

New solvent for polyamides and its application to the electrospinning of polyamides 11 and 12

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Abstract

Polyamides with long hydrocarbon chains, e.g. PA11 and PA12, are generally dissolved in phenolic or fluoric solvents that prevent these polymers from being electrospun and used in many applications because of their high boiling point and/or prohibitive cost. We demonstrate that a mixture of formic acid and dichloromethane can lead to the dissolution of various polyamides enabling their subsequent electrospinning. Nanofibers and nanoribbons of 130 nm and greater in average diameter were obtained and characterized using scanning electron microscopy and Raman spectroscopy.

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1. Introduction

Polyamide-11 (PA11) is one of the few polymers in existence that can be obtained from a “green” raw material, castor beans [1]. Given the predicted oil and natural gas shortages [2,3], we foresee PA11 to have a promising future in a growing range of applications. PA11 nanofibers could find applications in water filters, textiles and sound absorber materials. In general nanofibers in the environmental (filtration), biomedical, energy storage, and electronic fields [4]. Biomedical applications are the most sought after, especially for wound dressing, tissue scaffolds and drug delivery [5–7]. Because of their ease of processing and wide use in textiles and fiber production, many polyamides have been electrospun [7–17]. Most of them had a short hydrocarbon chain and would dissolve in pure formic acid (FA). The difficulty with polyamides with longer hydrocarbon chains like PA11 is that they do not dissolve in FA. These polymers are actually resistant to most

commonly used solvents, including strong mineral acids, organic acids and strong oxidizing agents. Manufacturers report a solvating effect, i.e. not necessarily leading to complete dissolution, with formic acid, phenols and some fluorochemicals. In fact, the remarkable chemical inertness of these polymers explains their use in highly corrosive environments (gas and oil pipelines, especially offshore pipelines in the case of PA11). While *m*-cresol can dissolve polyamides, the high boiling point makes electrospinning impossible, at least when employing a standard solvent evaporation method (coagulation in a liquid could be an alternative). Stephens et al., who studied the electrospinning of PA12, produced fibers, but had to use 1,1,1,3,3,3-hexafluoro-2-propanol, a very expensive and flammable solvent that prevents this process from any industrial application [18]. Li et al. were able to electrospin a terpolymer of nylon 6,6,6,1010 (obtained by copolymerization of nylon species) using 2,2,2-trifluoroethanol [13]. However, we were unable to dissolve PA11 or PA12 in this solvent.

The objective of this work was to find a solvent that would dissolve PA11 and PA12, would satisfy the electrospinning requirements (low boiling point) and be economically viable. Because of the amphiphilic nature of PA11, our idea was to

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combine hydrophilic and hydrophobic solvents. In this article, we demonstrate that a solution of FA and dichloromethane (DCM), a low boiling point and inexpensive solvent, was able to dissolve all the polyamide polymers tested and that the solution could be used to electrospin nanofibers of controlled diameter and morphology.

2. Experimental

2.1. Materials

PA11 (Rilsan[®], BESVOA grade) and PA12 (Rilsan[®], AESNO grade) were obtained from Arkema Inc. Their specific gravities were 1.02 and 1.05, respectively. In addition, a large number of Nylon[®] polymers were tested to confirm the efficiency of the solvent. For this purpose, a “Nylon kit” containing Nylon[®] 6, 6/6, 6/9, 6/10, 6/12, 11, 12 and 6(3)T poly(trimethyl hexamethylene terephthalamide) was purchased from Scientific Polymer Products Inc. Formic acid (88 vol.%) and dichloromethane (99.7%) were purchased from Mallinckroft and Alfa Aesar, respectively.

2.2. Equipment

A Nanofiber Electrospinning Unit (NEU from Kato) was used to produce the nanofibers, which were electrospun under various voltages ranging from 7.5 kV to 20 kV at spinning distances ranging from 5 cm to 15 cm in a horizontal syringe configuration. The syringe pump speed was adjusted between 20 and 30 $\mu\text{l}/\text{min}$. The target was either a stationary copper plate or a rotating drum covered with an aluminium foil.

