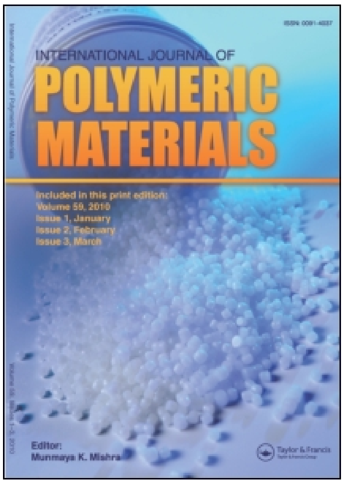
This article was downloaded by:
On: *19 January 2011*
Access details: *Access Details: Free Access*
Publisher *Taylor & Francis*
Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



International Journal of Polymeric Materials

Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713647664

Rapid Stabilization of Acrylic Precursors for Carbon Fibres Using Ammonia

D. M. Kiminta[a]

[a] Department of Chemical Engineering & Chemical Technology, Imperial College of Science, Technology and Medicine, (University of London), London, United Kingdom

To cite this Article Kiminta, D. M.(1993) 'Rapid Stabilization of Acrylic Precursors for Carbon Fibres Using Ammonia', International Journal of Polymeric Materials, 23: 1, 57 — 65

To link to this Article: DOI: 10.1080/00914039308009659

URL: http://dx.doi.org/10.1080/00914039308009659

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: http://www.informaworld.com/terms-and-conditions-of-access.pdf

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

Intern. J. Polymeric Mater., 1993, Vol. 23, pp. 57–65
Reprints available directly from the publisher
Photocopying permitted by license only

Printed in Malaysia

Rapid Stabilization of Acrylic Precursors for Carbon Fibres Using Ammonia

D. M. KIMINTA†

Department of Chemical Engineering & Chemical Technology, Imperial College of Science, Technology and Medicine, (University of London), Prince Consort Road, London SW72BY, United Kingdom

(Received February 10, 1993)

Polyacrylonitrile precursors have been successfully used for carbon fibres preparation by most industrial manufacturers for quite some time. During stabilization of these precursors, the methods applied and especially the chemical and physical changes that take place obviously dictate the eventual state of the products' properties. Because small angle x-ray scattering studies reveal the microporous nature of these fibres, the intense scattering patterns are remarkably unique for understanding the changes taking place as the fibres are stabilized. Ammonia was shown to accelerate the stabilization of some precursors. Stabilization of two acrylic fibres was studied both in air and air/ammonia atmospheres. Small Angle x-ray Scattering (SAXS) was used to study the changes of the microstructure. The study showed that the meridianol peaks which are not seen in the precursor fibres appear at the early stages of stabilization and then disappear as the stabilization progresses. The changes took place much faster in the ammonia stabilized samples, indicating the accelerating effect of ammonia. The SAXS scattering patterns also indicated the occurrence of molecular relaxation in the case of fibres stabilized in ammonia, indicating a plasticizing effect of ammonia.

KEY WORDS Carbon fibres, stabilization, acrylic precursors

INTRODUCTION

The precursor Polyacrylonitrile (PAN) has been used successfully for manufacturing carbon fibres. The demand for much stronger fibres and threads for apparels and sophisticated weaving of threaded high-strength materials especially for the aerospace industry has made the search for newer finer and stronger materials to continue year after year. Carbon fibres from non-textile precursors (cotton etc.) exhibit characteristic durable strength that has proved successful and one of these, (PAN), is the subject of this paper.

Making carbon fibres from Polyacrylonitrile includes the oxidation of the fibres so as to stabilize the polymer prior to pyrolysis. That is, the stabilizing of PAN into a condensed hetero-cyclic ring structure before further treating with high

---

†Formally at the University of Tennessee (Knoxville) and the Oak Ridge National Laboratory (ORNL), Tennessee (USA).

temperature. PAN is not exactly a ladder polymer but it conspicuously forms this structure after heating and if subjected to higher temperatures, some of the CH_2 groups get oxidized. Oxidative stabilization has disadvantages of many side reactions which result in the forming of complicated structures. PAN is a successful precursor polymer when used for manufacturing carbon fibres, paradoxically it lacks the two bonds structure and hence, to create a stronger ladder polymer, the precursor must be heated in air at temperatures above 200°C where its properties form a ladder structure that re-strengthens and modifies the main chain configuration. The ladder structure becomes more desirable especially during carbonization process because when present, it prevents melting and maintains thermal stability.

