THERMAL ANALYSIS OF PRISTINE AND CAFFEINE LOADED PA 4,6 NANOFIBROUS YARNS

[1,2]Juan Pablo PÉREZ AGUILERA, [1,2]Jaroslav MIKULE, [3]Luboš BĚHÁLEK, [2]Věra JENČOVÁ, [2]David LUKÁŠ

[1]Technical University of Liberec, Faculty of Mechatronics, Informatics and Interdisciplinary studies, Liberec, Czech Republic, EU, juan.pablo.perez.aguilera@tul.cz

[2]Technical University of Liberec, Faculty of Science, Humanities and Education, Department of Chemistry, Liberec, Czech Republic, EU

[3]Technical University of Liberec, Faculty of Mechanical Engineering, Department of Engineering Technology, Liberec, Czech Republic, EU

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Abstract

This work focuses on the research and development of composite multilayered AC electrospun materials for applications in technical, medical, and bioengineering fields. It investigates the effects of AC electrospinning on the thermal properties and morphology of Polyamide 4,6 (PA 4,6), both in its base pellet form and as nanofibrous materials with and without caffeine as a model drug. The high voltage applied during AC electrospinning can influence the crystallinity and thermal behavior of the material. Differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA) were employed to analyze thermal transitions, crystallinity, stability, degradation profiles, and as a tool to properly asses the loading of the model drug. Scanning electron microscopy (SEM) was used to examine fiber morphology and material structure. DSC analysis revealed that, compared to PA 4,6 pellets, the pristine nanofibrous material exhibited a decrease in normalized melting enthalpy and a slight increase in melting temperature, while the caffeine-loaded nanofibrous material showed an increase in normalized melting enthalpy and a decrease in melting temperature. TGA confirmed the proper loading of the model drug with initial weight loss corresponding to the PA 4,6:caffeine ratio of 8:2 in solution. The inflection point decreased for both electrospun materials when compared to the pellets. SEM analysis showed smooth, randomly oriented nanofibers, with a reduction in fiber diameter for the caffeine-loaded sample. This study provides clear insights into the effects of AC electrospinning and the addition of a model drug on the thermal properties and fiber morphology of PA 4,6. This serves as a solid base for the next steps in analyzing the release profiles of biologically active substances from composite/layered AC electrospun nanofibrous materials.

Keywords: AC electrospinning, polyamide 4,6, nanofibrous materials, caffeine-loaded nanofibers, thermal properties, nanofibrous yarns, fiber morphology, drug loading.

1. INTRODUCTION

The increasing demand for advanced materials with tailored properties has driven significant research into nanofibrous yarns, particularly those based on polyamide polymers. Among these, polyamide 4,6 (PA 4,6) has garnered attention due to its excellent mechanical strength, thermal stability, and chemical resistance. The unique morphology of nanofibers, characterized by a high surface area-to-volume ratio, enhances their potential applications in various fields, including textiles, filtration, and biomedical engineering [1].

Incorporating bioactive compounds into polymer matrices is a promising strategy to impart additional functionalities to nanofibrous structures [2]. Caffeine has been selected as a model drug for this study due to

its well-documented pharmacological properties and its suitability for investigating drug release profiles [3]. Loading caffeine into PA 4,6 nanofibrous yarns could provide valuable insights into the mechanisms of drug release and the influence of fiber morphology on the release kinetics, which are critical for developing effective drug delivery systems.

Thermal analysis plays a crucial role in understanding the thermal behavior of polymeric materials and their composites. Techniques such as differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA) allow for the evaluation of thermal transitions and stability, which are essential for assessing the performance of nanofibrous yarns under varying temperature conditions [4], [5]. This study aims to investigate the thermal properties of pristine and caffeine-loaded PA 4,6 nanofibrous yarns through comprehensive thermal analysis.

By elucidating the effects of caffeine loading on the thermal behavior of PA 4,6 nanofibers, this research seeks to contribute valuable insights into the design and optimization of multifunctional polymeric materials. Understanding these interactions will pave the way for developing innovative applications that leverage both the mechanical properties of PA 4,6 and the bioactive potential of caffeine as a model drug for future studies [6].

2. MATERIALS AND METHODS

2.1 Solution preparation

Polyamide 4,6 Stanyl® (PA 4,6) from Envalior was used as received for the unprocessed samples. For the non-functionalized solution, 14% wt PA 4,6 was dissolved in a 1:1 mixture of glacial acetic acid and formic acid (PENTA chemicals) and magnetically stirred for 24 hours. In the functionalized solution, 3.5% wt caffeine (C0750, Sigma-Aldrich) was added after dissolving the polymer, and the mixture was stirred under the same conditions.

