

Pyrolysis and Oxidation of PAN in Dry Air. Thermoanalytical Methods

Anna BIEDUNKIEWICZ*, Pawel FIGIEL, Marta SABARA

Institute of Materials Science and Engineering, West Pomeranian University of Technology, Szczecin, Poland

Received 10 October 2010; accepted 10 February 2011

The results of investigations on pyrolysis and oxidation of pure polyacrylonitrile (PAN) and its mixture with N,N-dimethylformamide (DMF) under non-isothermal conditions at linear change of samples temperature in time are presented. In each case process proceeded in different way. During pyrolysis of pure PAN the material containing mainly the product after PAN cyclization was obtained, while pyrolysis of PAN+DMF mixture gave the product after cyclization and stabilization. Under conditions of measurements, in both temperature ranges, series of gaseous products were formed.

For the PAN-DMF system measurements at different samples heating rates were performed. The obtained results were in accordance with the kinetics of heterogeneous processes theory. The process rates in stages increased along with the temperature increase, and TG, DTG and HF function curves were shifted into higher temperature range. This means that the process of pyrolysis and oxidation of PAN in dry air can be carried out in a controlled way.

Keywords: PAN, DMF, pyrolysis, oxidation, thermoanalysis.

INTRODUCTION

Polyacrylonitrile (PAN) is a widely used precursor for manufacturing carbon materials with very interesting mechanical, electrical and magnetic properties and high thermal and chemical resistance. These materials found application in aircraft and automotive industry, in electronics and as adsorbents and filters for water and gases treatment [1–28]. Nowadays PAN is also used as precursor during synthesis of transition metals and silicon carbides and nitrides. [2].

The age of carbon fibres derived from PAN started in year 1960, when A. Shindo, for the first time, subjected polyacrylonitrile to oxidation, before the pyrolysis process [13].

Products of PAN pyrolysis form thermally stable, organized molecular structures when they are processed by appropriate thermal treatment in low temperature called stabilization process. Stabilization is usually carried out in air. It prevents polymer from decomposition during carbonization in high temperature.

Properties of carbon material derived from PAN depend on conditions of pyrolysis, parameters of thermal treatment in high temperature and on the structure of applied polymer materials. Knowledge of characteristics of PAN thermal conversions proceeding in various systems is therefore crucial. Carbon forming from PAN is a composed process. In practice it is realized according to different procedures [5, 6, 9, 12, 14, 17, 20, 22, 24, 26]. During stabilization series of reactions proceed. Their sequence was determined on the basis of many scientific works initiated in the last century [12, 14, 16].

Reaction of cyclization was recognized as the most important process. This could be initiated in different ways, depending on type of atmosphere, presence of copolymers and other system components [8, 20]. In reaction of cyclization generated by nitrile groups

polymerization the material containing segments of short, ladder molecules connected by sequences of unchanged PAN polymer is formed (oligomerization). Nitrogen in the nitrile group forms the bound with the carbon of neighbouring nitrile group in the polymer chain and the six-element ring is formed.

The properties of carbon materials obtained in PAN pyrolysis and oxidation process depend on many factors. While manufacturing material according to the adopted procedure the course of PAN pyrolysis process has to be determined.

EXPERIMENTAL DETAILS

The investigations of pyrolysis and oxidation in dry air of solid PAN and PAN dissolved in DMF were carried out. PAN (purchased from Sigma-Aldrich) and DMF having a purity of 99.9 % (Sigma-Aldrich) were used. Synthetic air, (Messer, Germany) containing 20.5 % of oxygen and the rest of nitrogen was used. Impurities level was as follows: $H_2O < 10$ ppm, $CO_2 < 0.5$ ppm, $NO_x < 0.1$ ppm and hydrocarbons < 0.1 ppm by volume.

Thermogravimetric TG–DSC measurements were performed under non-isothermal conditions at linear change of sample temperature in time. SDT Q600 apparatus (TA Instruments) was used. Gaseous products were identified by mass spectrometry method using Thermostat GSD 301 (Pfeifer Vacuum) apparatus. Weighed amounts of the samples were in the range of 20 mg. The temperature was set between 25 °C and 800 °C. During the measurements temperature, TG, ΔTG and HF functions in time as well as the mass spectra of main gaseous products were recorded.