EXPERIMENTAL PROCEDURE

We heated the precursor fibres to 920°C using a tube oven and an Omega heater control-switch where the fibres were confined in a small spherical quartz-glass tube with inlets and outlets for inert gas (N_2) blown in at volumes of 10 cc/min to prevent and deter oxygen from flowing into the heating chamber. Both ends of the fibres were slightly tightened to keep the fibre under very weak tension during carbonization. This inlet and outlet for nitrogen flowing in was to necessitate an inert atmosphere around the samples placed in the glass-tube. The complexity of the nature of the structural and morphological changes taking place with the progress of stabilization were simplified when the samples were loaded on the ORNL 10 Metre for x-ray scattering to gather information necessary to characterize the fibre properties (see Figure 1). In this experiment, two commercial acrylic precursors, TB and CRT, the former containing two percent methyl acrylate (MA) comonomer and the latter containing 6% MA and 1% itaconic acid (IA) as coomonomers were used. The stabilization was carried out both in air and in air/ammonia (5% ammonia in air by volume). The 2% MA precursor was stabilized at 260°C and the 6% MA-2% IA precursor at 230°C. The stabilized fibres were investigated for the extent of stabilization by several techniques including the density determination, results of which are presented in this report.

Small Angle X-Ray Scattering Camera

The studying of these fibres would not have been possible without the use of the ORNL 10-Metre Small-Angle x-ray Camera at the National Centre for Small-Angle Scattering Research (NCSASR) at the Oak Ridge National Laboratory (ORNL). The camera utilizes a rotating-anode x-ray source with a crystal monochromatization of the incident beam. It has a pinhole collimation and a two-dimensional positive-sensitive proportional counter. Samples were prepared to fit into the camera's x-ray focal spot of 1 × 1 mm with a variation of focal spot-to-sample and the sample to detector distances of 0.5 m. The specimen chamber as indicated in the diagram (Figure 1) has rotating-wheels that hold up to 11 samples with an empty beam-hole for reference purposes. The geometry can be shortened or extended up to 10 meters depending on the type of sample and transmission needs. With up to 200 × 200 resolution elements, the detector has an area of 200 × 200 mm. In this

