

Eulalia Klata,
Krzysztof Babel*,
Izabella Krucińska

Technical University of Łódź
Department of Textile Metrology
ul. Żeromskiego 116, 90-543 Łódź, Poland
E-mail: ikrucins@p.lodz.pl

*Academy of Agriculture
Institute of Chemical Technology of Wood
ul. Wojska Polskiego 38/42, 60-637 Poznań, Poland
E-mail: kbabel@op.pl

Preliminary Investigation into Carbon Nanofibres for Electrochemical Capacitors

Abstract

This paper presents an investigation into the influence of the parameters of the thermal stabilisation process of polyacrylonitrile (PAN) nanofibres on the process of their pyrolysis. The manufacture of precursor nanofibres by electrospinning from a polyacrylonitrile/N, N-dimethylformamide (PAN/DMF) solution is also described. The diameters of the nanofibres obtained are within the range of 640 nm, whereas their degree of crystallinity, as determined by means of wide angle X-ray scattering, is 40%. The parameters of the thermal stabilisation and the pyrolysis processes of the precursor nanofibres are presented. Two processing variants of the thermal stabilisation of PAN nanofibres in an air stream were applied. The first variant of the stabilisation process was conducted at 225°C for 5-6 h, and the second variant step-wise for 9-10 h in a laboratory chamber dryer at a temperature of up to 280°C. The pyrolysis process was carried out in a thermobalance at a temperature of up to 700°C. Images of PAN precursor nanofibres and of the carbon fibres obtained from them are illustrated by SEM microphotographs.

Key words: polyacrylonitrile, carbon nanofibres, electrochemical capacitors.

Introduction

The performance of electrochemical capacitors produced from carbon fibres depends on the precursor material's properties, as well as on the microstructure and crystallinity of the finished material. Carbon, and especially activated carbon, is characterised by elements of a well-developed porous structure, and a large internal surface. Moreover, fibrous carbons are characterised by a partly arranged structure, which ensures good electron conductivity along the fibres, and by their nearly stable spatial arrangement which also ensures good contact among the fibres. Hitherto, activated carbon fibres have been obtained using the classical form of precursor fibres. The main aim of this paper is to present preliminary research into a technology for manufacturing activated carbon nanofibres. This technology is based on the processes of pyrolysis, and the activation of the precursor nanofibres made from a PAN polymer, which were stabilised beforehand. The research presented in this paper concerns only the pyrolysis process.

According to [1], we assume that the diameters of nanofibres are less than 1 micrometer. The diameters of typical carbon nanofibres are in the range from 100 nanometres up to 1 micrometre [2]. These very thin fibres ensure not only higher stiffness and higher tensile strength, but also a higher ratio of the surface area to their mass than those of classical fibres. These features are very important in the case of activated carbon designed for electrochemical capacitors. In dynamic processes where time is especially significant, for example that of

water adsorption from the gaseous phase, or for ion migration in electrochemical processes, compensation of diffusion effects inside the fibres is extremely important. Undoubtedly, fibrous nanostructures create such possibilities.

The formation of nanofibres by the electrospinning method results from the reaction of a drop of a polymer solution on the forces of an external electric field. This method enables the manufacture of fibres with transverse dimensions of nanometres. One of the first investigations into the phenomena of interaction of an electric field with a polymer drop were carried out by Zeleny [3] in 1914, whereas Formhals patented the spinning process in an electrical field in 1934 [4]. In 1964, Taylor [5,6] proved that for a given kind of liquid, a critical value of the applied voltage exists, at which the liquid drop flowing out from the nozzle is transformed into a cone under the influence of the electric field. The electric charges which diffuse in the liquid, forced by the electric field, cause a strong deformation of the liquid surface in order to minimise the total system's energy. The electric forces exceed the forces of surface tension in the regions of the maximum field strength and the maximum charge density, and the liquid forms a cone at the nozzle outlet. A thin stream of liquid particles is torn off from the end of the cone.

Taylor's further investigations have inspired many researchers who have observed the behaviour of different kinds of polymers in an electric field, which were the basis for developing technologies for manufacturing a new generation of fibres with very small transverse dimensions.