2.2 AC Electrospinning

The solutions were electrospun to create 100% nanofibrous yarns from PA 4,6 (Pristine NY) and from PA 4,6 functionalized with caffeine (Caffeine NY). The AC electrospinning was carried out using the set-up described in patent number 2022-370 [7] as depicted in **Figure 1**. The parameters for the electrospinning process are described in **Table 1**.

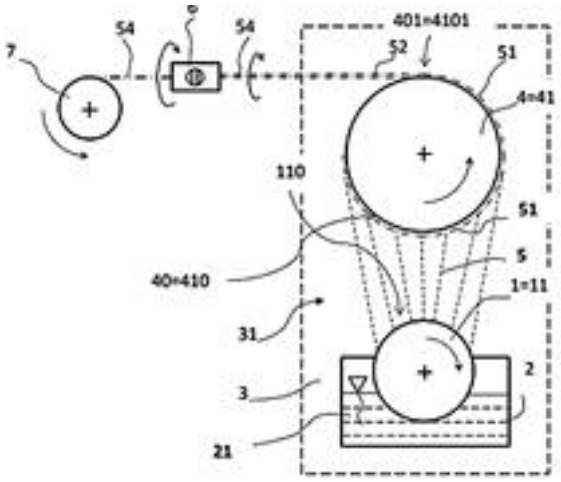


Figure 1 AC electrospinning device for the fabrication of 100% nanofibrous yarns utilizing a rotating disk electrode, rotating drum collector, a twirling device for yarn formation and a bobbin winder *[7]*

Table 1 AC electrospinning parameters for the production of Pristine NY and Caffeine NY.

Sample	Voltage (kV)	Frequency (Hz)	Winding speed (rpm)	Twirling speed (rpm)	Collector speed (rpm)	Ambient temperature (°C)	Relative humidity (%)
Pristine NY	40	100	0.85	10000	0.8	24	65
Caffeine NY	40	100	0.72	8000	0.7	25	55-60

2.3 Differential Scanning Calorimetry (DSC)

DSC is a thermal analysis technique that measures the heat flow into or out of a sample as a function of temperature or time. This technique is selected as it allows to analyze the thermal properties of the polymer materials being studied. More specifically their melting temperatures (Tm and Tc), specific heat capacity (Cp), purity, crystallinity, thermal conductivity, and thermal stability. DSC works by comparing the heat flow of a sample to that of a reference material, which is typically a thermally stable material. The difference in heat flow between the sample and the reference material indicates changes of state within the sample [8], [9], [10].

2.4 Thermogravimetric Analysis (TGA)

TGA is a thermal analysis technique that measures the change in mass of a sample as it is heated or cooled in a controlled environment. This technique provides invaluable insights into the thermal stability, composition, moisture content, and decomposition kinetics of materials [11], [12].

2.5 Scanning Electron Microscopy (SEM)

The SEM images were taken with a VEGA3 SBU – EasyProbe microscope, Tescan (Czech Republic) equipped with a Tungsten heated cathode as the electron gun and the secondary electron detector Everhart-Thornley type (YAG Crystal). The images were taken at High Vacuum Mode (SE) at a resolution of 8 nm at 15 kV.

3. RESULTS

The AC electrospinning set-up described in the patent successfully produced 100% nanofibrous yarns from PA 4,6 solutions, both with and without caffeine as an additive (at an 8:2 ratio in the dry material). The following section presents the results of the thermal and morphological analyses conducted on these samples.

3.1 Differential Scanning Calorimetry (DSC)

Table 2 DSC results for PA 4.6 in pellet form, pure caffeine, PA 4.6 pristine NY, and PA 4.6:Caffeine NY.

Sample	T_m N-Enthalpy 1(J/g)	T_m Peak 1(°C)	T_m N-Enthalpy 2(J/g)	T_m Peak 2(°C)
PA 4,6 Pellet	-	-	81.8 ± 2.5	288.3 ± 2.1
Caffeine	18.9	160.8	98.5	235.2
Pristine NY	-	-	65.8 ± 12.3	289.4 ± 0.9
Caffeine NY	26.4 ± 9.7	220.6 ± 11.7	100.2 ± 5.7	283.5 ± 1.7

Table 2 compares the thermal properties of the Pristine NY and Caffeine NY with the PA 4,6 pellets. The melting temperature of Pristine NY (289.4°C) is slightly higher than that of the pellet form by 1.1°C, suggesting that the electrospinning process may have enhanced molecular alignment in the nanofibers. However, the normalized enthalpy of Pristine NY decreases to 65.8 J/g, a 19.6% reduction compared to the pellet. This indicates a slight loss in crystallinity during electrospinning, as fewer polymer chains participate in the crystalline phase in the nanofibers.

