

COMPARATIVE DSC ANALYSIS OF VIRGIN AND NANOFIBER MATS OF PA6

Sai-Pavan Kanukuntla, Jaymin-Vrajlal Sanchaniya, Vitalijs Beresnevics

Riga Technical University, Latvia

sai-pavan.kanukuntla@rtu.lv, jaymin.sanchaniya@rtu.lv, vitalijs.beresnevics@rtu.lv

Abstract. Differential scanning calorimetry (DSC) is a useful technique for analysing the thermal behaviour of materials by measuring the heat transferred through a sample during temperature fluctuations. For polymers, understanding their thermal characteristics is crucial to determine their process capability, mechanical properties, stability at high temperatures, and suitability for specific applications. In this context, the electrospinning process involves heating polymers and subjecting them to high voltage, leading to changes in their thermal properties. Therefore, it is essential to identify these modifications to determine the thermal conductivity, stability, and temperature management of the nanofiber for specific applications. This study focuses on the analysis of polyamide (PA6) nanofibers produced by electrospinning using DSC and compares them to virgin PA6 to identify significant changes in thermal properties. The PA6 nanofibers were prepared by electrospinning PA6 polymer and collecting on a rotating drum at a needle tip of 20 cm to the collector centre distance. For comparison of thermal properties, the same virgin PA6 was used for DSC testing from which nanofibers were produced. The results show that the nanofiber mat's glass transition temperature increased by 3.2%, while the melting temperature decreased by 0.7%. Furthermore, the delta Cp (change in specific heat capacity) of the nanofiber mat was enhanced by 96%, and its thermal heat capacity and crystallinity increased by 16%. Therefore, this study provides insights into the alterations in the thermal characteristics of the nanofiber mat created by electrospinning.

Keywords: DSC, nanofibers, polyamide, thermal properties, polymers.

Introduction

Differential scanning calorimetry (DSC) is a method for measuring the heat flow through a sample while its temperature fluctuates [1]. It is frequently used in material science, chemistry, and physics to examine the thermal characteristics of a variety of materials, including polymers and different forms of polymeric materials, including nano fibers/materials [2-4].

Electrospinning is a commonly used technique for the manufacture of nanofibers in the realm of nanofiber applications [5-7]. With the help of the electrospinning process, nanofibers can be produced with enhanced physical characteristics [8-10]. During the electrospinning process, a polymer solution or melt is subjected to a high voltage, resulting in the creation of an electrically charged jet [11]. This jet is then attracted to a collector, where it condenses into a fibrous mat or film [12]. The electrospinning procedure can alter the polymer's thermal characteristics [13], including its melting point [14], glass transition temperature [15; 16], and thermal conductivity [17].

Due to its mechanical qualities and biocompatibility, polyamide 6 (PA6) is a thermoplastic polymer that is extensively employed in the manufacturing of nanofibers [18]. Electrospinning has been demonstrated to be an efficient approach for generating PA6 nanofiber with enhanced mechanical and thermal characteristics [19; 20]. Unfortunately, the impact of electrospinning on the thermal characteristics of PA6 nanofibers is little known.

In this study, PA6 nanofibers were produced by electrospinning, and their thermal behaviour was evaluated using DSC. The DSC study findings were compared to those of pure PA6 to determine any notable changes in thermal characteristics resulting from the electrospinning procedure. The thermal properties of electrospun PA6 nanofibers, including their glass transition temperature, melting point, and heat capacity, were examined.

The findings of this work will give insight in the thermal behaviour of electrospun PA6 nanofibers, therefore enhancing their performance in a variety of applications, including filtration [21-23], drug administration [24; 25], and tissue engineering [26; 27]. In addition, the research can contribute to fundamental knowledge of the electrospinning process and its impact on the thermal characteristics of PA6 nanofiber mats.

