1 \times 3\ cm^2$ stainless steel frames to prevent shrinkage. Each frame was immersed in the catalytic solution at 140°C for one minute, thereafter it was transferred to a boiling methanol bath for a 15 min washing period. This was followed by transferring to an oven for the oxidation process at 210°–220°C. Individual experiments destined to investigate effects of specific parameters deviated from the above conditions accordingly. For example, one sample excluded the methanol washing in order to study the effect of the presence of a higher concentration of the organotin initiator during the oxidation, thereby requiring dry conditions in the oven to prevent decomposition of the initiator. Other variables such as treatment times and temperatures were also examined.

Testing

The densities of the fibres were measured with a density gradient column of CCl_4 ($1.59\ g\ cm^{-3}$) and xylene ($0.89\ g\ cm^{-3}$) covering a density range of $1–1.5\ g\ cm^{-3}$. The column was calibrated with standard density floats (Techne Ltd.).

Thermal analysis was carried out with a Mettler thermoanalyser TA 3000 including differential scanning calorimeter DSC 30, thermogravimetric analyser TG 50 and thermomechanical analyser TMA 40. The specific operation conditions are listed below.

Filament tensile properties (modulus, yield, elongation and strength) were measured with an Instron universal testing machine. Tests were carried out with single filaments mounted on a cardboard frame whose sides had been cut prior to applying tension. The gauge length employed was 2.5 cm and the extension rate was $0.5\ cm\ min^{-1}$. Each result is an average of at least 40 tests.

The cross-sectional areas of fibres at various extents of stabilization were worked out from the densities assuming no shrinkage of the fibres during the stabilization and neglecting weight losses of 2% maximum.

RESULTS AND DISCUSSION

The study of the effect of catalytic initiation of the nitrile oligomerization reaction on the quality of the PAN fibre stabilization was based on a comparison between parallel samples. One sample was drawn from specimens which underwent catalytic treatment prior to the thermal oxidation, while the second sample, used as a reference, was subjected to the same thermal oxidation but with no pretreatment. The first sample was designated as 'treated' and the second as 'untreated'. In practice, the effect of catalytic initiation was evaluated by monitoring the differences between these samples showing various properties (colouration, density, mechanical and thermal properties) as functions of the thermal oxidation time.

Advancement of stabilization

An instant tool for assessing the advancement of stabilization is the gradual development of a range of colours (yellow, orange, brown, black) with the proceeding of the oligomerization reaction. In this study colour photography of treated and untreated sets was used as a qualitative means. It showed that the catalytic treatment resulted in saving 2–3 h of thermal oxidation. Moreover, whereas untreated fibres even after 5 h at 210°C produced only a dark brown colour, treated fibres turned black after 4 h.

Another common measure for the advancement of the stabilization reaction is the fibre density. *Figures 1* and *2* present the density results of treated and untreated samples as functions of the thermal oxidation time. In the first Figure methanol washing was applied to the treated fibre prior to the thermal oxidation, and in the second Figure treated fibres were washed only after the thermal oxidation. It is seen that the density of treated fibres after about 3 h of thermal oxidation is equal to that of untreated fibres after 5 h. Also, the treated fibres reach a threshold density after 5 h which is a prerequisite for a successful carbonization, while the density of the untreated fibres indicates an insufficient stabilization. The presence in excess of the organotin initiator during the thermal oxidation does not seem to have a significant effect on the densities. The slightly high densities in *Figure 2* result from a 10°C higher temperature in the thermal oxidation, as seen by comparing the untreated samples in *Figures 1* and *2*.