For Caffeine NY, the melting temperature decreases to 283.5°C, 4.8°C lower than the pellet. This suggests that the addition of caffeine disrupts the molecular alignment of PA 4,6 in the nanofibers. Interestingly, the enthalpy of Caffeine NY's second thermal transition increases to 100.2 J/g, which is 22.5% higher than that of the pellet. This suggests that, despite the lower melting temperature, the overall crystallinity of the caffeine-loaded nanofibers may be higher than that of the pure polymer. This could be attributed to the interaction between caffeine and the polymer matrix, which may promote more orderly packing of polymer chains.

Moreover, Caffeine NY displays two distinct thermal peaks: the first at 220.6°C, corresponding to caffeine, and the second at 283.5°C, representing PA 4,6. The shift in caffeine's melting point from its pure form (160.8°C and 235.2°C) suggests a significant interaction between caffeine and the polymer matrix, resulting in an increase in caffeine's melting temperature. The normalized enthalpy of the caffeine peak in Caffeine NY (26.4 J/g) is higher than that of pure caffeine (18.9 J/g), indicating effective integration of caffeine into the nanofiber matrix. This earlier thermal transition of caffeine suggests that it could be released at lower temperatures, while PA 4,6 remains structurally intact until its higher melting point. This has important implications for drug release applications, as it demonstrates the potential for controlled release of caffeine while maintaining the stability of the polymer matrix.

3.2 Thermogravimetric Analysis (TGA)

Table 3 illustrates the thermal degradation behavior of PA 4,6 in its pellet form, with the degradation onset (TD,2%, or temperature at 2% weight loss) occurring at 380.4°C. The polymer exhibits high thermal stability, with midpoint and inflection point temperatures at 431°C and 436.9°C, respectively, indicating a gradual degradation at elevated temperatures. In contrast, caffeine degrades much earlier, with a TD,2% of 218.2°C, and significantly lower midpoint (293°C) and inflection point (311.2°C) temperatures. This highlights the thermal instability of pure caffeine compared to PA 4,6.

For the nanofibrous yarn without caffeine (Pristine NY), the thermal stability is slightly reduced, with a TD,2% of 365°C, compared to 380.4°C for the PA 4,6 pellets. This reduction can be attributed to the higher surface area of the nanofibers, which makes them more susceptible to thermal degradation. The midpoint and inflection point temperatures for the Pristine NY are also slightly lower (414°C and 419°C), further reflecting its slightly reduced stability compared to the pellet form.

Table 3 Pure PA 4.6 pellet, pure caffeine, PA 4.6 pristine NY, and PA 4.6:Caffeine NY

Sample	$T_{D,2\%}$ (°C)	$T_{midpoint}$ (°C)	$T_{infl.point}$ (°C)
PA 4,6 Pellet	380.4 ± 0.9	431 ± 2.3	436.9 ± 3.4
Caffeine	218.2 ± 3.5	293 ± 6.6	311.2 ± 6.9
PA 4.6 Pristine NY	365 ± 10.1	414 ± 3.5	419 ± 2.6

Sample	$T^*_{midpoint}$ (°C)	$T^*_{infl.point}$ (°C)	$T_{midpoint}$ (°C)	$T_{infl.point}$ (°C)	First step wt loss [%]
PA 4.6:Caffeine NY	253 ± 6.6	260.7 ± 6.8	410 ± 3.5	415.7 ± 1.5	23.2 ± 0.5

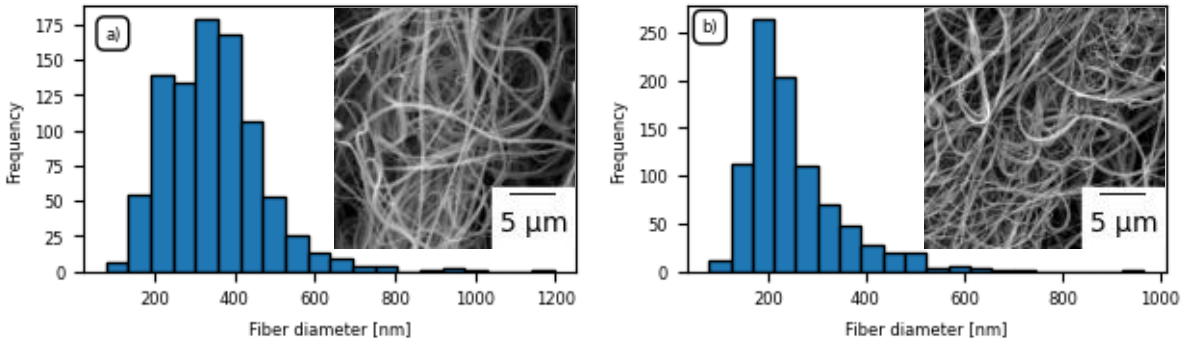
In the case of the caffeine-loaded nanoyarn (Caffeine NY), the first-step weight loss of 23.2% aligns well with the intended 20% caffeine loading, confirming successful caffeine incorporation. The first degradation step, with a Tmidpoint of 253°C and a Tinfl.point of 260.7°C, corresponds to the degradation of caffeine, consistent with its lower thermal stability. The second degradation step (Tmidpoint: 410°C, Tinfl.point: 415.7°C) is associated with the degradation of PA 4,6. These values are slightly lower than those of the pristine nanofibers, indicating that the addition of caffeine impacts the polymer's thermal stability, likely due to interactions between caffeine and the polymer matrix.

