

Effects of some acids, bases and salts on the morphology of polyurethane nanofibres

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Received 28 May 2018; revised received and accepted 28 February 2019

The polyurethane nanofibres have been prepared by electrospinning and the effects of different types of acids, bases, and salts on nanofibre diameters within the polyurethane solutions are studied. Nanofibre diameters are measured with the SEM and the changes in nanofibre morphology are investigated by considering the electrical conductivity, viscosity, and surface tensions of dopants. Deterioration is observed in the nanofibre morphology in the presence of acid, whereas the nanofibres obtained in the presence of salt are found smoother, longer and thinner. Homogeneous, fine and smooth nanofibres are obtained from salt-doped polyurethane solutions.

Keywords: Electrical conductivity, Electrospinning, Fibre morphology, Nanofibre, Polyurethane

1 Introduction

Electrospinning is a unique approach that employs electrostatic forces to obtain nanofibres from solutions and melts of natural and synthetic polymers. The electrospun nanofibres are ultra-fine and have a controllable porous structure and much larger surface areas than other fibres obtained by conventional methods^{1,2}. This method essentially relies on the application of electrical forces to overcome the weak surface tension forces of charged polymer solutions. Compared to other fibres prepared using conventional methods, electrospun nanofibres are successfully employed in medicine, tissue engineering, composites, fuel cells, and defense and security systems due to very small pores and quite large surface areas they feature³.

As per the need of nanofibres in various application areas, it is possible to improve/enhance the dimensions and surface structure of nanofibres. However, there are barely any study on this matter. A study on examining the dimensional stability of polyvinyl alcohol (PVA) nanofibres⁴ shows that NaCl and Fe(NO₃)₃ salts added to the solution medium cause a significant shrinking of the nanofibre diameter.

Polyurethane (PU) is a synthetic polymer obtained by putting a polyol with more than two hydroxyl group per molecule in an exothermic reaction with a diisocyanate or polymeric isocyanate in the presence

of a catalyst and additives. Polyurethane, a thermoplastic polymer, is utilized in biomaterials as it features excellent mechanical properties⁵. Electrospun polyurethane nanofibres are successfully used in wound dressings due to their superior oxygen permeability and barrier properties⁶.

Additives introduced to the medium during the electrospinning process may help the production of finer nanofibre mats with a large surface area and porous network structure by manipulating the PU fibre diameters for its application in wound dressing. In recent years, studies involving electrospun nanofibres and the increased diversity of application areas of nanofibres have made it necessary to elaborate the factors that affect fibre geometry and diameter. The present study is therefore aimed at investigating how the nanofibre size and morphology change when acid, base, and salt are added to the polyurethane solution medium; PU is a successfully utilized polymer as part of the electrospinning method. Nanofibre diameters are measured based on the SEM images. An attempt has also been made to explain the changes in dimensional stability and diameter with respect to the strength, electrical conductivity, viscosity, and surface tension of dopants.

2 Materials and Methods

2.1 Materials

The polyurethane (PU) solution (13% prepared in ethylacetate-DMF solvent mixture) was obtained commercially from a company called INOVENSO

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(Istanbul, Turkey). The acids, bases and salts utilized were of analytical grade and purchased from the Merck (Darmstadt, Germany) and BDH Chemicals Limited (Poole, England). List of acid, base and salt used are given in Table 1.

2.2 Instruments

Inovenso NE100 model electrospinning apparatus was utilized. Polymer solution was fed into the system through a syringe and 28 kV current at 1.20 mL/h flow rate was applied in order to inject the polymer solution, which accelerated towards the oppositely polarized collector. The distance between collector and nozzle was fixed at 18.5 cm.

SEM imaging of PU nanofibres was performed by using Carl Zeiss Supra 40 VP FESEM to observe morphological changes at an accelerating voltage of 15.00 kV. Polymer samples were coated with gold to make them conductive.

2.3 Preparation of PU Solutions with Acid, Base or Salt Additives

Acid, base, and salt solutions of 0.1 mL (each with 0.1 M concentration) were separately added to 13% PU solutions of 2.5 mL. The electrospinning apparatus was adjusted in line with the operation

parameters set based on previous experiences (voltage 28 kV, flow rate 1.20 mL/h, distance from nozzle to the collector 18.5 cm, and diameter of needle 1 mm) to obtain nanofibres.

3 Results and Discussion

As part of the electrospinning method, many parameters influence the formation of nanofibres from solutions or melts. Parameters^{7,8} influencing the nanofibre formation include solution parameters such as polymer's molecular weight, solution concentration, viscosity, electrical conductivity, and surface tension; and operational parameters such as the voltage applied, flow rate, and distance from nozzle to the collector. The effect of operational parameters on the diameter of polyurethane nanofibres has been reported in a previous study⁹. The present study relies on the effect of preset solution parameters. Table 1 shows the acids, bases and salts, and their effect on electrical conductivity, viscosity, and surface tension properties.