RESULTS AND DISCUSSION

Investigations on pyrolysis and oxidation of PAN are usually carried out by TG-DSC method. Comparing the DTA and DSC curves presented in works [4, 8, 20, 22] one can notice that shape of the first exothermal peak, related to stabilization process proceeding with oxide participation, is fuzzy or consists of two very close peaks. Elonga-

*Corresponding author. Tel.: +48-91-4494071; fax.: +48-91-4494356.
E-mail address: anna.biedunkiewicz@zut.edu.pl (A. Biedunkiewicz)

tion of heating time of PAN sample in air or increasing of upper temperature above 289 °C favours super-adsorption of oxygen, increase of carbonyl C=O groups number, structural defects and degradation of ladder structure of polymer [8, 9, 12]. Maximal degradation rate occurs at temperature of about 380 °C [9]. According to the authors of work [9] the upper temperature of stabilization should not exceed 289 °C.

Reaction of cyclization starts at temperature of 180 °C and proceeds slowly up to 220 °C, above which temperature it proceeds very rapidly up to the temperature of 289 °C [8]. The selected temperature from the range of 180 °C–289 °C and time or rate of sample heating determined sufficiently stable structure of carbon material after carbonization.

During preparation of carbides precursors DMF is used as the solvent of PAN [2]. This is the most polar solvent among the group of polyacrylonitrile solvents. It strongly solvates cations and less anions. Between PAN and DMF the strong intermolecular interaction is found, what facilitates solubility of polymer in it. A complex between PAN and DMF can be formed what hinders total evaporation of DMF during the sample drying. The total removal of DMF is possible at higher temperature under conditions of PAN pyrolysis. In work [6] the courses of the pyrolysis process of solid PAN and PAN dissolved in DMF were compared. Pyrolysis was carried out at temperature of 700 °C. The gaseous products were identified by chromatographic and mass spectroscopy method. In both cases similar gaseous products were obtained. It should be added that DMF also occurred in gaseous phase what indicates strong interaction between DMF and PAN molecules. Presence of DMF in PAN pyrolysis process reduces the thermal effect of cyclization process, causes increase of initial temperature of cyclization and the maximal reaction rate of the reaction is shifted into lower temperature range.

During the heat treatment of PAN-DMF mixture in argon two peaks occurred at DTG curve [28–30]. The first, endothermic peak referred to the conversion proceeding with mass loss and was connected with evaporation of DMF, and the second exothermic peak was connected with process of PAN cyclization.

According the state-of-art, in case of solid PAN at lower temperature cyclization and stabilization can take place. It is possible to obtain a mixtures of the products of these processes. Their identification is important for process synthesis of carbon fibres designing and also for synthesis carbides from precursor which contains PAN dissolved in DMF [2, 31]. Identification of cyclization and stabilization products is possible in oxidation process in air at higher temperature using TG-DSC-MS method. Additionally, the comparison of course of pyrolysis process of pure PAN and mixtures of PAN and DMF in air is necessary.

In case of PAN-DMF system the samples were first heated at 110 °C to strip the major part of mainly non-bonded DMF. Under measurement conditions evaporation of non-bonded rests of DMF, PAN cyclization and proceeding in parallel desorption of DMF with its decomposition, then stabilization of PAN and oxidation of conversions products can take place.

In Fig. 1 the charts of TG_u and HF in time for both cases are presented. In case of pure PAN in HF curve the high exothermal peak occurs referring to cyclization. The process proceeded with mass loss.

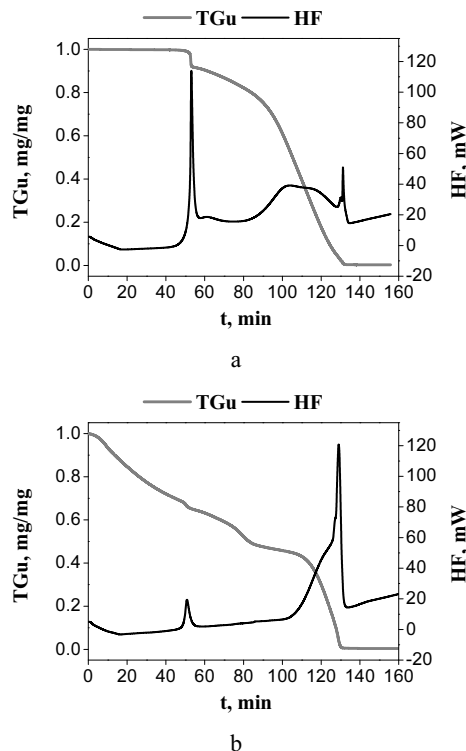


Fig. 1. Normalized TG_u and HF functions in time and temperature. Sample heating rate: 5 K/min, a – PAN, b – PAN+DMF

In case of PAN+DMF system the peak is low and shifted into the lower temperature range. The heat released during PAN cyclization was used during DMF desorption proceeding in parallel with cyclization.