3.3 Scanning Electron Microscopy (SEM)

Figure 1 clearly shows that the addition of caffeine results in a significant reduction in the average fiber diameter, from 347 nm in the pristine nanoyarn to 251 nm in the caffeine-loaded nanoyarn, a decrease of approximately 28%. This indicates that caffeine influences the electrospinning process, leading to the production of thinner fibers. Although there is some variability in fiber diameter, the standard deviations suggest that the caffeine-loaded nanoyarn (±98 nm) has a more consistent fiber distribution compared to the pristine nanoyarn (±125 nm). This points to caffeine possibly promoting more uniform fiber formation during electrospinning, even as the average diameter decreases.

One explanation for the reduction in fiber diameter is that caffeine may alter the viscosity of the PA 4,6 solution. Typically, lower viscosity solutions tend to yield thinner fibers during electrospinning. If caffeine reduces the overall solution viscosity, this could account for the smaller fiber diameter observed. Additionally, caffeine may affect the electrical properties of the polymer solution, as changes in conductivity can influence the stretching and elongation of the electrospun jet, leading to finer fibers. The interaction between PA 4,6 and caffeine might also induce phase separation or alter polymer chain interactions, contributing to the observed differences in fiber formation and size.

The caffeine-loaded nanoyarn displayed thinner fibers, as seen in **Figure 1**, which could have several implications. Thinner fibers result in a higher surface area-to-volume ratio, potentially advantageous for applications like drug delivery, where increased surface area may enhance drug release or interaction with biological environments. A reduction in fiber diameter might also impact the mechanical strength and flexibility of the nanoyarn. Thinner fibers can sometimes reduce mechanical robustness, but this will depend on how caffeine affects the crystallinity and overall fiber structure.



Sample	Average [nm]	St. deviation [nm]
Pristine NY	347	125
Caffeine NY	251	98

Figure 2 Fiber diameter histogram and SEM image for a) Pristine NY and b) Caffeine NY

4. CONCLUSION

The custom AC electrospinning setup successfully produced PA 4,6 nanofibrous yarns, both in pristine form and with caffeine as an additive. The DSC analysis showed that the electrospinning process slightly increased the melting temperature of the pristine nanoyarn, suggesting enhanced molecular alignment. However, the reduction in enthalpy values indicates a decrease in crystallinity, likely caused by the electrospinning process itself. For the caffeine-loaded nanoyarn, DSC revealed a lower melting temperature of PA 4,6, which points to some disruption in the polymer's crystalline structure. Despite this, the increased enthalpy suggests that caffeine may promote a secondary crystalline phase or improve the overall stability of the nanofibers. The two

distinct thermal transitions observed for caffeine in the nanoyarn demonstrate its potential for controlled drug release, with caffeine melting at a lower temperature than the PA 4,6 matrix.

TGA confirmed the successful incorporation of caffeine into the nanofibers, with a degradation profile reflecting both caffeine and PA 4,6. The addition of caffeine slightly reduced the thermal stability of the nanoyarn compared to pristine PA 4,6. This decrease in stability is likely due to the interaction between caffeine and the polymer matrix. Finally, SEM revealed that caffeine loading significantly impacted the fiber morphology, reducing the average fiber diameter and leading to thinner, more uniformly distributed fibers. This reduction in fiber size could enhance surface-related properties, such as drug release, while potentially affecting the mechanical and thermal behavior of the nanoyarn. The observed changes suggest that caffeine influences the electrospinning process, likely through modifications to the viscosity, conductivity, or interaction with the polymer solution. These findings provide a comprehensive understanding of the thermal and morphological behavior of PA 4,6 nanofibers with caffeine. This foundation is valuable for future research on drug release mechanisms and the thermal performance of nanofibrous materials.

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