Scanning Electron Microscopy (SEM) was performed using a Zeiss Supra VP-50 field emission SEM. Images were

collected using an In-lens detector at 1–2 kV with a working distance of ~ 4 mm. The low voltage allowed for direct imaging of the nanofibers on the aluminium foil substrate they were electrospun onto without applying a conductive coating. The images were analyzed and the fiber and ribbon diameters were measured using Adobe Acrobat 8.0.

Raman spectra were acquired using a Renishaw 1000/2000 Raman micro-spectrometer (1800 l/mm grating) in back-scattering geometry. The excitation source was a diode laser (785 nm) focused through a 50 \times objective to a spot size of approximately 2 μm , giving a power of 2 mW. All spectra were collected with one accumulation of 30 s. The measured spectra were analyzed using Wire 2.0 software from Renishaw.

3. Results and discussion

Despite the large number of solvent combinations tested, one hydrophilic (e.g. acetic, formic, nitric, sulfuric and

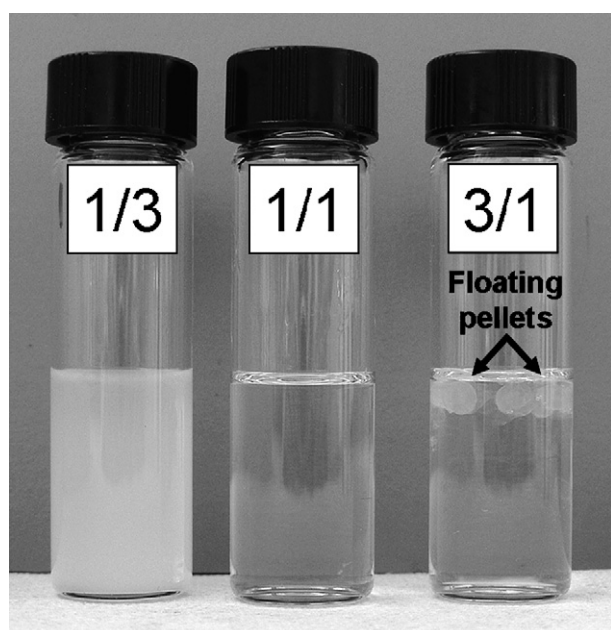


Fig. 1. Vials containing 4 ml FA/DCM at different volume ratios with PA11 pellets (100 mg) after 45 min of sonication.