The HF function curves in the range of reaction course of PAN conversion products oxidation are also different. In case of pure PAN first the wide peak referring to cyclization products combustion occurs and then a minor peak connected with combustion of cyclization products and PAN stabilization [4, 8, 30]. In case of PAN+DMF systems this relation is shifted in favour of second product. Performed measurements indicated also that under non-isothermal conditions process of polymer stabilisation did not proceed to completion.

In Fig. 2 TG and DTG functions in time are presented. In DTG curve concerning pure PAN two peaks occur. The first one refers to PAN cyclization and the second to oxidation of PAN conversion products at low temperature [4, 7, 20]. In case of PAN-DMF system in DTG curve four peaks are present. The first one concerns removal of free DMF rests, second one is connected with PAN cyclization process, the third one refers to desorption of DMF with its decomposition and the fourth one to oxidation of PAN conversion products formed at lower temperature.

An important complement of these measurements was identification of gaseous products. In both cases similar volatile products were evolved. In the range of lower temperature these were: CO₂, CH₃, NO, C₃H₅, C₃H₆, C₂H₂O. In case of PAN+DMF system also DMF was

registered. During oxidation of PAN conversion products the following compounds were formed: CO_2 , NO_2 , C_3H_5 , CH_3CO , $\text{C}_2\text{H}_5\text{O}$, COOH , $\text{C}_2\text{H}_7\text{N}$. In both temperature ranges HCN and NH_3 were not registered among evolved gases.

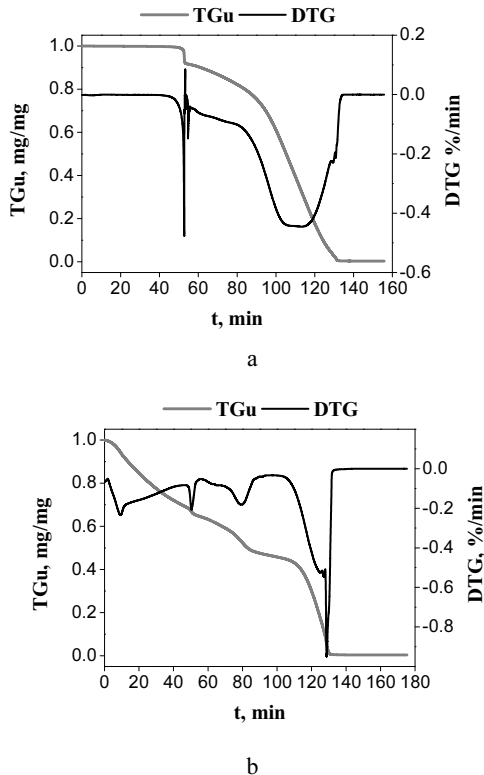


Fig. 2. Normalized TG_u and DTG functions in time. Sample heating rate: 10K/min, a – PAN, b – PAN-DMF system

In Fig. 3 mass spectra of the main gaseous components recorded during the proceeding of above mentioned processes is shown. The presented charts distinguish well both systems. It is evident that CO_2 in case of pure PAN was evolved during cyclization (first peak in the curve), during oxidation of PAN cyclization products (the first wide part of second peak) and during oxidation of the product after cyclization and stabilization (narrow part of second peak). Also other areas of the mass spectra curves are different.

In Fig. 4 mass spectra charts of products formed during the oxidation of PAN cyclization and stabilization products in dry air have been compared.

During combustion in both cases similar products were formed. It should be added that such products, except of NO_2 , were formed also during the PAN cyclization and DMF conversion. Course of PAN conversion depends also on sample heating rate. The influence of sample heating rate is shown at the example of PAN-DMF system.