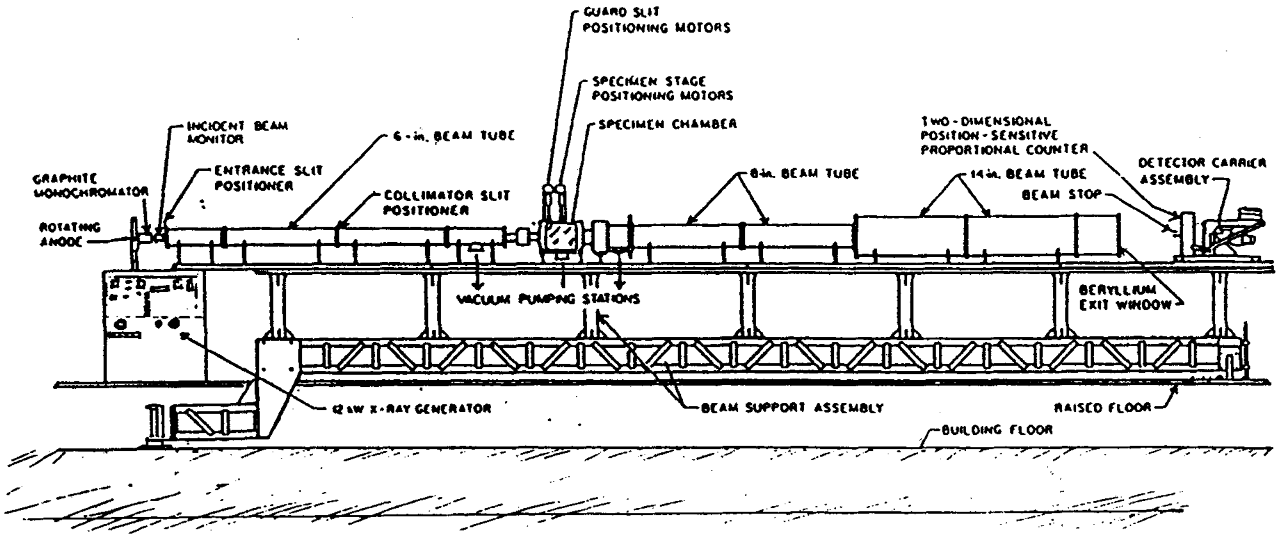


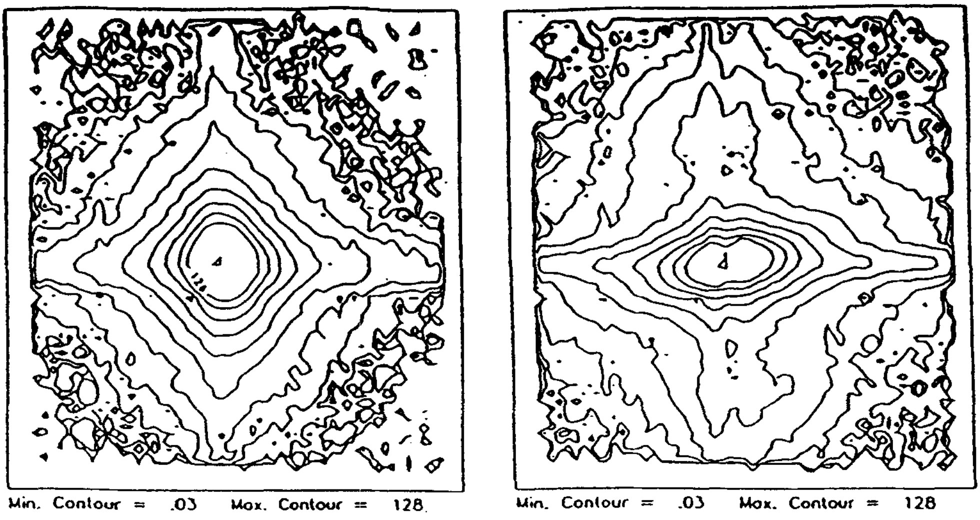
FIGURE 1 Small angle x-ray scattering camera at ORNL (from Reference 7).

experiment, we controlled the specimen chamber with a computer and were able to rotate samples around the beam and collected the required data. This information was used to generate contour plats that are included in this report. Other factors of importance were the angular resolutions and the x-ray source operating voltages of 45 kV and 100 mA. With flux incident on the specimen being at a level of 1.0 × 10^6 photons s^{-1}, computing system is able to gather more than enough information on the samples.

X-Ray Scattering Pattern of Polyacrylonitrile

As stabilization progressed, meridional peaks appeared for an instant and then disappeared later. Typical examples of the contour maps generated from the programme (10 metre SAXS system) have been reproduced and presented. An isointensity plot is given by Figure 2A. The precursor fibre in this case was completely stabilized and the plot does not show any meridional peak. On isointensity Figure 2B, a distinct meridional peak appeared as indicated. It should be noted here that this phenomenon was observed only at the intermediate stages of stabilization.