The process commonly described as thermal stabilisation, which leads to the loss of thermoplasticity, is one of the most significant stages in the process of manufacturing carbon fibres from polyacrylonitrile (PAN) precursors. PAN is a linear polymer without branches which melts and decomposes under thermal processing [7-9]. Thermal stabilisation in an air stream is the method most often used [10]. This is a complex process carried out in some stages whose theoretical basis has not as yet been entirely established [11-13]. The idea of intermolecular nitrile cyclisation of the polymer chain, which consists in nitrogen incorporation into the structural rings at a temperature of about 210°C, the oxidation leading to dehydrogenation with liberation of water as well as to intermolecular crosslinking, is at present predominant [14]. The aim of the investigation described in this paper is to carry out preliminary research into establishing the influence of the parameters of the PAN nanofibre oxidation process on the process of pyrolysis. We obtained carbon nanofibres from PAN nanofibres manufactured by electrospinning, which were collected as a web during the electrospinning process. These fibres, after subjected to an activation process (not described in this paper), can be used for producing composite electrode materials, for example those destined for use in electrochemical capacitors. The PAN nanofibres obtained in the form of a nonwoven were tested by the WAXS method. Microphotos of the PAN precursor nonwoven, as well as of the carbon nonwovens, were taken. The technological conditions of the thermal stabilisation and the pyrolysis are further discussed.

■ Experiment

Preparing the PAN solution

Electrospinning was conducted from a 15-17 wt% spinning solution of polyacrylonitrile (PAN) in N,N-dimethylformamide (DMF). PAN was a commercial product from the Aldrich company, whereas the N,N-dimethylformamide came from the Polish company POCH (Polskie Odczynniki Chemiczne). The solution was obtained by total polymer dissolution at room temperature.

Manufacturing nanofibres from PAN solution

The web composed of PAN nanofibres was formed with the use of a laboratory prototype stand especially designed for manufacturing nonwovens by the electrospinning technique. Two electrodes are the basic system elements; one of these, connected to a syringe for extruding the polymer, enables the polymer drops to achieve a suitable electric potential. The constant polymer flow is ensured by compressed air. The next important element of this system is the second, take-up electrode, in relation to which the electric potential of the polymer is applied, and on which the fibres are deposited during the nonwoven manufacturing process. This electrode can be of different shapes; we suggest the shape of a flat plate. Both electrodes are mutually insulated. The whole system is insulated from external electric fields by a screen, which serves as a Faraday-cage and additionally isolates the structure against air swirls.

Thermal stabilisation and pyrolysis

The thermal stabilisation process of the nonwoven manufactured from PAN nanofibres was carried out in a quartz tube placed in a laboratory chamber dryer. The tube was connected with an air pump, which forced a specific airflow around the sample being processed. Two processing variants for thermally stabilising the PAN nanofibres in an air stream were applied. The first variant, qualified as 'mild processing', consists in heating the fibres at 225°C for 5-6 h. The second variant was implemented by heating the fibres in stages: the first stage involved heating at a temperature of up to 240°C for 2 h, the next consisted in increasing the temperature up to 260°C over 30 minutes, and maintaining this temperature for 4 h, and the final stage involved temperature increase up to 280°C over 30 minutes, and maintaining these condi-

tions for 2-3 h. The airflow rate was set at about 80 l/h. Independent of the further, final pyrolysis for obtaining carbon fibres; a preliminary pyrolysis test was carried out to check the effectiveness of the thermal stabilisation of the PAN fibres. This effectiveness was estimated on the basis of a thermogravimetric analysis carried out with the use of a Setsys TG-DSC 15 SETARAM analyser. The measurements were carried out in an open platinum crucible in a protective atmosphere of helium. Samples with a mass of about 7 mg were heated up to the temperature of 700°C, with an increased velocity of about 3°C/min, and the temperature was increased more slowly only within the range of 250°C to 400°C (about 2°C/minute).

Characteristic of the PAN nanofibres and the carbon fibres obtained

The diameters of PAN and carbon nanofibres were determined by means of SEM microphotography. The supermolecular structure of PAN nanofibres was analysed by the wide angle X-ray scattering method (WAXS). The investigations were carried out with the use of a USD 63 Seifert diffractometer. The X-ray diffraction patterns were recorded in an angle range from 2° to 60° with a step of 0.1° using CuK α radiation. The impulse counting time was 20 s, the current intensity was 30 mA, and the accelerating voltage was 40 kV. The diffraction maxima partition was carried out on the basis of the Hindeleh & Johnson method [15]



Figure 1. PAN fibre precursor nonwoven and fibre cross-section image, SEM microphotograph.

with the use of the Rabiej program [16]. The crystallinity degree was determined by comparing the domains which originated from the crystalline part with the total domain (from the crystalline and the amorphous regions).

■ Discussion of the Research Results

We obtained nanofibres in the shape of nanofibrous material (in the form of a web) directly from the polymer by electrospinning. The transverse dimensions of the fibres were about 640 nm, as can be seen in Figure 1. On the basis of this preliminary research, it is visible (as also in Figure 2) that the nanofibres obtained are characterised by a nearly circular cross-section.