The measurements were carried out at sample heating rate 2 K/min (sample weight 19.59 mg), 5 K/min (sample weight 19.58 mg) 10 K/min (sample weight 20.45 mg). The second sample, after completion of the process, was heated for 3 hours under isothermal conditions.

The results of TG_u and DTG function presented in Fig. 5 indicate, that registered variables are continuous functions of temperature and time. In Fig. 6 however DTG and HF function charts are shown.

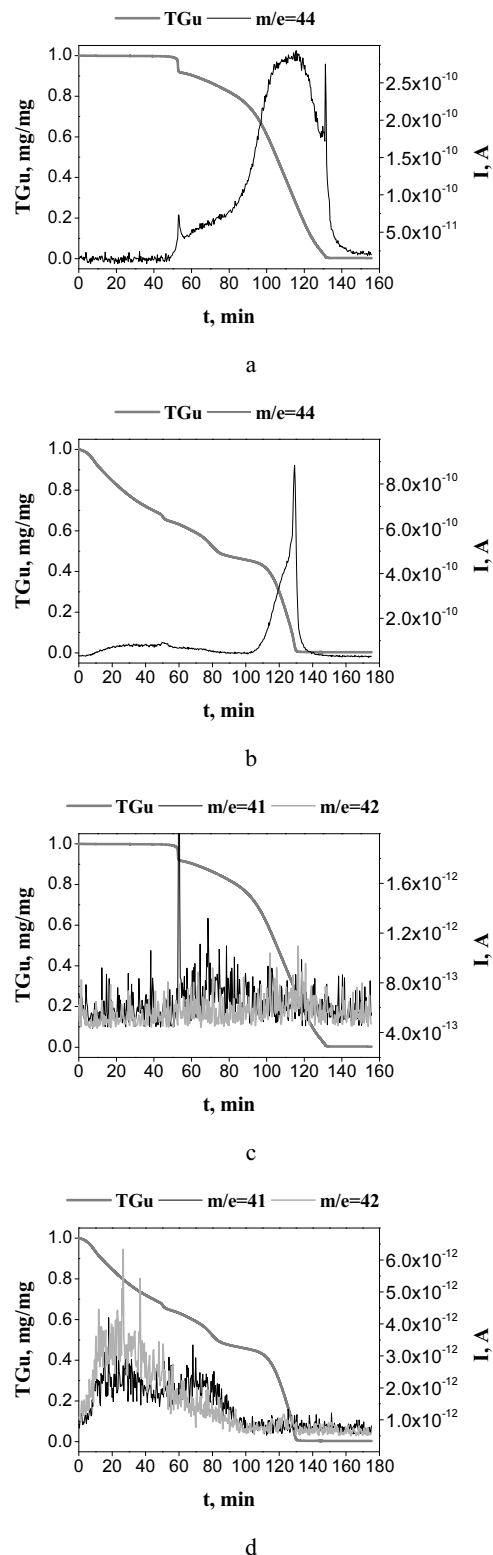


Fig. 3. Normalised TG_u function and mass spectra: a – $m/e = 44$ (CO_2) concerns pure PAN system, b – $m/e = 44$ (CO_2) concerns PAN –DMF system, c – $m/e = 42$ (C_3H_6 , $\text{C}_2\text{H}_2\text{O}$) concerns pure PAN system, d – $m/e = 42$ (C_3H_6 , $\text{C}_2\text{H}_2\text{O}$) concerns PAN –DMF system. Sample heating rate: 5 K/min

At the used sample heating rates process stages were separated. In accordance with the theory of heterogeneous processes kinetics DTG and HF function curves were shifted into the higher temperature range while increasing

sample heating rate. This means that the conversions can be conducted in a controllable way. It is evident that synthesizing precursors the samples can be heated up to the