There are two possible explanations for the appearance of meridional scattering: One of them explains the phenomenon by the two phase morphology of the precursor, where the stabilization reactions occur in the less ordered region in the early stages leading to electron density differences between the ordered and less ordered regions.[3] Explanation given for the other appearance is that the electron density differences are between the two phases resulting from the intermolecular packing cyclized and aromatized domains, the cyclized domains have lower density while the aromatized ones have a higher density.[4] Studying the samples stabilized in an inert environment, where aromatization is less likely to occur, it may be



A B

FIGURE 2 Isointensity plots of the fiber before the onset of stabilization (A) and at the intermediate stage of stabilization (B).

possible to determine which explanation is correct about the behaviour of the precursor polymer. This study clearly indicated faster changes in the morphology of the fibres in the presence of ammonia, which is associated with the faster kinetics of stabilization. The equatorial scattering of the fibres stabilized in ammonia and in air were observed to be different. Equatorial scattering is generally known to be from the microvoids in the precursor fibre and typically they are elongated and oriented in the fibre direction. When comparisons of these fibres were made (generated SAXS patterns), that is, those stabilized in air and in ammonia, it was evident that the higher amount of relaxation took place in the case of ammonia stabilized fibres. This can be attributed to the plasticizing effect of ammonia. This is an indication of higher mobility of the molecules during the high temperature reaction process resulting in the relaxation of the orientation in the starting precursor.

RESULTS

Two acrylic precursors had different copolymer composition and showed different effects of ammonia on the stabilization kinetics. As shown in Figure 3, the density increase was much faster in the presence of ammonia for the 2% MA precursor fibre. As observed, in the presence of ammonia, the critical density was achieved in about half the time required for the stabilization of the precursor in air. Although the itaconic acid containing precursor showed some acceleration of stabilization in the presence of ammonia, the effect was much less than in the case of non acidic precursor. This has been attributed to the faster initiation of cyclization by the in situ acidic groups in the case of fibres containing itaconic acid monomer, thereby overwhelming the effect of ammonia. Observing from the contour plots of graphitized samples see contour plots (Figures 2A, 2B and 4), an increase in scattering appears to exist which is thought to be formation of microstructural voids. From

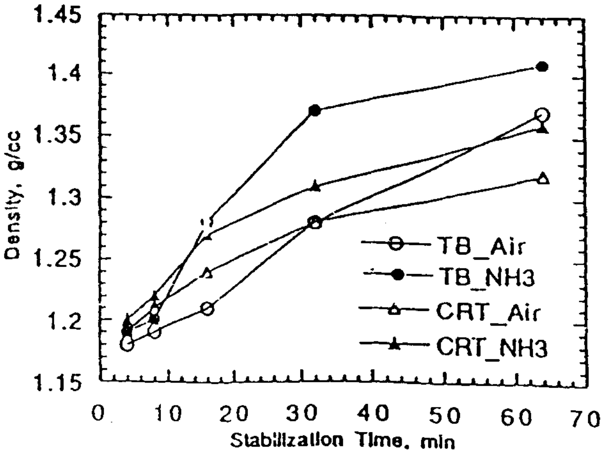


FIGURE 3 Change in density during stabilization for two precursors (from Reference 8).