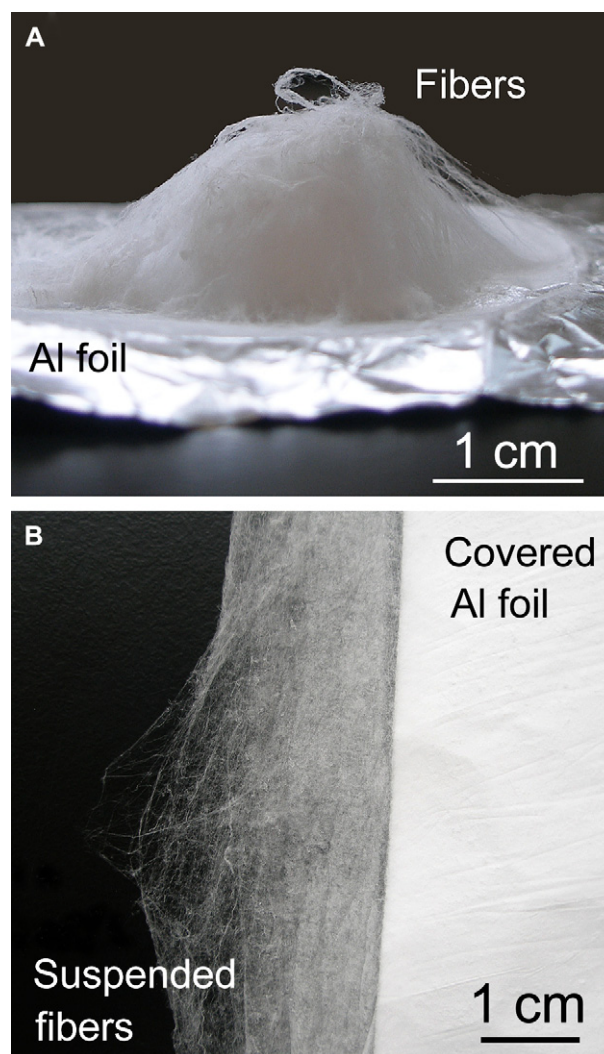


Fig. 2. PA11 electrospun nanofiber mats of 5 wt.% in FA/DCM (1/1); electrospinning performed (A) on a static collection plate for 10 min; the total fibers' length is about 70 km and (B) on a rotating drum for 1 h (total surface covered: 20 \times 30 cm Al foil) showing fiber collection on the aluminium foil. Other fibers, dangling off the aluminium foil, allow the fiber mat to be observed.

hydrochloric acids), the other hydrophobic (e.g. tetrahydrofuran, dichlorobenzene, dichloromethane and toluene), only a combination of FA and DCM led to the dissolution of PA11 pellets. Fig. 1 shows 3 vials containing FA and DCM at different volume ratios and the same amount of PA11 pellets. The vials were bath-sonicated for 45 min. The 1/3 FA/DCM ratio leads to a cloudy suspension indicating a poor solubility. In the 3/1 ratio solution, the PA11 pellets are almost unchanged, except some swelling. However, the 1/1 ratio solution appears transparent and is stable over time, indicating a complete dissolution of the PA11 pellets. Additional tests were performed on different Nylon[®] polymers to ensure that the observed dissolution was not specific to the Rilsan[®] polyamides. While Nylon[®] 6, 6/6, 6/9, 6/10, 6/12 and 6(3)T would dissolve in both pure FA and FA/DCM (1/1), Nylon 11 and 12 would only dissolve in FA/DCM (1/1). Since all the polyamides tested (Rilsan[®] and Nylon[®]) were successfully dissolved and given their significant structural differences, we conclude that the combination of FA and DCM could be a universal solvent for the whole polyamide family.

In order to understand better the dissolution mechanism, Nylon 6 has been dissolved in different volume ratios of FA/DCM. Interestingly, while pure FA to 3/2 (FA/DCM) volume ratio mixtures led to rapid dissolution of the pellets, higher

ratios (including 1/1) did not dissolve the pellets. Because the hydrocarbon chain is shorter in the case of Nylon 6 compared to PA11, a higher concentration of FA is needed. This result suggests that to maximize the solubility of polyamides, the DCM content should increase with the length of the hydrocarbon chains. Note that the Nylon 6 pellets dissolved faster in the 3/2 (FA/DCM) solution than in pure FA, confirming the efficiency of this solvent. In this optimized solvent combination (1/1 ratio), it was possible to dissolve PA11 at a concentration as high as 20 wt.%.

PA11 has been electrospun at concentrations from 2 wt.% to 5 wt.% using the 1/1 volume ratio of solvents. Fig. 2 shows two different mats of electrospun fibers obtained on a static plate and a rotating drum. The “pyramid” of fibers in Fig. 2A was formed in 10 min. (10 cm working distance, 20 kV) and had a weight of 18.0 mg. Assuming that all fibers are ribbon-shaped (see Fig. 3), we can approximate their cross-section by a rectangle of about 900×300 nm (Fig. 3 and Table 1). Given the density of PA11 (1.05 g/cc), we find that the “pyramid” contains about 70 km of fibers, that were formed at a velocity of about 110 m/s. Fig. 2B shows the same solution electrospun on a rotating drum (20 m/min). A mat of 20×30 cm was formed with a dense and thick coverage in 1 h. This high electrospinning velocity increases the potentials for commercial applications.