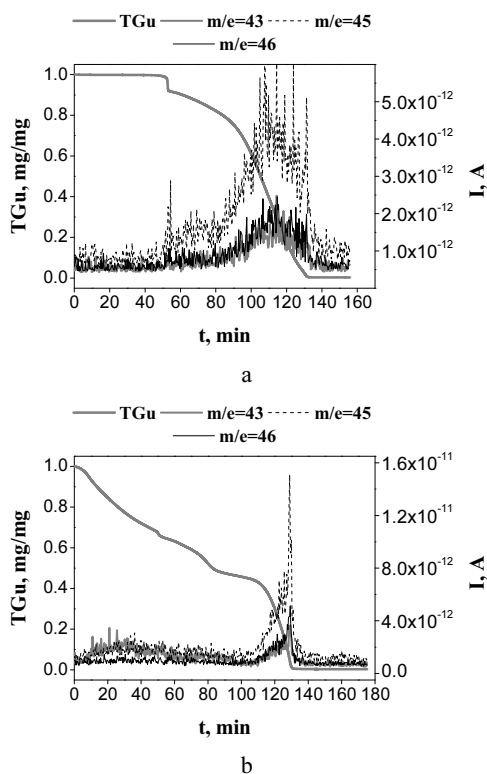


Fig. 4. Normalised TG_u function and mass spectra: $m/e = 43$ (C_3H_7 , CH_3CO), $m/e = 45$ (C_2H_2O , $COOH$, C_2H_7N) and $m/e = 46$ (NO_2). a – PAN, b – PAN-DMF. Sample heating rate: 5 K/min

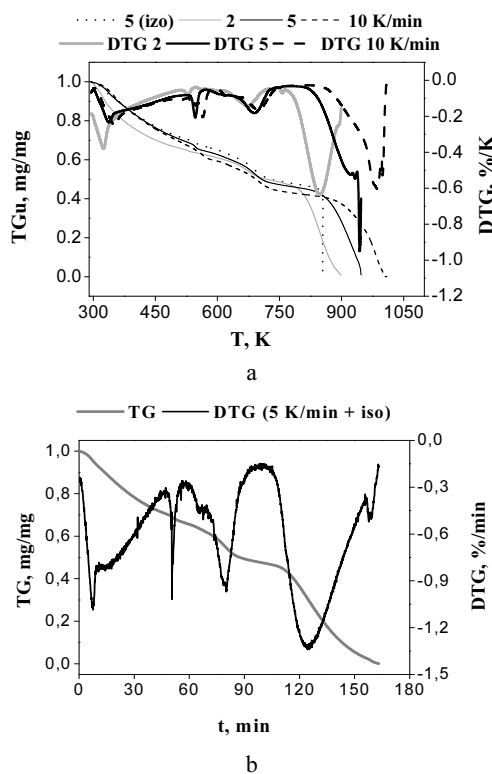


Fig. 5. TG_u and DTG functions. Pyrolysis of PAN-DMF in dry air: a – dependency on temperature, b – dependency on time

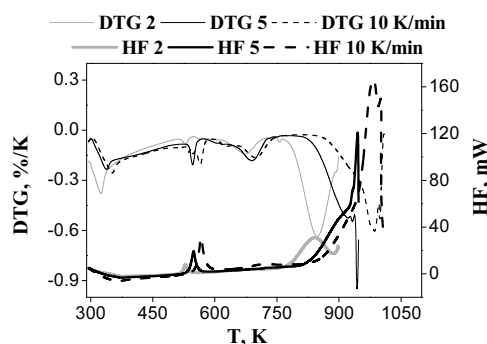


Fig. 6. DTG and HF functions chart. Oxidation of PAN-DMF in dry air

temperature range of 400 °C without generation of PAN cyclization and stabilization products conversion. This temperature was taken as suitable temperature for preparing precursors of carbides synthesis.

CONCLUSIONS

The results of investigations of pure PAN and PAN+DMF mixture pyrolysis and oxidation in dry air were presented. At the lower temperature range up to about 680 K cyclization and stabilization of PAN took place. At higher temperature oxidation of PAN conversion products formed at lower temperature proceeded. The course of processes was different. In case of pure PAN two stages, while in case of PAN+DMF system four stages were recorded.

In HF function curve obtained for pure PAN the high exothermal peak resulting from PAN cyclization occurred. Cyclization proceeded with the sample mass loss. During oxidation of PAN conversion products formed at lower temperature a double peak occurred in HF function curve. The first wide part referred to oxidation of cyclization products and the second narrow part of the peak concerned oxidation of PAN cyclization and stabilization products. In this case material containing mainly PAN cyclization product was obtained.

In case of PAN+DMF mixtures in HF function curve a peak connected with cyclization process occurred. The heat released during cyclization was used during desorption of DMF with its decomposition. In the range of oxidation course of PAN conversion products a narrow asymmetric peak was registered. In this case material after cyclization and stabilization was mainly obtained.