Materials and methods

PA6 (CAS: 25038-54-4, PA6 standard density: 1.06-1.16 g·cm⁻³) and formic acid (CAS: 64-18-6) are chemicals supplied from Sigma-Aldrich (Germany). PA6 solution was created by adding 10% wt/wt of PA6 granules to the solvent formic acid and stirring it for 5 hours at +40 °C and 400 rpm with a

magnetic stirrer (Thermo Scientific™ Cimarec + TM Stirring Hotplates Series, USA). To remove air bubbles and stabilise the solutions, they were left at room temperature for one hour.

Electrospinning solution at $+22 \pm 1$ °C using the Fisherbrand™ Single Syringe Pump, a needle-based electrospinning equipment, Danbury, CT 06811, United States, and a flat plate collector produced composite mats. Utilized were a 3-mL plastic syringe and a 27G needle. The electrospinning parameters were 25 kV voltage, $0.5 \text{ mL}\cdot\text{h}^{-1}$ flow rate, and 20 cm between the syringe tip and the collector plate's centre. Aluminium foil was put to the plate to collect nanofibers. Before performing any tests or characterizations, all samples were held for 48 hours at a temperature of $+22.1 \pm 1$ °C and relative humidity of less than 60% [1].

Differential scanning calorimetry (DSC) measurements were conducted with DSC 214 Polyma (Netzsch, Germany) in nitrogen (N₂, CID 947) atmosphere at a flow rate of $30 \text{ mL}\cdot\text{min}^{-1}$. The nanofibers and pure PA6 were cut precisely, placed in the crucible, and stored for 48 hours at $+22 \pm 1$ °C and relative humidity of less than 60%. The samples were heated from -40 °C to $+230$ °C at a rate of $15 \text{ K}\cdot\text{min}^{-1}$. The average mass was determined using laboratory scales KERN ABT 100-5NM (Germany; max till 101 g, discreteness 0.000001 g) [1].

Specific heat capacity means the amount of heat required to increase the temperature of one gramme of mass by one degree Celsius. Specific heat capacity (C_p) may be expressed as follows using DSC:

$$DSC = m * C_p * sensitivity * HR, \quad (1)$$

where m – sample mass;

C_p – specific heat capacity;

HR – heating rate.

DSC may be used to compute (according to ASTM E 1269 or the ratio technique) the specific heat capacity of a material based on three measurements (baseline, sapphire, and sample).

Results and discussion

Fig. 1 displays the DSC graphs of virgin PA6 and the nanofiber mat during second heating. The moisture content of virgin PA6 and the formic acid employed in the electrospinning method to create the nanofiber mat evaporated during the first heating cycle, and a second heating cycle was investigated to determine the thermal characteristics.

A polymer specimen undergoing DSC analysis is generally heated at a consistent pace from a low temperature to a high temperature $+230$ °C. The polymer experiences thermal changes during the initial heating cycle, which can considerably impact its thermal behaviour. During the initial heating cycle, the thermal history of the sample is imprinted, and this might influence the findings of DSC analysis.

Typically, a second heating cycle is done after the initial heating cycle has been finished to address this issue. The second heating cycle allows for the elimination of thermal history effects, giving the experiment a new start. The polymer suffers thermal changes; however, the thermal history effects are eliminated by heating the sample from a low temperature to a high temperature again.

The second reason, why the second heating cycle is necessary for the DSC study of polymers (Fig. 1), is that it permits the controlled detection of thermal transitions. The polymer may experience thermal breakdown or crosslinking during the initial heating cycle, resulting in permanent alterations to its thermal performance. These permanent modifications might impact the accuracy and repeatability of DSC analysis findings.

