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LATVIAN JOURNAL OF PHYSICS
AND TECHNICAL SCIENCES
2024, N 4

DOI: 10.2478/lpts-2024-0031

COMPARATIVE ANALYSIS OF THERMAL CHARACTERISTICS: VIRGIN POLYACRYLONITRILE (PAN) VERSUS ELECTROSPUN PAN NANOFIBRE MATS

J. V. Sanchaniya

Institute of Mechanical and Biomedical Engineering,
Riga Technical University,
6B Kipsala Str., Riga, LV-1048, LATVIA
E-mail: jaymin.sanchaniya@rtu.lv

The utility of polymers in the fabrication of nanofibres via electrospinning is well established. Paramount to their application is understanding of their thermal properties, as these dictate not only their processability but also their mechanical robustness, stability under elevated temperatures, and suitability for intended applications. The electrospinning process, which involves heating polymers and subjecting them to high voltage, inherently modifies their thermal characteristics. This study attempts to elucidate these alterations, particularly by focusing on polyacrylonitrile (PAN) nanofibres. Employing techniques such as thermogravimetric analysis (TGA) and Differential Scanning Calorimetry (DSC), the study compares the thermal properties of electrospun PAN nanofibre mats with those of their virgin counterparts. The PAN nanofibres were synthesised by electrospinning the PAN polymer solution and collecting the resultant mat on a flat plate collector. For a comparative analysis, virgin PAN, from which nanofibres were derived, underwent identical thermal testing. The findings reveal a reduction in the glass transition temperature of PAN nanofibres by approximately 3–5 % compared to virgin PAN. In addition, a significant reduction in heat capacity of about 42 % was observed in the nanofibres. Additionally, the TGA results indicated solvent evaporation at approximately 110 °C. Therefore, this investigation sheds light on the nuanced alterations in the thermal characteristics of PAN nanofibre mats as a result of the electrospinning process, providing vital insights for their application in various thermal management scenarios.

Keywords*: Electrospinning, differential scanning calorimetry (DSC), nanofibres, PAN (polyacrylonitrile), thermogravimetric analysis (TGA).*

1. INTRODUCTION

Electrospinning emerges as a pivotal technique in the nanofibre fabrication landscape, particularly in the context of nanofibre applications [1]. This process enables the production of nanofibres with superior physical attributes. It involves subjecting a polymer solution or melt to a high voltage, engendering the formation of an electrically charged jet. This jet, under the influence of the electric field, travels towards a collector, where it solidifies into a fibrous mat or film. In particular, the electrospinning process is known to induce modifications in the thermal properties of the polymer, such as alterations in its melting point, glass transition temperature, and thermal conductivity [2].

Electrospun polyacrylonitrile (PAN) nanofibers are utilised in a wide range of applications, for example, air & water filtration [3]–[5], drug delivery [6]–[8], wound dressing [9], nanocomposite fabrication [10]–[12], antibacterial textiles [13]–[15] integrated with silica dioxide and succinite (Baltic amber), and the creation of protective clothing [16]. Given these applications, the nanofibres are often subjected to thermal stresses, underscoring the necessity to understand their thermal stability when exposed to heat.

Thermogravimetric analysis (TGA) is instrumental in this study as it measures the change in mass of a sample over time as a function of temperature, offering insights into physical phenomena such as phase transitions, which typically encompass transitions between solid, liquid, and gaseous states, as well as absorption, desorption, and chemical phenomena like thermal decomposition reactions. Complementarily, differential scanning calorimetry (DSC) is employed to ascertain the crystallisation and glass transition temperatures of the polymers.

The objective of this study is to perform a comparative analysis of the thermal characteristics of virgin PAN and PAN nanofibres. Using TGA and DSC analyses, a comprehensive understanding of how electrospinning influences the thermal properties of PAN is sought, thereby contributing valuable insights into the field of polymer science and nanotechnology.

2. MATERIALS AND METHODOLOGY

This study meticulously examines the thermal characteristics of virgin polyacrylonitrile (PAN) and electrospun PAN nanofibres that are produced as previously mentioned by the authors [11], [17], [18]. The materials used for the synthesis of these nanofibres comprised PAN powder and N, N-dimethylformamide (DMF). Specifically, polyacrylonitrile (average molecular weight: 150,000 (MW); CAS number: 25014-41-9) and N, N-dimethylformamide (ACS reagent quality, 99.8% purity; CAS number: 68-12-2) were procured from Sigma-Aldrich Chemicals, Merck KGaA, Darmstadt, Germany.