For PAN+DMF system measurements under non-isothermal conditions were performed at different sample heating rates in time. The obtained results are in accordance with theory of heterogeneous processes kinetics. Along with the increase of sample heating rate conversion rate in stages increased and the TG, DTG and HF function curves were shifted into higher temperature range. This means that pyrolysis and oxidation of PAN can be conducted in a controllable way.

Acknowledgments

Financial support of the work by the Ministry of Science and Higher Education within the project No. N N507 444334, 2008–2011, is gratefully acknowledged.

REFERENCES

1. Wang, Yu, Santiago-Aviles, J. J., Furlan, R., Ramas, J. Pyrolysis Temperature and Time Dependence of Electrical Conductivity for Electrostatically Generated Carbon Nanofibers *IEEE Transaction on Nanotechnology* 2 (1) 2003: pp. 39–43.
2. Biedunkiewicz, A. Aspects of Manufacturing of Ceramic Nanomaterials of Type TiC/C, TiC, TiC-SiC-C and Ti(C,N)-Si(C,N)-Si₃N₄ by sol-gel method Ed. WPUT., Szczecin, 2009.
3. Beyler, C. L., Hirschler, M. M. Thermal Decomposition of Polymers (Charper 7). Overview and Background SFPE Handbook of Fire Protection Engineering. 3rd ed, Editor-in-chief: Philip J. Di Nanno, PE NFPA, Quincy MA, 2001: pp. 110–131.
4. Sazanow, Yu. N., Nud'ga, L. A., Novoselova, A. V., Ugolkov, V. L., Fedorova, G. N., Kulikova, E. M., Gribanov, A. V. Carbonization of Polyacrylonitrile Composites with Nitrogen-containing Cellulose Derivatives *Russian Journal of Applied Chemistry* 77 (4) 2004: pp. 639–644.
5. Memetea, L. T., Billingham, N. C., Then, E. T. H. Hydroperoxides in Polyacrylonitrile and Their Role in Carbon-fibre Formation *Polymer Degradation and Stability* 47 1995: pp. 189–201.
6. Mittal, J., Konno, H., Inagaki, M., Bahl, O. P. Denitrogenation Behaviour and Tensile Strength Increase During Carbonization of Stabilized PAN Fibres *Carbon* 39 (9) 1998: pp. 1327–1330.
7. Fitzer, E. PAN- Based Carbon Fibers – Present State and Trend of Technology from the Viewpoint of Possibilities and Limits to Influence and to Control the Fiber Properties by the Process Parameters *Carbon* 27 (50) 1989: pp. 621–645.
8. Fitzer, E., Müller, D. J. The Influence of Oxygen on the Chemical Reactions During Stabilization of PAN as Carbon Fiber Precursor *Carbon* 13 1975: pp. 63–69.
9. Tse-Nao, K., Ching-Chyuan, Y., Wen-Tong, C. The Effect of Stabilization of PAN- Based Carbon Films *Carbon* 11 (4) 1993: pp. 583–590.
10. Morita, K.-T., Miyachi, H., Hiramatsu, T. Stabilization of Acrylic Fibers by Sulfur Atoms Mechanism of Stabilization *Carbon* 19 1981: pp. 11–18.
11. Deurebergue, A., Oberlin, A. TEM Study of Some Recent High Modulus PAN-Based Carbon Fibers *Carbon* 30 (7) 1992: pp. 981–987.
12. Bahl, O. P., Manocha, L. M. Characterization of Oxidized PAN Fibers *Carbon* 12 1974: pp. 417–423.
13. Chang, P.-H., Labes, M. M. New Route of Graphite Flakes and Films: Pyrolysis of Aromatic and Heteroaromatic Compounds under Dehydrogenation Conditions *Chemistry of Materials* 1 1989: pp. 523–525.
14. Ko, T.-H., Day, T.-C., Perng, J.-A. The Characterization of PAN-Based Carbon Fibers Developed by Two-Stage Continuous Carbonization *Carbon* 31 (5) 1993: pp. 765–771.
15. Tsuchiya, Y., Sumi, L. Thermal Decomposition Products of Polyacrylonitrile *Journal of Applied Polymer Science* 21 1977: pp. 975–980.