The thermal characteristics of PA6 granules and the nanofiber mat are displayed in Table 1. The glass transition temperatures of virgin PA6 and PA6 nanofiber mat were $+55.3$ °C and $+57.1$ °C, respectively. Both materials melted at around $+223.5$ °C and $+221.8$ °C. Delta C_p change in the specific heat capacity at glass transition temperature was $0.155 \text{ J}\cdot(\text{g}\cdot\text{K})^{-1}$ for virgin PA6 granules and $0.320 \text{ J}\cdot(\text{g}\cdot\text{K})^{-1}$ for the PA6 nanofiber mat. Crystallinity and thermal heat capacity both increased by 16% in the PA6 nanofiber mat compared to PA6 granules; the values increased from $69.01 \text{ J}\cdot\text{g}^{-1}$ to $80.33 \text{ J}\cdot\text{g}^{-1}$ for heat capacity, and crystallinity changed from 36.50% to 42.34%, respectively.

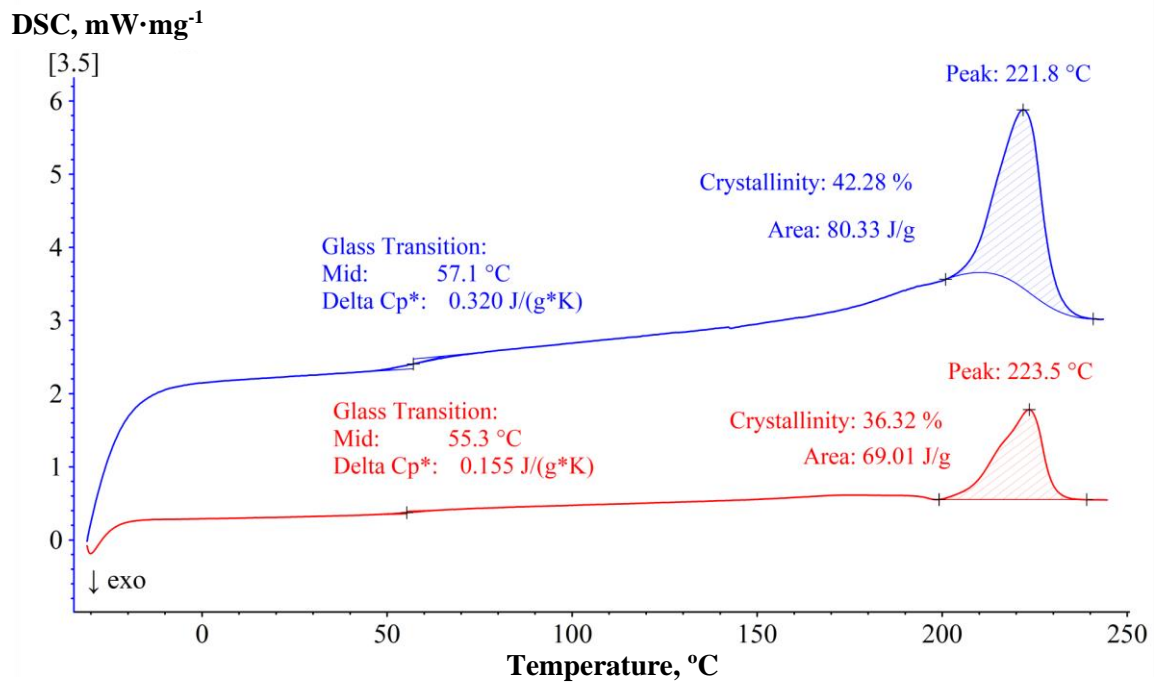


Fig. 1. DSC results of second heating of virgin PA6 granules and PA6 nanofiber mat

Table 1

Thermal properties of virgin PA6 granules and PA6 nanofiber mat

Material	T_g , °C	T_m , °C	Delta C_p , $J \cdot (g \cdot K)^{-1}$	H , $J \cdot g^{-1}$	X_c , %
Virgin PA6 granules	55.3	223.5	0.155	69.01	36.32
PA6 nanofiber mat	57.1	221.8	0.320	80.33	42.28

DSC examination of pure polyamide pellets often exhibits a melting peak, which corresponds to the energy required to break the intermolecular interactions that hold the polymer chains together in a crystalline lattice. Most polyamide nanofibers have a higher ratio of the surface area to volume than pure polyamide, which changes how they behave when heated. Particularly, compared to pure polyamide, polyamide nanofibers can display a greater degree of crystallinity, a narrower melting temperature variation, and a higher glass transition temperature [28].