For thermogravimetric analysis (TGA), a TG 209 F1 Libra® thermomicrobalance (NETZSCH, Selb, Germany) was used. The samples, each weighing between 5 and 6 mg, were placed in crucibles of aluminium oxide (Al2O3). The temperature was gradually increased from 20 °C to 800 °C at a rate of 10 °C / min, in an inert nitrogen atmosphere with a flow rate of 30 ml / min.

Differential scanning calorimetry (DSC) was performed using a DSC 214 Polyma differential scanning calorimeter (NETZSCH, Selb, Germany), also under a nitrogen atmosphere with an identical flow rate. The DSC involved the precise placement of the virgin PAN powder and the PAN nanofibre mat in the crucible. The thermal cycle began with an initial heating from -50 °C to 150 °C, aimed at expelling impurities and moisture. This was followed by cooling to -50 °C and a subsequent reheating to 150 °C to determine the glass transition temperature. Each heating and cooling cycle was interspersed with an isothermal step.

The DSC protocol adhered to ASTM E1356 standards. The heating rate was maintained at 10 °C / min in a range of -50 °C to 150 °C, in accordance with methodologies previously described by the authors in [17]. To verify the weight of the samples, a KERN ABT 5NM laboratory scale (KERN&Sohn GmbH, Balingen, Germany) was used. This scale, with a maximum capacity of 100 g and a discreteness of 0.000001 g, bears the serial number WB22G0101 and was calibrated according to the certificate number B61-389-2023-03/1, dated 24 March 2023.

This methodology provides a comprehensive framework for assessing the thermal properties of both virgin and electrospun PAN, thereby facilitating a thorough comparative analysis.

3. RESULTS AND DISCUSSION

The thermal behaviour of virgin polyacrylonitrile (PAN) and PAN nanofibres was investigated using TGA and DSC.

The TGA curve for virgin PAN (Fig. 1) comprises a green graph representing mass loss as a function of temperature and a red graph depicting the first derivative, which aids in precise temperature determination. In particular, up to 289.5 °C, no significant mass loss was observed in the virgin PAN. The onset of degradation was marked at 291.6 °C. The total mass loss from 25 °C to 299.8 °C was 14.15 % and from 299.8 °C to 374.4 °C, it was 22.78 %. Subsequently, a mass loss of 19.70 % was recorded from 374.4 °C to 566.0 °C, followed by a loss of 3.65 % from 566.0 to 799.6 °C. At 800 °C, the residual mass was recorded as 39.42 %.

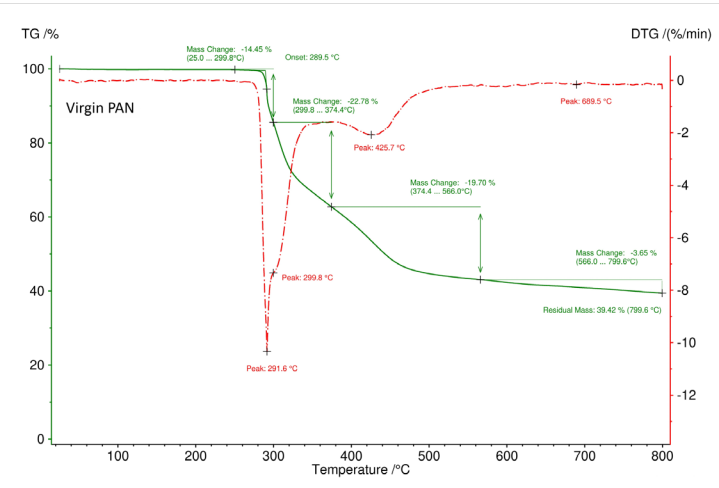

Fig. 1. TGA and DTG of virgin PAN.

The TGA curve of PAN nanofibres (Fig. 2) showed an initial mass loss at 110.6 °C, approximately 3.08 %, attributed to the evaporation of the solvent DMF. The total mass loss from 25.0 °C to 158.7 °C was 3.08 %, and from 158.7 °C to 297.6 °C it was 1.66 %. In the temperature range of 264.2 °C to 297.6 °C, the mass loss was 14.26 %. From 297.1 °C to 371.6 °C, the loss was around 22.96 %, and from 371.6 °C to 552.0 °C it was 20.23 %. In the range of 551.3 °C to 799.5 °C, the mass loss was 5.61 %, leaving a residual mass of 32.63 %.