The hypothesis that the activity of the initiator would be confined to the fibre surface was checked by scanning electron microscopy combined with X-ray energy dispersion analysis applied to treated fibres to detect the location of Sn atoms. An example is given in *Figure 3* showing the distribution of tin over the fibre cross-section after a 1 min catalytic treatment without either methanol washing or thermal oxidation. It is seen that the penetration of the organotin compound into the fibre is negligible. Moreover, it is pointed out that when the standard methanol washing cycle was applied, it resulted in Sn concentrations of less than 0.5 wt%, undetectable by the technique with our equipment. In view of these observations a two-step process for the nitrile oligomerization in the treated fibres is assumed. It consists of an initiation step whose mechanism is identical to that

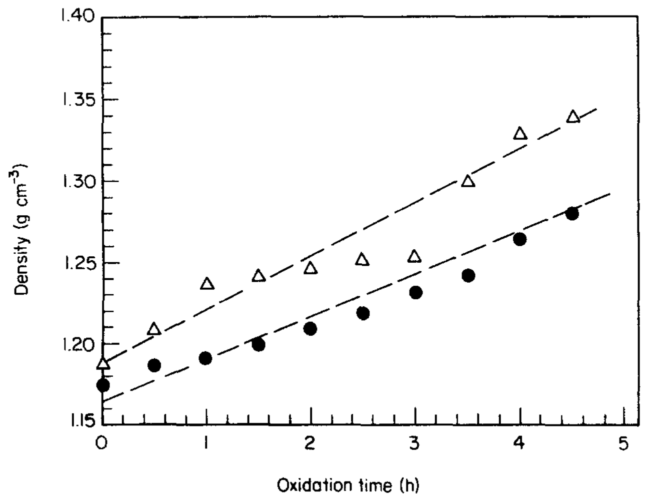

Figure 1 The densities of treated (△) and untreated (●) fibres as a function of the oxidation time. The fibres were washed with methanol prior to the thermal oxidation

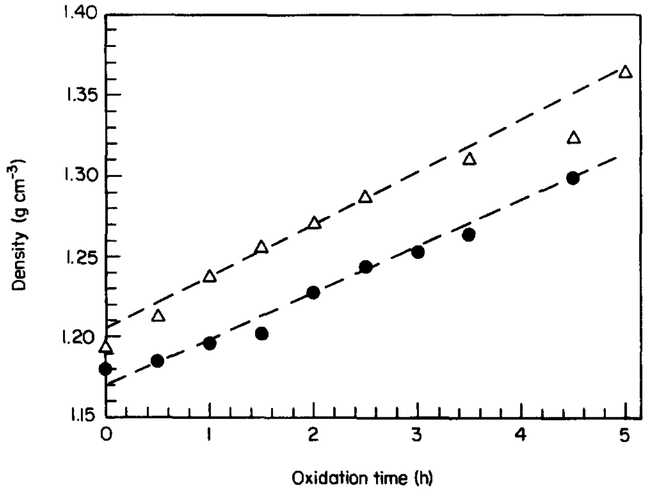

Figure 2 The densities of treated (△) and untreated (●) fibres as a function of the oxidation time. The catalyst was not washed away, and remained in excess during the thermal oxidation

discussed in ref. 3, dealing with catalytic stabilization of swollen fibres, and of a propagation step which is active in the unswollen fibre during the thermal oxidation. The latter step takes place after the organotin catalyst has completed its role as an initiator, and has been washed away with methanol producing Sn concentrations of less than 0.5 wt%. A number of possible mechanisms for the propagation step may be postulated. A most probable one is based on the observations that thermal oxidation with no pre-washing of the initiator does not result in any significant improvement, and that the methanol washing cannot remove all the initiator. It is reasonable to assume that both initiation and propagation steps require only an effective quantity of the initiator, which is chemically bound to the nitriles as shown in ref. 3. The mobility of the relatively bulky dibutyltin dimethoxide molecule in the PAN network during the propagation step is possible due to the fact that this step coincides with the thermal oxidation at 220°C—much above the T_g of the polymer.

Effect of stabilization on thermal behaviour

The stabilization process comprises a series of exothermal or endothermal reactions some of which may be accompanied by a weight change. The nitrile oligomerization and the oxidation of the main backbone are exothermal, while polymer degradation and fusion are endothermal events. Weight gains may result from additions of initiator molecules and of oxygen during the thermal oxidation step, while weight losses may be attributed to degradation and evolution of gases such as NH_3, HCN and CO_2. It is feasible that the extent of stabilization, i.e. nitrile oligomerication and main backbone oxidation will show in the thermal stability of the partially stabilized PAN fibre. For example, a PAN fibre pre-stabilized at 220°C for 7 h under N_2 has exhibited a flat d.t.a. curve and a weight loss of only 20% up to 500°C compared with a sharp exotherm and a 60% weight loss of unstabilized fibre[6].