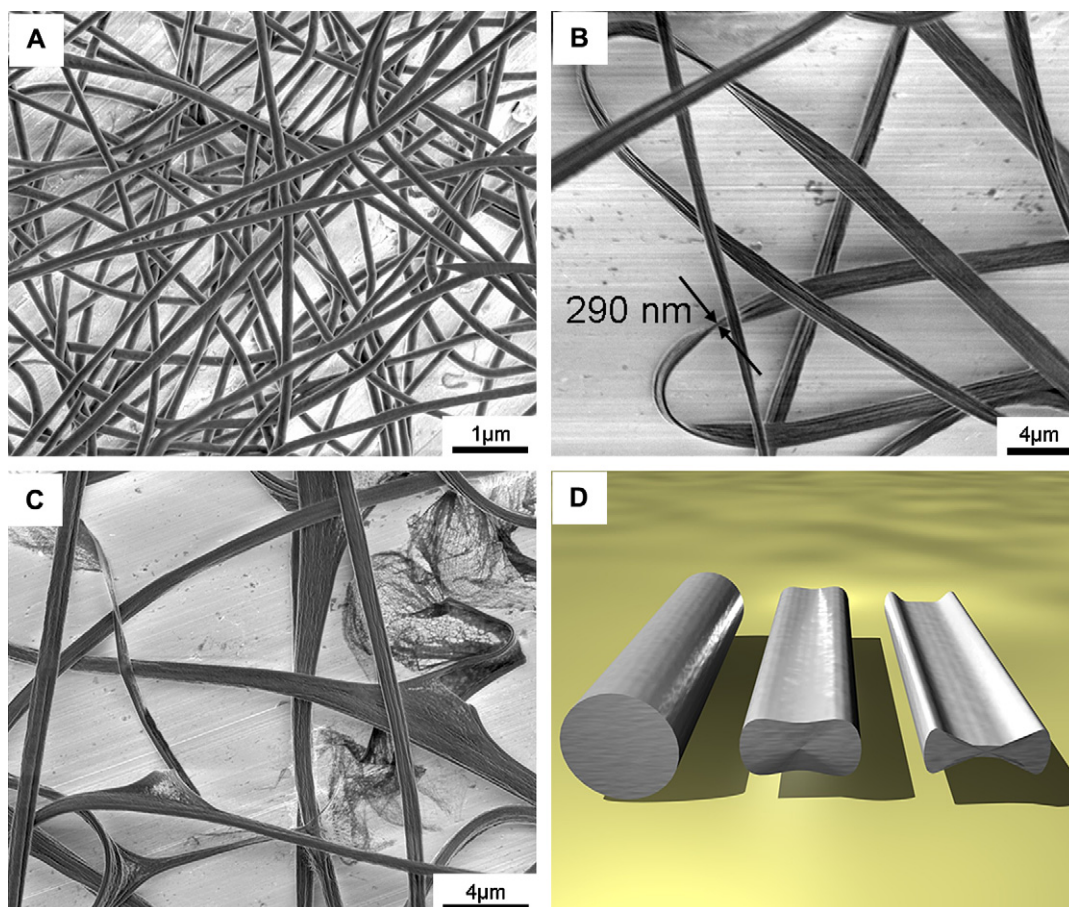


Fig. 3. SEM images of electrospun PA11 fibers of (A) 2 wt.% (cylindrical shape), (B and C) 5 wt.% (ribbon shape with ridges), and (D) a schematic of the ribbon formation mechanism (after Koombhongse et al. [19]).

Table 1
Average width of fibers and ribbons at various concentrations with accompanying statistics

PA11 concentration (wt.%)	Electrospun fiber shape	Average width (nm)	Standard deviation (nm)
2	Cylinder	133	40
3	Ribbon	259	56
4	Ribbon	539	116
5	Ribbon	877	251

SEM images of 2–5 wt.% PA11 solutions are shown in Fig. 3. While low concentrations (<2 wt.%, not shown) did not produce continuous fibers, the 2 wt.% solution (Fig. 3A) produced small (~ 130 nm) cylindrical fibers, the shape generally observed with electrospinning. By increasing the polymer concentration to 5 wt.% (Fig. 3B and C), the apparent diameter increased to ~ 1 μm and a large proportion of electrospun fibers were ribbon-shaped. A 10 wt.% solution was also tested and led to mostly ribbons but the variation in width was too large to accurately measure the average diameter (ribbons from 2 μm to 20 μm were obtained). Fig. 3C shows ribbons as well as branching and web-like structures. Note that some ribbons possess lines (ridges) that run parallel to the length of the fiber. This effect is explained by the fast evaporation of the solvent during the electrospinning process, leading to the formation of a solid skin that shrinks and collapses upon the evaporation of the remaining solvent [19,20]. This effect, as seen in schematic in Fig. 3D, is also responsible for the formation of the ribbons. First, circular fibers are formed (left). Then, due to the fast solvent evaporation, a solid skin is formed, which traps the solvent inside the fiber. The resulting slow evaporation leads the structure to collapse and form ribbon (middle and right).