SEM images of acid-doped PU nanofibres are given in Fig. 1. Certain deteriorations are clearly visible on the images of nanofibres obtained from acid-doped PU solutions. Deteriorations worsen with higher acid strength. The first two images exhibit relatively smooth nanofibre structures. As can be seen in Table 1, K_a values of CH_3COOH and H_3PO_4 are 1.8×10^{-5} and 7.1×10^{-3} respectively; these are weak acids in comparison to others. CH_3COOH -doped PU nanofibres exhibit a smoother and beadless structure, while H_3PO_4 -doped PU nanofibres indicate clearly visible fibre nodes and bead formations. Again, K_a and electrical conductivity are directly proportional quantities. Hence, nanofibre morphology and fibre length exhibit a significant deterioration with higher acids strength, which is associated with an increased electrical conductivity of the solution. However, the small conductivity value leads to insufficient jet formation in the solution, which results in a bead formation together with the fibre¹⁴. Changes in nanofibre diameter are given in Fig. 2 (a) with respect to the electrical conductivity.

The change in electrical conductivity of the solution with the addition of strong or weak electrolytes to the solution medium affects the net charge density carried by the solution jet as part of the electrospinning operation. When the jet's charge increases, the material is exposed to stronger elongation forces, resulting in less bead formation and providing finer fibres¹⁵.

Table 1 — Related electrical conductivity and surface tension properties^{10,11}

Dopant	Electrical conductivity(κ) mS/cm (in 0.1 N)	Surface tension ^{12,13} (γ), mN/m	Viscosity (η) mPa.s (in 0.5 M)	Strength K
Acids				
CH_3COOH	0.46	27.00	1.063	1.8×10^{-5}
H_3PO_4	-	-	1.138	7.1×10^{-3}
H_2SO_4	22.5	67.90	1.112	1.0×10^3
HNO_3	35.0	72.80	1.010	2.4×10^1
HCl	35.1	65.95	1.029	1.3×10^6
HClO_4	38.6	69.01	-	Large
Bases				
NH_3	0.33	-	1.015	1.8×10^{-5}
$\text{Ba}(\text{OH})_2$	18.0	-	-	> 1
NaOH	18.3	-	1.112	> 1
KOH	21.3	-	1.058	> 1
$\text{Ca}(\text{OH})_2$	-	-	-	> 1
$\text{Mg}(\text{OH})_2$	-	-	-	> 1
Salts				
CH_3COONa	6.11	-	1.171	-
Na_2SO_4	7.84	194.5	1.244	-
NaNO_3	8.72	119.2	1.025	-
NaCl	9.20	113.3	1.052	-
KClO_4	11.52	-	-	-
Na_3PO_4	-	-	1.662	-