Our d.s.c. measurements indicated that the catalytic treatment was in fact equivalent to a determined period of thermal oxidation as implied by the density results. This is examplified in *Figure 4* which compares d.s.c. traces of an original (white) fibre and a treated (without oxidation) fibre. It is observed that the effect of the treatment is to enhance stabilization reflected in a shorter range of endothermal response (degradation and fusion) and a wider range of exothermal response (nitrile oligomerization). Also, the maximum exothermal reaction is shifted to a lower temperature of 300°C compared with 340°C of the untreated fibres.

The assumption that fibre fusion was responsible in

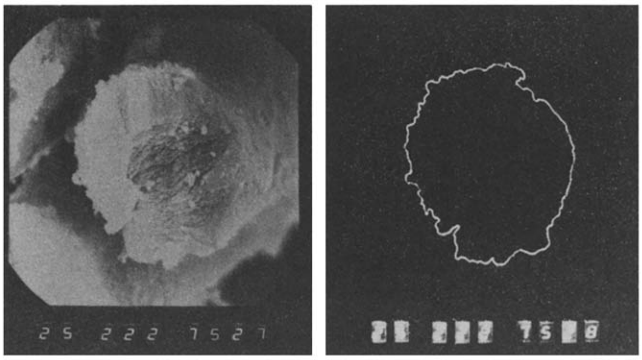

Figure 3 A scanning electron micrograph of a cross-section of a treated fibre (left) examined by an X-ray energy dispersion analysis (right) to detect location of Sn atoms (white spots). It is seen that the penetration of the dibutyltin dimethoxide compound into the fibre is limited, and most of the Sn is present on the fibre surface (outside the white line), and on surfaces of neighbouring fibres

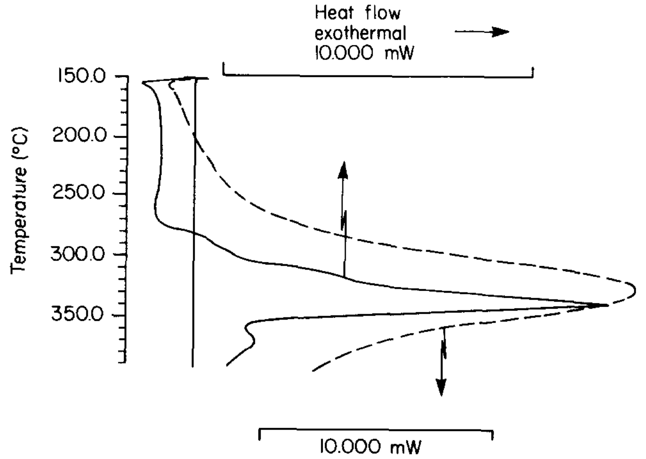

Figure 4 D.s.c. traces of original (white) fibre (–) and of treated (without oxidation) fibre (– –)

part for the endothermal reaction was tested by thermomechanical analyses of untreated and treated fibres. The fibres were placed between two inconel discs, and under such conditions fusion was indicated by shrinkage when the fused fibres complied to the pressure of the probe. *Figure 5* shows that the untreated fibre begins to fuse at about 270°C, while no signs of fusion are shown by the treated fibre (without thermal oxidation). It was concluded that the catalytic treatment was efficient enough to result in stabilization even during the short heating period in the thermomechanical analyser at a heating rate of 10°C/min.

Next, the effect of the catalytic treatment on the stabilization was examined by thermogravimetric analysis. *Figure 6* presents examples of t.g./d.t.g. traces for white and partially stabilized fibres which represent the following general picture. The relevant weight loss event pertinent to the stabilization process occurs in the temperature range 270°–370°C, while a total polymer degradation starts at $\sim$500°C, resulting in a weight loss of $\sim$100%. *Figure 7* compares the weight loss in the temperature range 200°–450°C of treated and untreated samples as a function of thermal oxidation time. It is seen that the weight loss decreases with the extent of stabilization until an asymptotic value of 17% is attained. Whereas the untreated sample requires 2.5 h of thermal oxidation to reach a stage of minimum weight loss, it only takes 0.5 h for the treated sample, indicating again that the catalytic treatment is equivalent to about two hours of thermal oxidation.