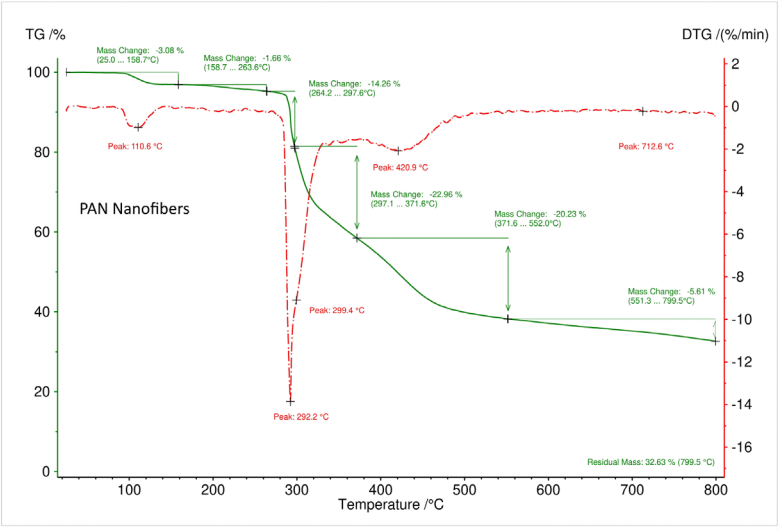

Fig. 2. TGA and DTG of PAN nanofibre mat.

During the first heating cycle in DSC (Fig. 3), virgin PAN absorbed 30.06 J / g, while PAN nanofibres absorbed 26.88 J/g. Two peaks were observed in the heat absorption profile, potentially due to solvent evaporation, corroborating the temperature range observed in the TGA graph of the PAN nanofibre mat (Fig. 2).

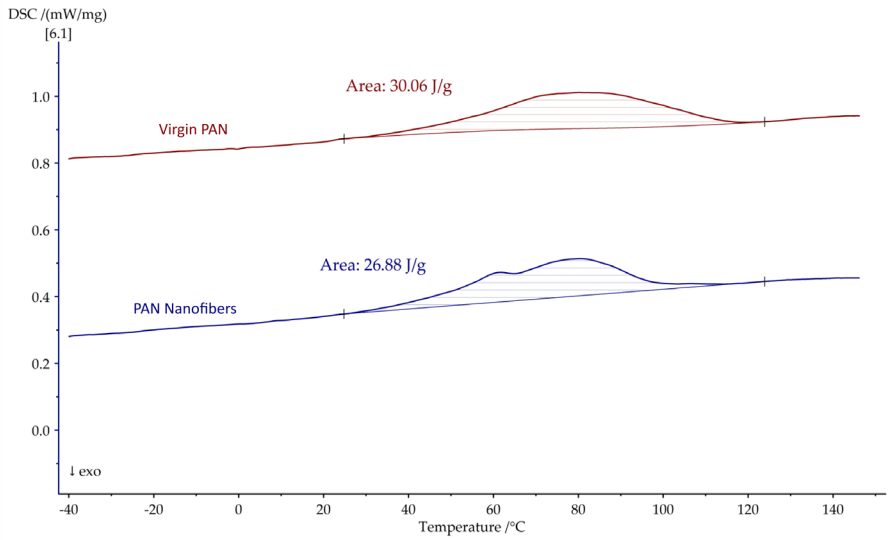

Fig. 3. The 1st heating cycle of virgin PAN vs PAN nanofibres in DSC.

In the first cooling cycle, represented in Fig. 4, the glass transition temperature for virgin PAN was observed at 97.9 °C, while for PAN nanofibres, it was 94.9 °C, indicating a reduction of approximately 3 %.

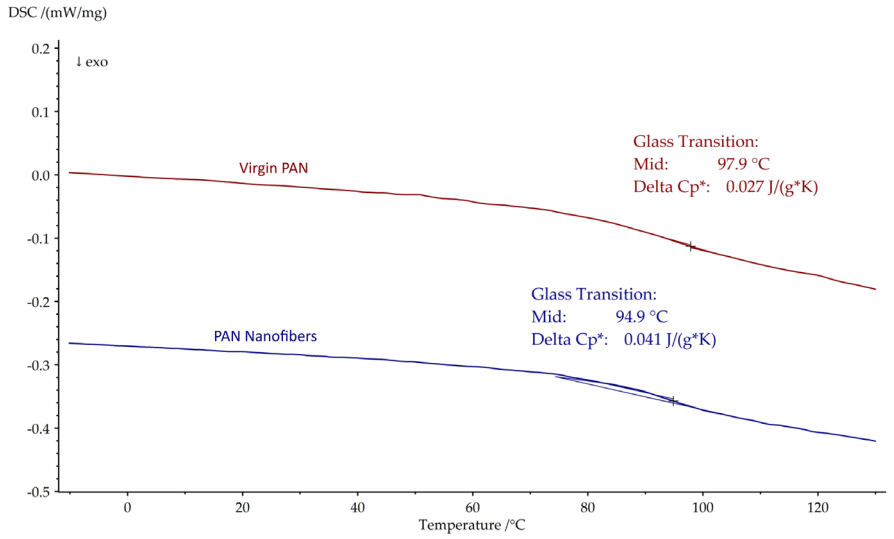

Fig. 4. The 1st cooling cycle of virgin PAN vs PAN nanofibres in DSC.