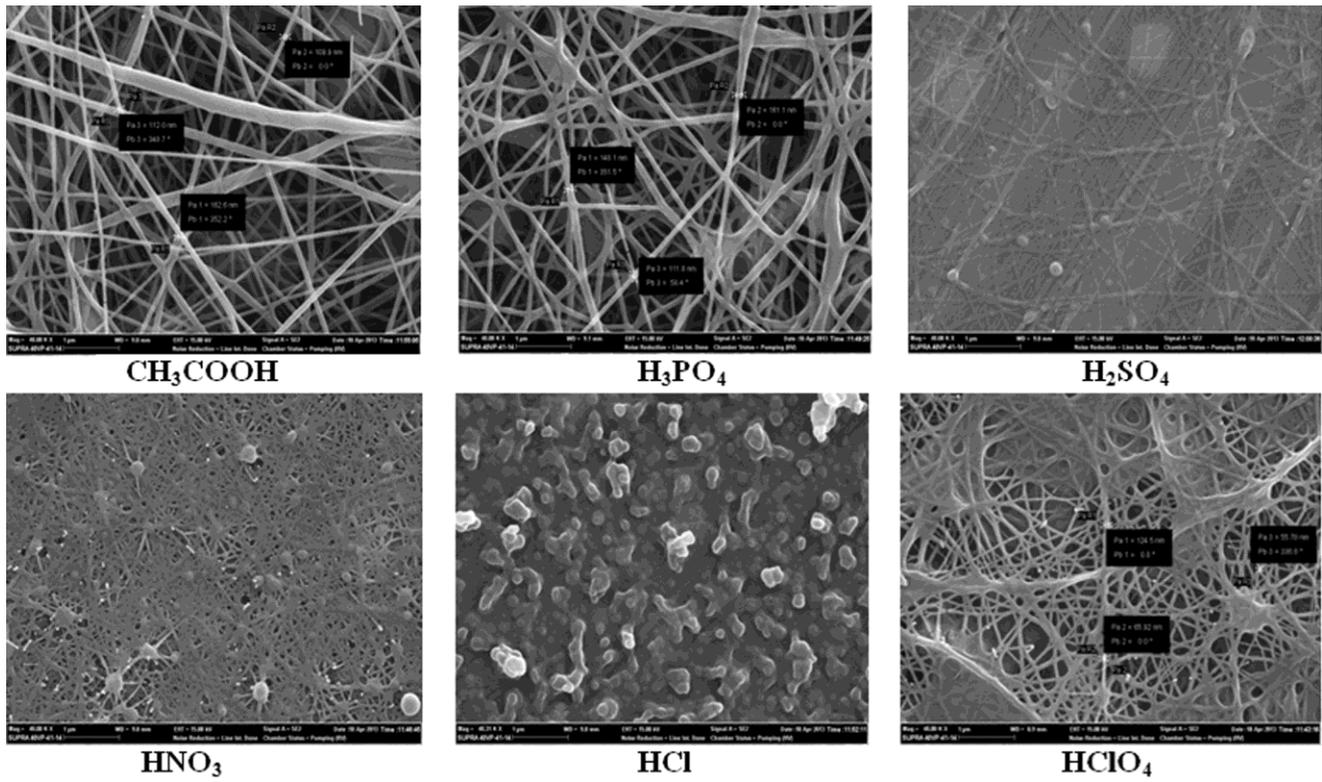


Fig. 1 — SEM images of PU nanofibres doped with different acids

SEM images of base-doped PU nanofibres are shown in Fig. 3. Unlike acid-doped PU nanofibres, all bases yield different nanofibre structure. Here, the fundamental difference lies in the adverse effect on the PU nanofibre morphology caused by H^+ ions (acid-doped) which are associated with acid ionization. OH^- ions produced by base ionization are not as effective as H^+ ions in terms of affecting the fibre morphology. As the basic strength grows, the medium's harsh acidity level decreases, and a quite smooth fibre geometry is obtained in the absence of any factor to adversely affect the nanofibre morphology. However, the nanofibre diameter increases linearly, depending on the increase in electrical conductivity [Fig. 2 (b)], and unlike acid-doped PU nanofibres, this change is due to the difference caused by H^+ and OH^- ions in the solution.

SEM images of salt-doped PU nanofibres are presented in Fig. 4. Compared to the nanofibres obtained by two other types of additives, this group exhibits the longest nanofibres with the smoothest geometry. CH_3COONa yields the finest nanofibres. As stated above, the salt anion associated with weak acid decreases the medium's electrical conductivity, and this provides smoother and thinner nanofibres

with the help of balanced electrical forces within the solution. As can be seen in Fig. 2 (c), the change in electrical conductivity of the solution with salt addition affects the nanofibre diameter. At first sight it is possible to say that the diameter of nanofibres varies linearly with electrical conductivity. However, literature¹⁵ shows that the increase in electrical conductivity increases the elongation capacity of the solution, allowing the production of smoother fibres with smaller diameters. But it is opposite in this study. The reason for this difference is that different salts having different ionic strengths have been used instead of changing the concentration of an individual salt. However, it is not yet possible to explain the reasons for this difference in this study. Zhang *et al.*¹⁶ demonstrated that the increase in solution conductivity with the addition of salt contributes to the nanofibre formation. Adding salt has a positive effect on the electrospinning procedure. A study⁴ examining the effect of NaCl added to an aqueous PVA solution on the nanofibre formation reported that even a trace of NaCl sharply increases the solution's conductivity, thereby affecting the net charge of the solution jet during the electrospinning procedure. A different study investigating the effects of solution

conductivity on P(LLA-Cl) mixed nanofibres found that nanofibre diameter decreases as the solution conductivity increases¹⁷. Another study examined how the addition of NaCl to a PCl solution affected the nanofibre diameter. Adding salt to polymer solutions increases the solution's conductivity and surface charge density of the solution jet. This reduces

the bead formation and fibre diameter. The fibre diameter decreased and a beadless fibre appearance was observed under higher NaCl concentrations¹⁸. Findings in present study are in line with those reported by the aforementioned studies. In conclusion, adding an electrolyte such as acid, base or salt to polymer solutions during electrospinning changes the solution's conductivity and hence the nanofibre geometry.