16. Bashir, Z. A Critical Review of the Stabilization of Polyacrylonitrile *Carbon* 29 (8) 1991: pp. 1081–1090.
17. Kowbel, W., Hippo, E., Muridie, N. Influence of Graphitization Environment of PAN Based Carbon Fibers on Microstructure *Carbon* 27 (2) 1989: pp. 219–226.
18. David, L. I., Ismail, A. F. Influence of the Thermostabilization Process and Soak Time During Pyrolysis Process on the Polyacrylonitrile Carbon Membranes for O₂/N₂ Separation *Journal of Membrane Science* 213 2003: pp. 285–291.
19. Surianarayanan, M., Panduranga, Rao, S., Vijayaraghavan, R., Raghvan, K. V. Thermal Behaviour of Acrylonitrile Polymerization and Polyacrylonitrile Decomposition *Journal of Hazardous Materials* 62 1998: pp. 187–197.
20. Martin, S. C., Liggat, J. J., Snape, C. E. In Situ NMR Investigation into the Thermal Degradation and Stabilisation of PAN *Polymer Degradation and Stability* 74 2001: pp. 407–412.
21. Nielsen, M., Jurasek, P., Hayashi, J., Furimsky, E. Formation of Toxic Gases During Pyrolysis of Polyacrylonitrile and Nylons *Journal of Analytical and Applied Pyrolysis* 35 1995: pp. 45–51.
22. Surianarayanan, M., Uchida, T., Wakakura, M. Evolved Gases by Simultaneous TG-MS Technique and Associated Thermal Hazard in Drying of Polyacrylonitrile *Journal of Loss Prevention in the Process Industries* 11 1998: pp. 99–108.
23. Setnescu, R., Jipa, S., Setnescu, T., Kappel, W., Kobayashi, S., Osawa, Z. IR and X-ray Characterization of Ferromagnetic Phase of Pyrolysed Polyacrylonitrile *Carbon* 37 1999: pp. 1–6.
24. Fitzer, E., Frons, W., Heine, M. Optimization of Stabilization and Carbonization Treatment of PAN Fibres and Structural Characterization of the Resulting Carbon Fibers *Carbon* 24 (4) 1986: pp. 387–395.
25. Paulauskas, F. L., Spruiell, J. E. Structure and Properties of Carbon Fibres Produced Using Microwave-Assisted Plasma Technology. Part I *SAMPE Journal* 40 (4) 2004: pp. 6–14.
26. Chen, J., Harrison, I. R. Modification of Polyacrylonitrile (PAN) Carbon Fiber Precursor via Post-Spinning Plasticization and Stretching in Dimethylformamide (DMF) *Carbon* 40 (1) 2002: pp. 25–45.
27. Laffont, L., Monthieux, M., Sern, V., Mathur, R. B., Guimon, C., Guimon, M. F. An EELS Study of the Structural and Chemical Transformation of PAN Polymer to Solid Carbon *Carbon* 42 (12-13) 2004: pp. 2485–2494.
28. Saufi, S. M., Ismail, A. F. Development and Characterization of Polyacrylonitrile (PAN) Based Carbon Hollow Fiber Membrane *Songklanakarin Journal of Science and Technology* 24 2002: pp. 843–854.
29. Aviles, M. A., Gines, J. M., del Rio, J. C., Pascual, J., Perez-Rodriguez, J. L., Sanchez-Soto, P. J. Thermal Analysis of Acrylonitrile Polymerization and Cyclization in Presence of N,N-dimethylformamide *Journal of Thermal Analysis and Calorimetry* 67 2002: pp. 177–188.
30. Sanchez-Soto, P. J., Aviles, M. A., del Rio, J. C., Gines, J. M., Pascual, J., Perez-Rodriguez, J. L. Thermal Study of the Effect of Several Solvents on Polymerization of Acrylonitrile and Their Subsequent Pyrolysis *Journal of Analytical and Applied Pyrolysis* 58-59 2001: pp. 155–172.
31. Biedunkiewicz, A., Gabriel, U., Figiel, P., Grzesiak, D. Application of Thermal Analysis in Nanotechnology. Carbonization and Purification of nc-TiC_x in Argon Atmosphere *Journal of Thermal Analysis and Calorimetry* 101 (2) 2010: pp. 701–706.

Presented at the International Conference
"Baltic Polymer Symposium 2010"
(Palanga, Lithuania, September 8–11, 2010)