Higher crystallinity of polyamide nanofibers is a result of their nanofiber diameter, which permits improved molecular orientation and packing efficiency. Due to the existence of smaller crystallites in polyamide nanofibers, which melt at lower temperatures than the larger crystallites in pure polyamide, the melting temperature range is narrower. Due to their higher degree of crystallinity and smaller crystallite size, polyamide nanofibers have a lower melting point [28].

In summary, the improved thermal properties of PA6 nanofiber mats are due to the fact that nanofibers have a higher surface-to-volume area. PA6 nanofiber mats have enhanced thermal characteristics due to the increased surface area per unit volume of the nanofibers. The glass transition temperature and melting temperature were found to increase and decrease, respectively, as determined by DSC. Both the glass transition temperature and the melting temperature of PA6 nanofibers are affected by the degree of crystallinity.

Conclusions

The results shown in Table 1 indicated that the nanofibers fabricated from virgin PA6 have a substantial effect on their thermal characteristics. The glass transition temperature of the PA6 nanofiber mat was found to be greater than that of virgin PA6, showing that the nanofibers contribute to enhanced thermal stability. This may have important impacts for the usage of PA6 in high-temperature applications, such as in the automotive and aerospace sectors.

In addition, the thermal heat capacity and crystallinity of the PA6 nanofiber mat were greater than those of PA6 granules. The greater thermal heat capacity means that the nanofiber mat can store more thermal energy, which might affect its utility in applications requiring thermal insulation. The rise in crystallinity suggests that the nanofibers may have served as nucleation sites, so stimulating the creation of organised crystalline structures inside the material. This might enhance its mechanical qualities and increase its deformation resistance under stress.

The results indicate that the glass transition temperature of the PA6 nanofiber mat was 3.2% higher and the melting temperature was reduced by 0.7%. The nanofiber mat's delta Cp was enhanced by 96%, while its thermal heat capacity and crystallinity were also increased by 16%.

Electrospinning of virgin PA6 into nanofibers may improve the thermal characteristics and make it more suitable for use in demanding industrial applications, according to the research.

Acknowledgements

The research was supported by the Riga Technical University DAD grant and SAM grant pro-gram, project no. 2-04887, 2-04890, 2-04121 and 2-04891.

Author contributions

Conceptualization, J.V.S.; methodology, J.V.S., V.B; validation, J.V.S.; investigation, J.V.S. and S.P.K.; data curation, J.V.S.; writing – original draft preparation, J.V.S.; writing – review and editing, J.V.S. and S.P.K.; visualization, J.V.S.; funding acquisition, J.V.S. and S.P.K. All authors have read and agreed to the published version of the manuscript.