The X-ray diffraction pattern which we obtained for the tested PAN nanofibres,

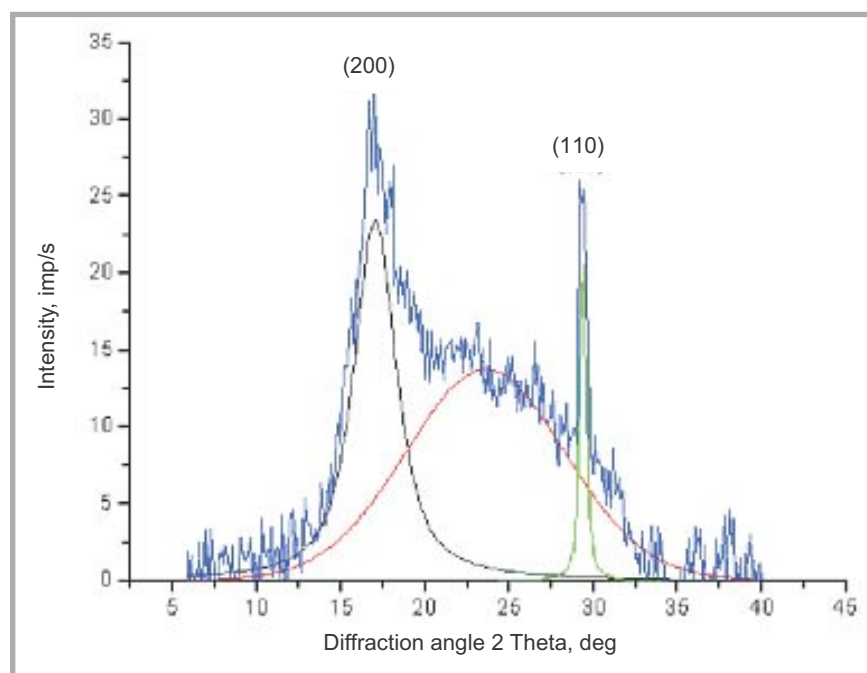


Figure 2. Diffraction pattern of PAN nanofibres.

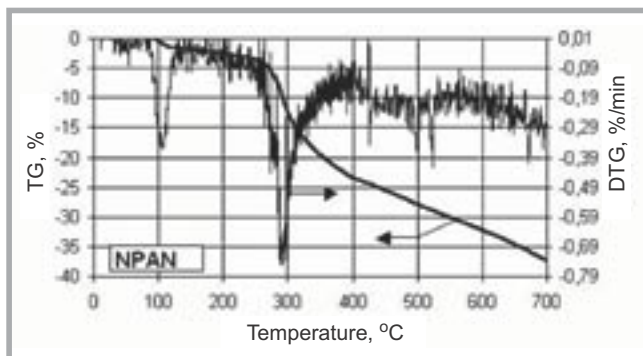


Figure 3. Thermogravimetric analysis of the precursor PAN nanofibres.

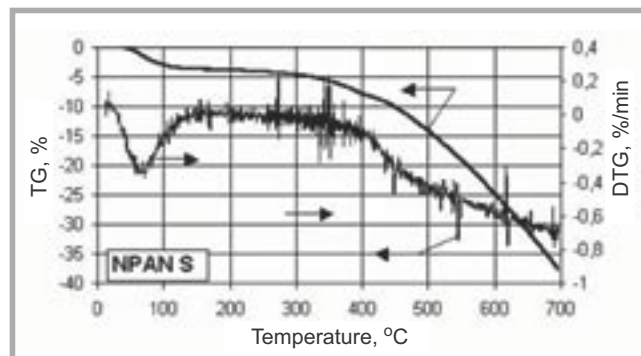


Figure 4. Thermogravimetric analysis of the PAN nanofibres stabilised at 280°C.

together with the decomposition on diffraction maxima and the presentation in what a degree the theoretical diffraction curve fitted to the experimental method, is shown in Figure 2.

The reflections originated from the network planes of Miller factors (200) for the angle $2\theta \approx 17^\circ$ and (110) for the angle $2\theta \approx 29.5^\circ$. The peak, which originated from the (110) planes, was smaller than the peak which originated from the (200) planes, but it was at the same time sharper. This latter feature is not visible in the case of typical PAN fibres. The crystallinity degree of the precursor nanofibres was 40%, whereas the crystallite dimensions measured perpendicular to the (200) planes were 29.5 Å, and 187.1 Å perpendicular to the (110) planes.