Branching observed in Fig. 3C is due to instabilities of the electrospinning jet [19]. The splitting of the ribbons into nano-webs, as seen in Fig. 3C, was probably due to the fast phase separation between polymer and solvent, the solvent rich regions being apparently transformed into pores [21].

The diameter (width) of fibers electrospun at 1 kV/cm (10 cm distance between the needle and the collection plate) at varying concentrations was estimated from SEM images and can be seen in Fig. 4A. A clear linear trend (on a log scale) can be observed. This increase in average diameter is common as the concentration increases [22,23]. However, in the case of biaxial fibers like ribbons, the diameter measurements are also influenced by the tilt angle of the ribbons. This is the reason why only the largest visible width of the fibers was recorded. The results, obtained from no less than 100 fibers per sample, are compiled in Table 1.

To check if the electrospinning changed the polymer structure, the as-received PA11 pellets and electrospun fibers were compared using Raman spectroscopy. As seen in Fig. 4B, the pellets exhibit peaks at 1108 cm^{-1} and 1122 cm^{-1} corresponding to the *trans*-C–C symmetric stretching in the polymer chain of the γ conformation [18]. The contribution at ~ 1630 cm^{-1} comes from the amide I peak (C=O vibrations) and the contribution at ~ 1300 cm^{-1} comes from the amide III

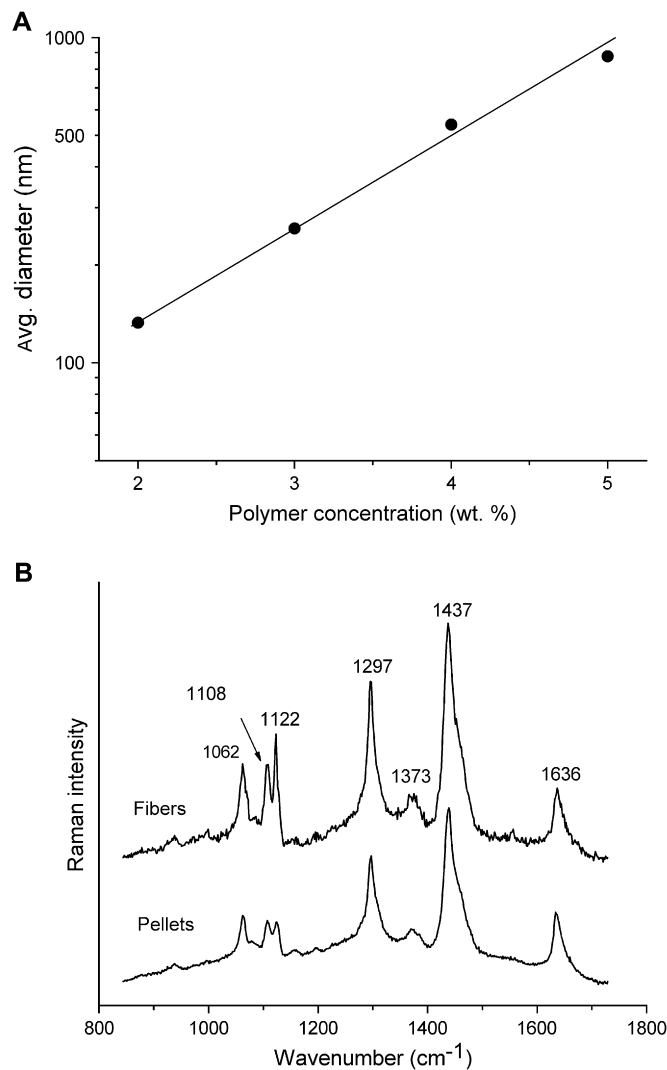


Fig. 4. Characterization of PA11. (A) Average diameter (width) of electrospun fibers and ribbons vs. polymer concentration. (B) Raman spectra of PA11 fibers and pellets.