References

- [1] Lasenko I., Sanchaniya J. V., Kanukuntla S. P., Ladani Y., Viluma-Gudmona A., Kononova O., Lulis V., Tipans I., Selga T. The Mechanical Properties of Nanocomposites Reinforced with PA6 Electrospun Nanofibers. *Polymers (Basel)*, vol. 15, no. 3, 2023, DOI: 10.3390/polym15030673.
- [2] Rajhi A. A. Mechanical Characterization of Hybrid Nano-Filled Glass/Epoxy Composites. 2022. *Polymers*, vol. 14, no. 22, p. 4852, Nov. 2022, DOI: 10.3390/polym14224852.
- [3] Lulis V., Kononova O., Macanovskis A., Stonys R., Lasenko I., Krasnikovs A. Experimental investigation and modelling of the layered concrete with different concentration of short fibers in the layers. *Fibers*, vol. 9, no. 12, 2021, DOI: 10.3390/fib9120076.
- [4] Lulis V., Annamaneni K. K., Kononova O., Korjakins A., Lasenko I., Karunamoorthy R. K., Krasnikovs A. Experimental Study and Modelling on the Structural Response of Fiber Reinforced Concrete Beams. *Appl. Sci.*, vol. 12, no. 19, p. 9492, Sep. 2022, DOI: 10.3390/app12199492.
- [5] Lasenko I., Grauda D., Butkauskas D., Sanchaniya J. V., Viluma-Gudmona A., Lulis V. Testing the Physical and Mechanical Properties of Polyacrylonitrile Nanofibers Reinforced with Succinite and Silicon Dioxide Nanoparticles. *Textiles*, vol. 2, no. 1, pp. 162-173, 2022, DOI: 10.3390/textiles2010009.
- [6] Sanchaniya J.V., Kanukuntla S.P., Modappathi P., Macanovskis A. Mechanical behaviour numerical investigation of composite structure, Consisting of polymeric nanocomposite mat and textile. 21st Int. Sci. Conf. "Eng. Rural Dev". Proc., vol. 21, pp. 720-726, 2022, DOI: 10.22616/erdev.2022.21.tf225.
- [7] Viluma-Gudmona A., Lasenko I., Sanchaniya J. V., Podgornovs A. Electro-resistant biotextile development based on fiber reinforcement with nano particles. "Eng. Rural Dev", vol. 20, pp. 804-812, 2021, DOI: 10.22616/ERDev.2021.20.TF182.
- [8] Viluma-Gudmona A., Lasenko I., Sanchaniya J. V., Abdelhadi B. The amber nano fibers development prospects to expand the capabilities of textile 3D printing in the general process of fabrication methods. "Eng. Rural Dev", vol. 20, pp. 248-257, 2021, DOI: 10.22616/ERDev.2021.20.TF051.
- [9] Deitzel J. M., Kleinmeyer J., Harris D., Beck Tan N. C. The effect of processing variables on the morphology of electrospun. *Polymer (Guildf)*, vol. 42, pp. 261-272, 2001.
- [10] Grauda D., Bumbure L., Lyashenko I., Katashev A., Dekhtyar Y., Rashal I. Amber particles as living plant cell markers in flow cytometry. *Proc. Latv. Acad. Sci. Sect. B Nat. Exact, Appl. Sci.*, vol. 69, no. 3, pp. 77-81, 2015, DOI: 10.1515/prolas-2015-0011.