Mechanical properties

The purpose of measuring the mechanical properties was two-fold. Like the other investigated properties the mechanical properties may serve as an indicator and a measure of the advancement of the stabilization process, and thus they offer an additional means for comparing treated and untreated fibres. The second reason for measuring the mechanical properties was to ensure that the new treatment did not harm the fibre in any way, and did not affect its suitability as a carbon fibre precursor.

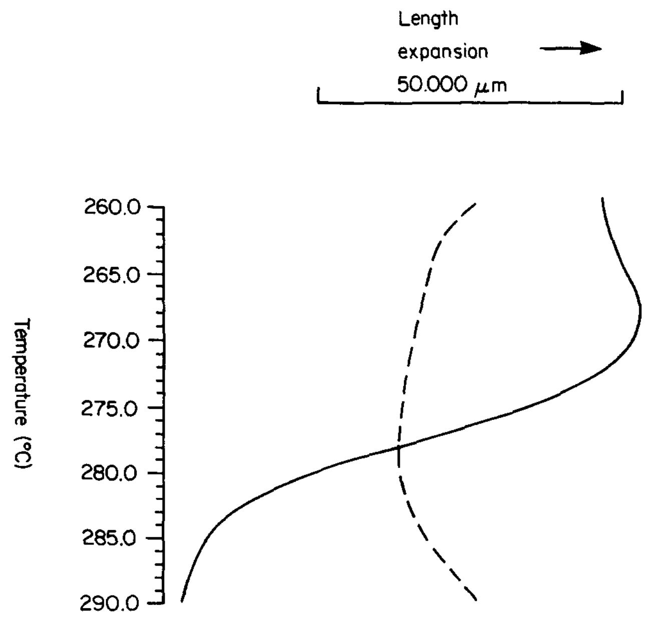

Figure 5 Tm traces of original (white) fibre (—) and of treated (without oxidation) fibre (- -)