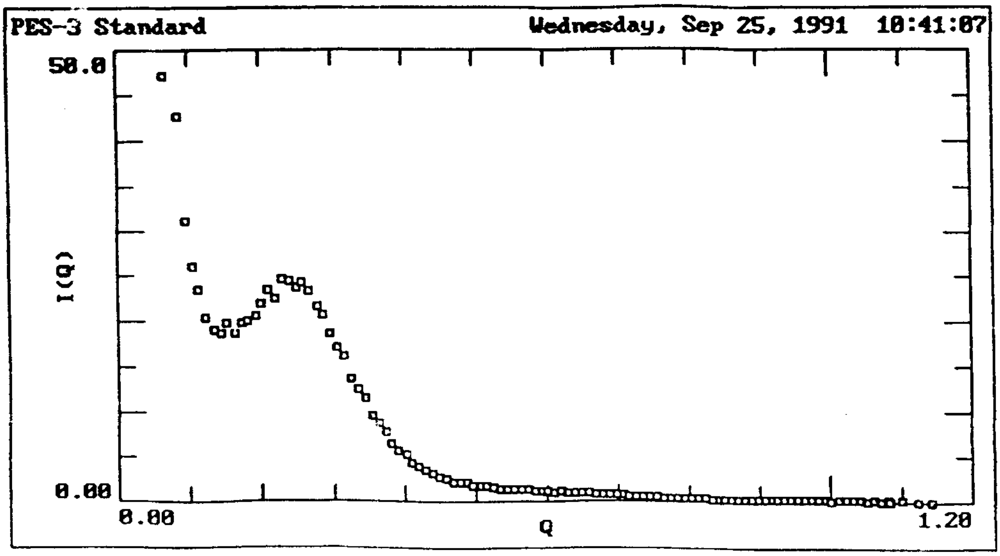


FIGURE 4

the isointensity contour plots, there exists differences between fibres stabilized in air and those stabilized in ammonia with respective slight differences due to stabilization periods on both cases.

DISCUSSION OF RESULTS

This study was aimed at investigating the effect of ammonia in the stabilization environment on the rates of appearance and disappearing of meridional scattering. Normalized transmittance was not the same for the fibres stabilized to different extent in the two environments. As can be seen from Table I, empty beam has transmittance 1.00 and the precursor a value of 0.418. As the stabilization starts the transmittance increases, the value reaches the maximum at an intermediate stage and then decreases before levelling off. This process of increasing and reaching the maximum of transmittance value occurs much faster in the case of ammonia stabilization which had been expected. In addition, there is a difference in that the maximum intensity reached is of lower value for the ammonia stabilized than for the air stabilized ones. This is due to the differences in the chemical structure of the stabilized fibres in to the differences in the chemical structure of the stabilized fibres in the two cases. Other explanations if any exist were not known at the time of this study. Our hope in concluding the study was that the ambiguity about what causes the meridional scattering can be resolved or rather, encourage further investigations by those involved with the composite materials studies. Another objective was to make use of small angle x-ray scattering facilities in order to understand various microstructural changes that had taken place during stabilization in the two environments. Obviously, these changes affect the structure and final properties of the carbon fibres being manufactured. Generally speaking, SAXS is

TABLE I

Transmittance During SAXS for the 2% MA Precursor (TB) Fiber Stabilized in Air and Air/Ammonia.

Sample Description	Transmittance	Comments
No Sample	1.000	———
Precursor Fiber	0.418	No Meridional Peak
Stab. in Air_4 min	0.465	No Meridional Peak
Stab. in Air_8 min	0.679	No Meridional Peak
Stab. in Air_16 min	0.815	Meridional Peak Starts
Stab. in Air_64 min	0.589	Distinct Meridional Peak
Stab. in Ammonia_4 min	0.762	Meridional Peak Starts
Stab. in Ammonia_8 min	0.525	No Meridional Peak
Stab. in Ammonia_16 min	0.643	No Meridional Peak
Stab. in Ammonia_64 min	0.400	No Meridional Peak

TABLE II

Sequen. Number	Carbon Fiber ID	Igs	Is	T m	Fibre Thickness	Stabil. (minutes)
44250	CF - N1	438.7	359.2	0.418	1.00	precursor
44251	CF - N3	489.0	265.0	0.679	1.00	air- 8min.
44252	CF - N4	498.8	191.5	0.815	1.00	air- 16 "
44253	CF - N6	508.8	176.6	0.861	1.00	air- 32 "
44254	CF - N8	503.5	346.3	0.589	1.00	air- 64 "
44255	CF - N9	496.4	222.2	0.585	1.00	air-128 "
44256	CF - N13	475.1	343.3	0.762	1.00	NH_3-4min
44257	CF - N14	523.3	350.9	0.525	1.00	NH_3- 8 "
44258	CF - N15	482.8	376.1	0.643	1.00	NH_3- 16"
44259	CF - N17	452.8	391.3	0.400	1.00	NH_3-64 "
44261	EMPTY Beam	487.8	56.4	1.000	1.00	NO Sample
44260	CF - N2	500.2	418.4	0.465	1.00	air-4min.