peak (C=N/C=O vibrations). The electrospun fibers exhibit weak or no signal from the *trans*-amide conformation (1310–1350 cm^{-1} and 1440–1490 cm^{-1}), indicating that the amide region is in a *gauche*-conformation. The *trans*-hydrocarbon and *gauche*-amide conformations suggest a non-planar conformation [18]. No significant difference was found between the Raman spectra of bulk and electrospun PA11, indicating that they have the same chain conformation [18]. Note, however, that the more intense and narrow peaks in the electrospun sample (ES) at 1108 cm^{-1} and 1122 cm^{-1} indicate a higher crystallinity of the fibers.

To show that the proposed solvent may have a wide usage and is not unique for PA11, we applied the same protocol to PA12, which was dissolved in the same solvent mixture ratio and electrospun at concentrations of 1–3 wt.%. At low concentrations, the polymer was not forming continuous fibers. A 2.5 wt.% (Fig. 5B) solution of PA12 was electrospun into ribbon-shaped fibers. Raman spectra in Fig. 5A shows a higher crystallinity of the electrospun fibers compared to pellets,

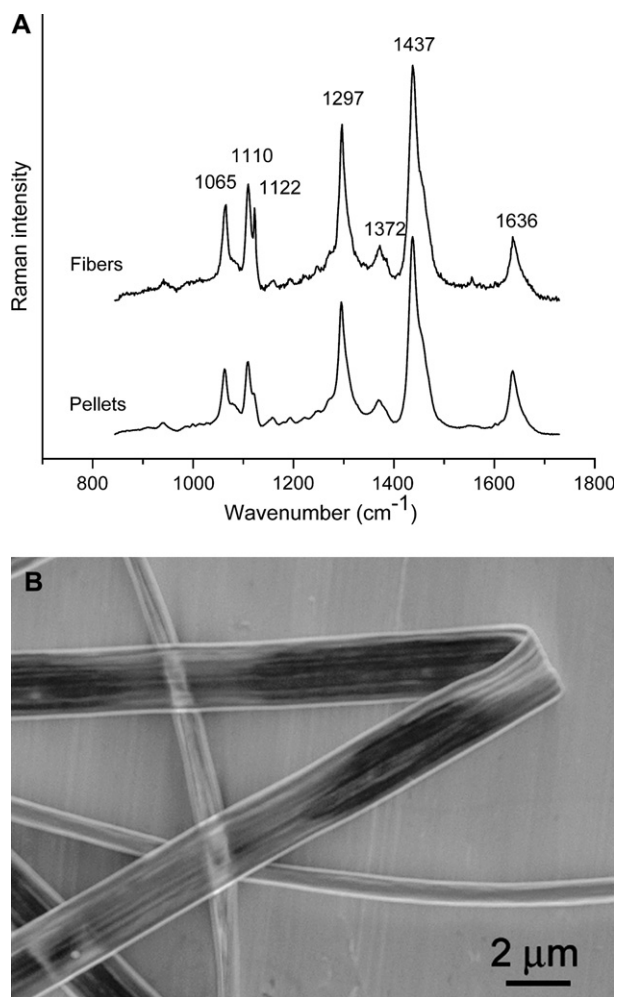


Fig. 5. Characterization of PA12. (A) Raman spectra of PA12 fibers and pellets and (B) SEM image of a PA12 fiber from a 2.5 wt.% solution.

similar to the case of PA11 (Fig. 3). The similarities are drawn between PA11 and PA12 to demonstrate that FA/DCM is an efficient solvent for polyamides and is suitable for large-scale production of nano- and microfibers due to the economics of a less expensive solvent.

4. Conclusion

It has been shown that the combination of FA and DCM is a new solvent for polyamides. PA11 and PA12, which are the most difficult polyamides to dissolve, were electrospun to form nanofibers and nanoribbons. Raman spectroscopy showed a higher crystallinity of the electrospun PA11 and PA12 nanofibers as compared to the original pellets. The

electrospun fiber diameters can be tailored from ~ 130 nm (2 wt.%) to over 800 nm (5 wt.%).

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