The second heating cycle of DSC (Fig. 5) revealed a glass transition temperature of 101.8 °C for virgin PAN and approximately 96.0 °C for PAN nanofibres, a reduction of about 5 %. The change in heat capacity (Delta Cp*) showed a notable difference: for virgin PAN, it was 0.202 J / (gK), while for the PAN nanofibres, it was 0.116 J/(gK), marking a reduction of 42 %.

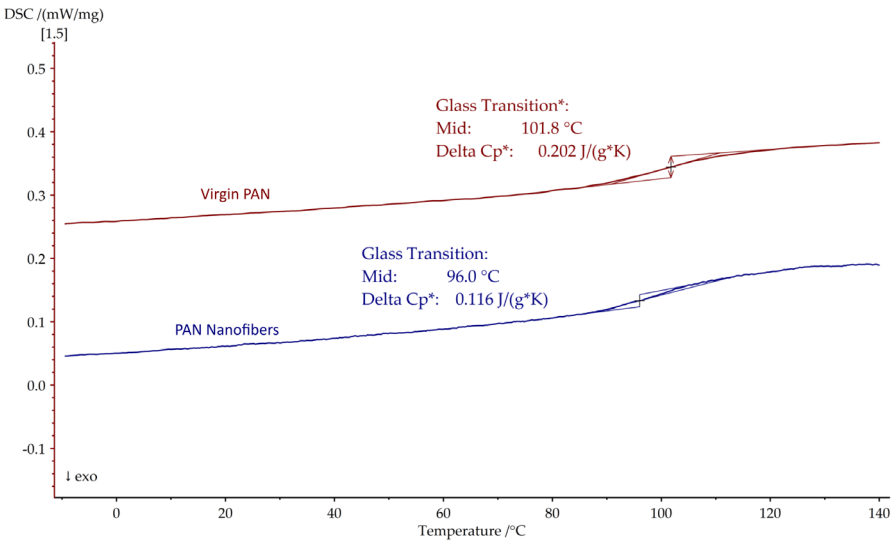

Fig. 5. The second heating cycle of virgin PAN vs PAN nanofibres in DSC.

These results collectively offer a comprehensive insight into the thermal characteristics of virgin PAN and PAN nanofibres, highlighting the impact of the electrospin-

ning process on their thermal stability and transition temperatures.

The comparative analysis of the thermal properties of virgin polyacrylonitrile (PAN) nanofibres and electrospun PAN nanofibres, as elucidated by TGA and DSC, reveals significant insights. The electrospinning process evidently impacts the thermal stability and transition temperatures of PAN. The increased glass transition temperature in the nanofibre mats, as compared to those of virgin PAN, suggests enhanced thermal stability, possibly attributable to the morphological changes induced by electrospinning. The observed decrease in melting temperature and the reduced heat capacity in nanofibres indicate alterations in the crystalline structure and thermal behaviour, which was observed in the case of polyamide nanofibres [19]. These changes have profound implications for the application of PAN nanofibres in areas that require thermal resilience. The early onset of solvent evaporation in nanofibres, as detected in TGA, further underscores the influence of processing methods on the properties of the materials. Overall, the findings underscore the necessity of considering these thermal characteristic variations when employing PAN nanofibres in practical applications, particularly those subjected to thermal stress.

4. CONCLUSIONS

This investigation has comprehensively analysed the thermal characteristics of virgin PAN and electrospun PAN nanofibres, using thermogravimetric analysis and Differential Scanning Calorimetry. The results indicate significant alterations in the thermal properties as a result of the electrospinning process. The glass transition temperature in the PAN nanofibres showed a reduction of approximately 3–5 % compared to virgin PAN, suggesting a decrease in thermal stability. The melting temperature and heat capacity also showed notable changes, with the heat capacity experiencing a 42 % reduction in the nanofibres. These variations in thermal properties, including the early onset of solvent evaporation in nanofibres, underscore the impact of electrospinning on the thermal behaviour. These findings are vital for applications where PAN nanofibres are exposed to thermal conditions, informing material selection and processing techniques in industries such as filtration, drug delivery, and protective clothing.

ACKNOWLEDGEMENTS

The research/publication has been supported by the Doctoral Grant programme of Riga Technical University.

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