As can be seen from the thermal analysis results of non-stabilised nanofibres (Figure 3), the pyrolysis process takes place within the temperature range of about 260°C to 400°C, whereas the velocity maximum of the mass loss lies at a temperature of about 290°C. The fibres melt in this region, lose their fibrous form, and at the same time lose about 18% of their mass. The pyrolysis stabilises itself upon

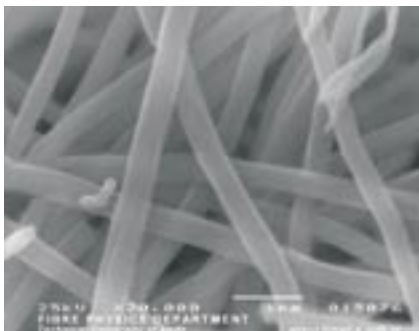


Figure 5. Image of carbon fibres obtained as result of the pyrolysis conducted at a temperature of up to 700°C.

further slow heating of the sample, and is characterised by a uniform loss of mass.

The fibres stabilised at a temperature of 225°C melt, which indicates too low a processing temperature. In contrast to these fibres, those stabilised at the temperature of 280°C disintegrate, while preserving the fibrous structure. The pattern of mass changes during heating to the temperature of 700°C (Figure 4) show the loss of the region of active pyrolysis with a rapid mass loss, and the pyrolysis pattern is stabilised throughout the whole temperature range observed. The increase in the decomposition velocity at temperatures over 400°C is caused by the increase in the heating velocity of the sample. Thus, we may assume that the stabilisation at a temperature of 280°C caused the incorporation of oxygen in the fibre structure and the loss of its melting ability, and also that the further continuation of pyrolysis at higher temperatures proceeds typically and similarly to the pyrolysis of classical PAN fibres.

As a result of the pyrolysis carried out, carbon fibres were obtained which had the image presented in Figure 5. An analysis of the diameters of the fibres obtained allows us to state that a 25% change of the diameter of the PAN fibres had occurred as the result of pyrolysis. The diameters of the carbon fibres were about 480 nm.

Summary

Our preliminary investigation allows us to state that PAN precursor nanofibres can be processed (for obtaining carbon nanofibres) by thermal stabilisation and pyrolysis. However, the thermal-time conditions for these processes must be significantly milder than those for processing traditional polyacrylonitrile fibres. Electrospinning is a suitable meth-

od for obtaining PAN nanofibres, as well as their further processing into carbon nanofibres of circular cross-section.

Acknowledgement

The authors would like to thank H. Wrzosek from the Technical University of Łódź for carrying out the SEM images.

References

1. Grafe T., Graham K., presented at the INTC 2002 International Nonwovens Technical Conference (Joint INDATAPPI Conference), Atlanta, Georgia, September 24-26, 2002.
2. Chun I., Reneker D.H., Fong H., Fang X., Deitzel J., Beck Tan N., Kearns K., *Journal of Advanced Materials*, 1999, 31, 36-41.
3. Zeleny J. *Phys. Rev.*, 1914, 3, 69-91.
4. Formhals A., *Process and apparatus for preparing artificial threads*. US Patent No. 1,975,504, 1934.
5. Taylor G.I. *Proc. R. Soc. Lond. A.* 1964, 280, 383-97.
6. Taylor G.I. *Proc. R. Soc. Lond. A.* 1969, 31, 453-75.
7. Jain M.K., Balasubramanian M., Desai P., *J. of Mat. Science*, 1987, 22, 301-312.
8. Donnet J.-B., Bansal R.C., *Carbon fibers*, Marcel Dekker INC, New Jorc, Basel, 1990.
9. Peebles L.H., *Carbon fibers - formation, structure and properties*, CRC Press, Boca Raton, London, Tokyo, 1996.
10. Balasubramanian M., Jain M.K., Bhattacharya S.K., Abhiraman A.S., *J. of Mat. Science*, 1987, 22, 3864-3872.
11. Fizer E., Frohs W., Heine M., *Carbon*, 1986, 24, 387-395.
12. Ogawa H., Saito K., *Carbon*, 1995, 33, 783-788.
13. Gupta A., Harrison I.R., *Carbon*, 1997, 35, 809-818.
14. Beltz L.A., Gustafson R.R., *Carbon*, 1996, 34, 561-566.
15. Hindleleh A.M., Johnson D.J., *Polymer*, 1974, 15, 697.
16. Rabiej S., *Eur. Polym.*, 1991, 27, 947.

Received 08.05.2004 Reviewed 22.11.2004