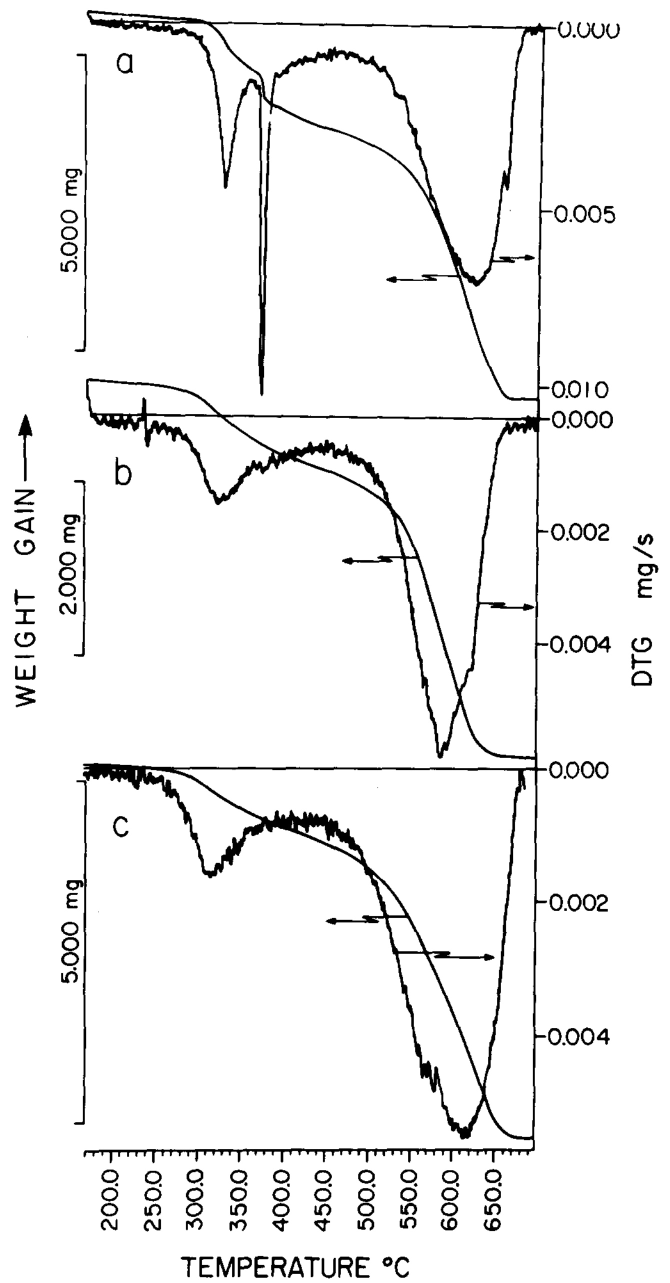

Figure 6 T.g./d.t.g. traces of (a) the original (white) fibre, (b) a treated (without oxidation) and (c) an oxidized for 2.5 h fibre (with no catalytic treatment)

Figure 8 presents load-extension curves of an original PAN fibre and of a stabilized fibre. It is seen that the yield stress and the modulus increase with the stabilization, and that the ultimate elongation, and strength decrease, in general agreement with Watt's observartions[7]. *Figure 9* presents the results of the mechanical properties. Indeed, the yield stress and the modulus increase and the ultimate elongation and stress decrease with the oxidation time. (It is noted that in previous studies where only catalytic oligomerization of the nitriles in the swollen fibre has been applied with no thermal oxidation the ultimate extension of the stabilized fibre has increased[3,4]. The data in general do not exhibit smooth trends, resulting from relatively large scatter. This scatter also affected the results of t-tests (pairs) comparing treated and untreated samples, which produce a significant difference only with the yield stress. Still, comparisons of the linear regression lines drawn for treated and untreated samples show a clear difference

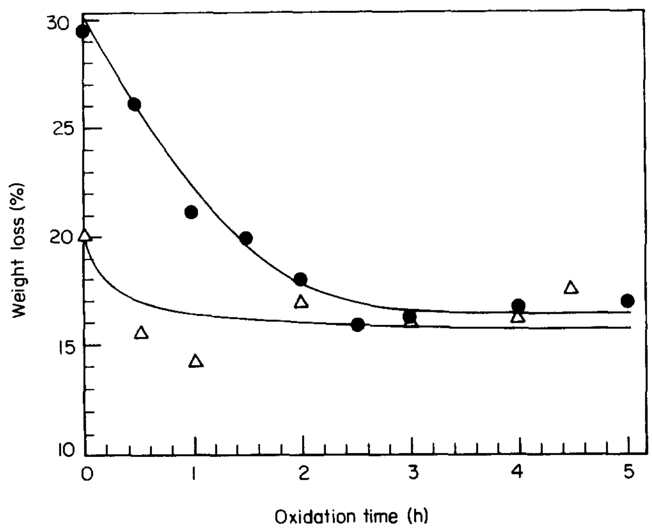

Figure 7 The weight loss in the temperature range 200°–450°C during t.g. experiments as a function of the thermal oxidation time of treated (△) and untreated (●) fibres

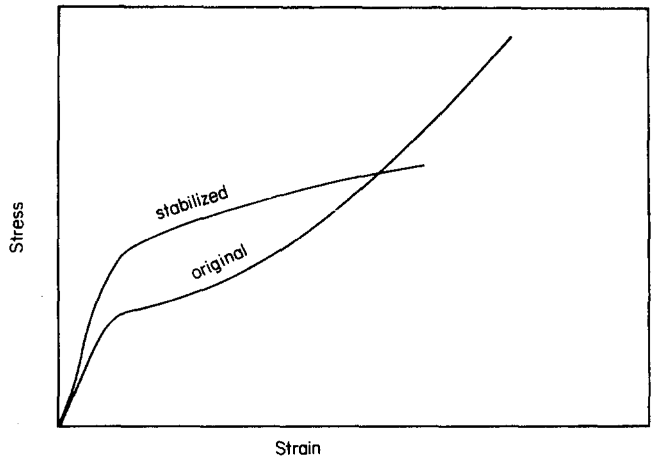

Figure 8 Stress–strain traces of the original PAN fibre and of a fully stabilized fibre

between the two samples and indicate that property changes of the first precede those of the latter by 1–2 h of thermal oxidation.