- [11] Wang L., Ryan A. J. Introduction to electrospinning. *Electrospinning Tissue Regen.*, pp. 3-33, 2011, DOI: 10.1533/9780857092915.1.3.
- [12] Sanchaniya J.-V., Kanukuntla S.-P., Simon S., Gerina-Ancane A. Analysis of mechanical properties of composite nanofibers constructed on rotating drum and collector plate. 21st Int. Sci. Conf. "Eng. Rural Dev". Proc., vol. 21, pp. 737-744, 2022, DOI: 10.22616/erdev.2022.21.tf227.
- [13] Selatile K., Ray S. S., Ojijo V., Sadiku R. E. Morphological, Thermal, and Mechanical Properties of Electrospun Recycled Poly(ethylene terephthalate)-g¹raphene Oxide Composite Nanofiber Membranes. *ACS Omega*, vol. 6, no. 32, pp. 21005-21015, 2021, DOI: 10.1021/acsomega.1c02578.
- [14] Arinstein A., Liu Y., Rafailovich M., Zussman E. Shifting of the melting point for semi-crystalline polymer nanofibers. *Epl*, vol. 93, no. 4, 2011, DOI: 10.1209/0295-5075/93/46001.
- [15] Nauman S., Lubineau G., Alharbi H. F. Post processing strategies for the enhancement of mechanical properties of enms (Electrospun nanofibrous membranes): A review. *Membranes (Basel)*, vol. 11, no. 1, pp. 1-38, 2021, DOI: 10.3390/membranes11010039.
- [16] Liang Y., Cheng S., Zhao J., Zhang C., Sun S., Zhou N., Qiu Y., Zhang X. Heat treatment of electrospun Polyvinylidene fluoride fibrous membrane separators for rechargeable lithium-ion batteries. *J. Power Sources*, vol. 240, pp. 204-211, 2013, DOI: 10.1016/j.jpowsour.2013.04.019.
- [17] Zeighampour F., Khoddami A., Hadadzadeh H., Ghane M. Thermal conductivity enhancement of shape-stabilized phase change nanocomposites via synergistic effects of electrospun carbon nanofiber and reduced graphite oxide nanoparticles. *J. Energy Storage*, vol. 51, no. January, p. 104521, 2022, DOI: 10.1016/j.est.2022.104521.
- [18] Gaidukovs S., Lyashenko I., Rombovska J., Gaidukova G. Application of amber filler for production of novel polyamide composite fiber. *Text. Res. J.*, vol. 86, no. 20, pp. 2127-2139, 2016, DOI: 10.1177/0040517515621130.
- [19] Yoon J. W., Park Y., Kim J., Park C. H. Multi-jet electrospinning of polystyrene/polyamide 6 blend: thermal and mechanical properties. *Fash. Text.*, vol. 4, no. 1, 2017, DOI: 10.1186/s40691-017-0090-4.
- [20] Nirmala R., Navamathavan R., El-Newehy M. H., Kim H. Y. Preparation and characterization of electrospun ultrafine polyamide-6 nanofibers. *Polym. Int.*, vol. 60, no. 10, pp. 1475-1480, 2011, DOI: 10.1002/pi.3105.
- [21] Lv D., Wang R., Tang G., Mou Z., Lei J., Han J., De Smedt S., Xiong R., Huang C. Ecofriendly Electrospun Membranes Loaded with Visible-Light-Responding Nanoparticles for Multifunctional Usages: Highly Efficient Air Filtration, Dye Scavenging, and Bactericidal Activity, *ACS Appl. Mater. Interfaces*, vol. 11, no. 13, pp. 12880-12889, 2019, DOI: 10.1021/acsmi.9b01508.
- [22] Roche R., Yalcinkaya F. Electrospun Polyacrylonitrile Nanofibrous Membranes for Point-of-Use Water and Air Cleaning. *ChemistryOpen*, vol. 8, no. 1, pp. 97-103, 2019, DOI: 10.1002/open.201800267.
- [23] Roche R., Yalcinkaya F. Incorporation of PVDF nanofibre multilayers into functional structure for filtration applications. *Nanomaterials*, vol. 8, no. 10, 2018, DOI: 10.3390/nano8100771.
- [24] Debabrata G. D., Chakrabarti G. Thermoresponsive Drug Delivery Systems. Characterization and Application. Elsevier Inc., 2018. DOI: 10.1016/B978-0-12-814029-1.00006-5.
- [25] Stack M., Parikh D., Wang H., Wang L., Xu M., Zou J., Cheng J., Wang H. Electrospun nanofibers for drug delivery. Elsevier Inc., 2018. DOI: 10.1016/B978-0-323-51270-1.00025-X.
- [26] Wang X., Ding B., Li B. Biomimetic electrospun nanofibrous structures for tissue engineering. *Mater. Today*, vol. 16, no. 6, pp. 229-241, 2013, DOI: 10.1016/j.mattod.2013.06.005.
- [27] Do A. V., Khorsand B., Geary S. M., Salem A. K. 3D Printing of Scaffolds for Tissue Regeneration Applications. *Adv. Healthc. Mater.*, vol. 4, no. 12, pp. 1742-1762, 2015, DOI: 10.1002/adhm.201500168.
- [28] Lasenko I., Sanchaniya J.V., Kanukuntla S.P., Delpouve N., Viluma-Gudmona A., Tipans I., Gobins V., Krasnikovs A. The Effect of Annealing on Mechanical and Thermal Properties of PAN Nanofiber mats. *Multidiscip. Digit. Publ. Inst.* 2023, DOI: unpublished work.