To get transmission coefficient, the following information is necessary:-

Igc: Intensity of the beam through glassy carbon.
Imt: The Empty beam with no carbon sample.
Idc: The Dark current, no beam gets to the Detector.
Igcs: Intensity of the beam through glassy carbon plus sample.
Is: Intensity of the beam through Sample alone.

Imt = 56.4 cps.
Idc = 24.6
Igc = 487.8cps

X-Ray Power: 40 kV; 100 ma
SDD: 5.126 metres.

used for the study and examination of these fibres because of its superb capability of identifying features of the fibres at microstructural level. Fluctuations in electron densities is a matter of interest for gathering information on this study. The Isointensity curves obtained from these samples indicate a meridional small angle changes in respect to the different heating time of the fibres. That is, the intensity of the meridional scattering differ on these samples. (see Figures 2A and 2B). The N_2 gas is blown into the glass-tube to prevent combustion within the glass tube placed in the oven chamber which had a maximum temperature of 1175°C.

The objective of this work was to study the changes in morphology of the acrylic precursors which had been rapidly stabilized for carbon fibres. The isointensity contour patterns presented in this report indicate our finding of a previously reported behaviour[1-6] whereby using small angle x-ray scattering, the samples we examined (stabilized differently as indicated in Table II) and samples stabilized at a shorter time period (in presence of ammonia), displayed a meridional scattering pattern that was not present on the scattering patterns of samples stabilized for a longer period. The use of ammonia, about 5%[5] rather than air reduces the period in half. Use of SEM, SAXS and WAXS for this investigation is strongly recommended.

CONCLUSION

The observations made on this study suggests that an important change takes place during the stabilization of acrylic fibres where active sites form atoms into the polymer, hence initiating polymerization of nitrile groups that form condensed heterocyclic ring structure. Appearance of a periodic superstructure was noticed along the fibre-axis as the heating continued just below 285°C. Mayer and Ruland[6] also have reported cyclization and aromatization reaction resulting in shrinkage between 200 and 300°C. The samples that were heated in the tube-oven with oxygen free nitrogen exhibited an extreme sensitivity toward oxygen when below 100°C. On the synchroton scattering and time resolved studies of the structural changes taking place during the stabilization reactions, we strongly believe that by using about 5% ammonia with air in the stabilization environment, time required to stabilize can be reduced in half. Also, it is our assumption that the conditions and method of arranging and rearranging the fibre structure which is possible only during stabilization, can possibly design or custom-tailor or influence the forming microstructures of the fibre for suitable specific use of the end product (carbon fibres).

Acknowledgment

A part of this work was completed at the Imperial College (University of London) Chemical engineering laboratories which we thankfully acknowledge, as well as the Small Angle X-ray Scattering facility at the Oak Ridge National Laboratory (USA) which we profoundly acknowledge with gratitude for the help received during the student's training at ORNL.

References

1. W. Ruland, *J. of Polym. Sci.*, **C28**, 143 (1969).
2. M. E. Fillery and P. H. Goodhew, *Nature Phys. Sci.*, **233**, 118 (1971).

3. S. B. Warner, D. R. Uhlmann and L. H. Peebles, *J. of Mater. Sci.*, **14**, 1893 (1979).
4. W. Watt, Int. Conf. Carbon (London, 1970).
5. R. S. Beer, *J. Amer. Chem. Soc.*, **65**, 1784 (1943).
6. M. Mayer and W. Ruland, *1990 International Conference, Paris*, p. 324.
7. R. W. Hendricks, *J. of Appl. Cryst.*, **11**, 15–30 (1975).
8. D. M. Kiminta and G. Bhat, *1991 ORNL Annual Report (Summer '91) (ORNL/SURA)*, Paper presented at Oak Ridge National Laboratory (ORNL) on Oct. 4, 1991.
9. J. W. Johnson, P. G. Rose and G. Scott, *Int. Conf. Carbon* (London, 1970).