CONCLUSION

Dibutyltin dimethoxide is markedly efficient in promoting the initiation of nitrile oligomerization. It generates 2 h shorter thermal oxidation times at 220°C and better overall stabilizations. The dibutyltin dimethoxide treatment is highly relevant to Acrilan which normally is a 'slow oxidizer'. It enables thermal oxidation at temperatures above 220°C with no fibre fusion, projecting an even further shortening of the thermal oxidation treatment when these higher temperatures are applied. Considering the commercial applicability of the process, it is noted that the reported effects were also observed with a treated fibre which was stored for one day prior to ther thermal oxidation. This opens an option to employ the proposed treatment in the precursor plant and use the pretreated precursor in the carbon fibre plant.

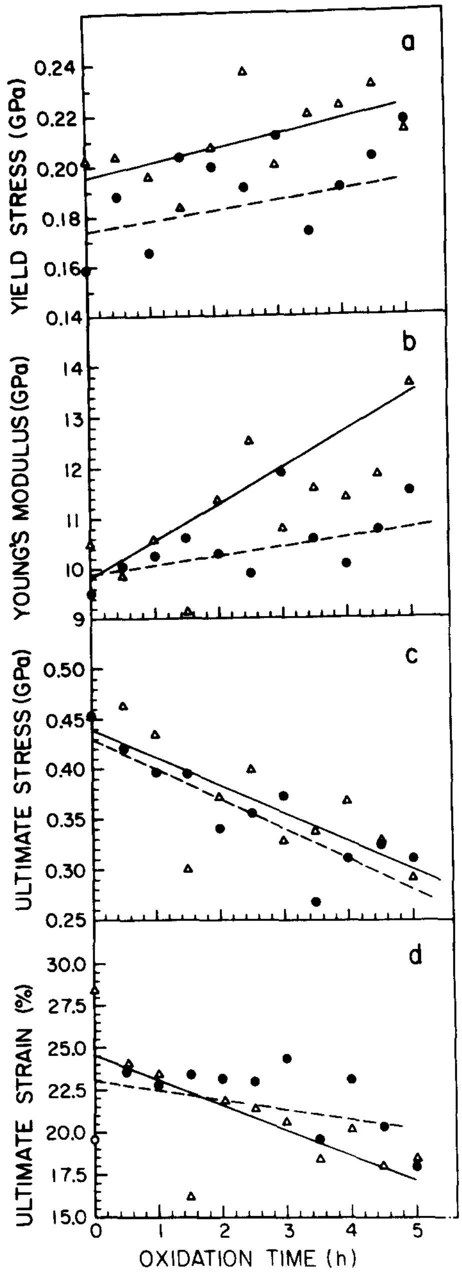

Figure 9 The mechanical properties of treated (△) and untreated (●) fibres as a function of the thermal oxidation time

REFERENCES

1 Goodhew, P. J., Clarke, A. J. and Bailey, J. E. *Mater. Sci. Eng.* 1975, **17**, 3
2 Henrici-Olivé, G. and Olivé, S. 'The Chemistry of Carbon Fiber Formation from Polyacrylonitrile', Adv. Polym. Sci., 'Industrial Developments', Springer-Verlag, Berlin, Heidelberg, 1983, Vol. 51, p. 3
3 Cohen, D., Marom, G. and Zilkha, A. *Eur. Polym. J.* 1976, **12**, 795
4 Wand, J., Marom, G. and Zilkha, A. 'A Process for the Preparation of Carbon Fibres from Polyacrylonitrile Fibres', The Hebrew University of Jerusalem, Casali Institute of Applied Chemistry, Report No. 7804, 1978
5 Alleston, D. L. and Davies, A. G. *J. Chem. Soc.* 1962, 2050
6 Grassie, N. and McGuchan, R. *Eur. Polym. J.* 1971, **7**, 1357
7 Watt, W. *Proc. Roy. Soc. (London)* 1970, **A319**, 5