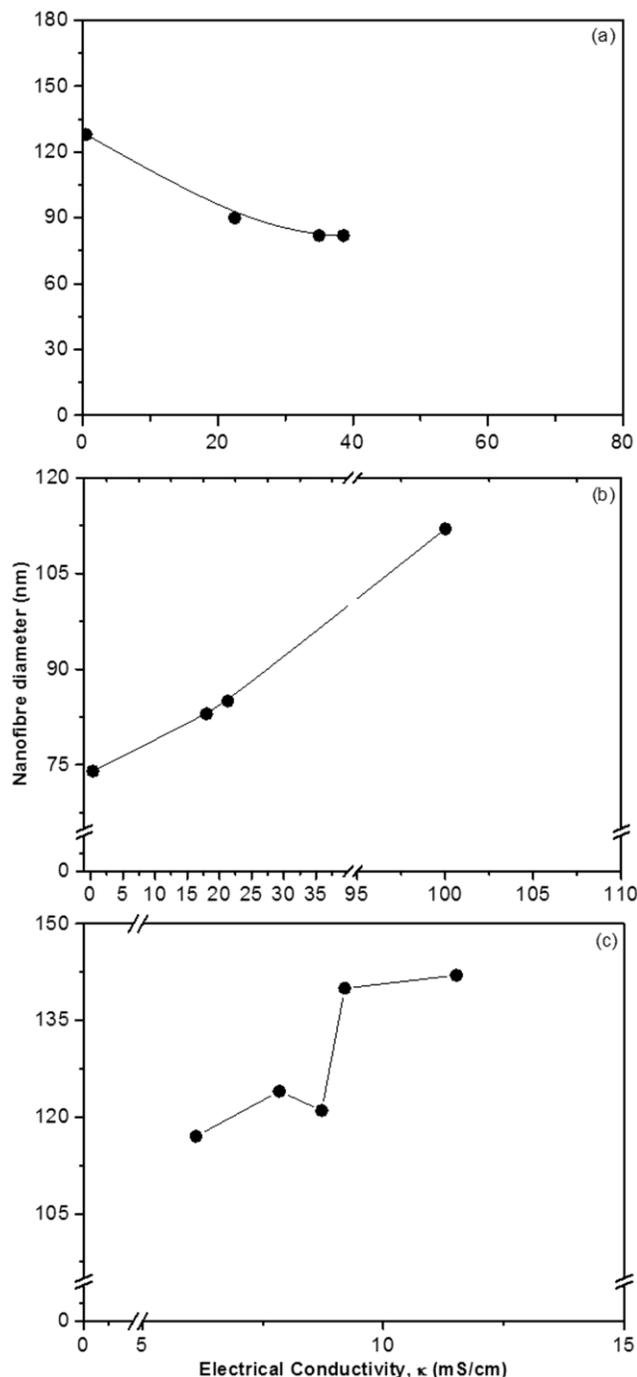


Fig. 2 — Change in diameter of nanofibres with electrical conductivity of (a) acids, (b) bases and (c) salts

Surface tension is another significant parameter for solution that affects the nanofibre size. Being a function of the solvent components of a solution, it plays an important role in electrospinning. One may obtain beadless and continuous fibres if the relevant polymer solution has a low surface tension. Different solvents offer different contributions to the surface tension. In general, a high surface tension hinders the electrostatic spinning procedure due to the formation of sprayed drops and instability of the jet¹⁹. Formations of drops, beads and fibres depend on surface tension. A lower surface tension of the polymer solution enables a more successful electrospinning procedure¹⁴. Figures 5 (a) and (b) show how the diameter of nanofibres obtained from acid- and salt-doped PU solutions change with surface tension. Both types of doping result in a larger nanofibre diameter, depending on a reduced surface tension. The most important effect of surface tension on electrospinning is 'whether it causes bead formation or not'. The charged solution must cope with the surface tension in order to start electrospinning. While the surface tension attempts to decrease the solution's surface area per unit mass, electrical forces strive to increase the surface area on the jet during elongation²⁰. When electrical forces overcome the surface tension, the solution jet is sprayed towards the collector and the fibre starts to elongate. This process provides beadless fibres with a smooth geometry. In the present study, it is observed that bead formation in the images of nanofibres is obtained from the PU solutions including acids and salts with high surface tensions.

Viscosity is another solution parameter that affects the nanofibre diameter. It increases under higher solution concentrations. A higher viscosity yields a larger nanofibre diameter. On the other hand, a higher viscosity makes it more difficult to spray the solution and it exhibits large bead formations. However, one may observe discontinuous nanofibres under an extremely low viscosity¹⁵. The solution's viscosity

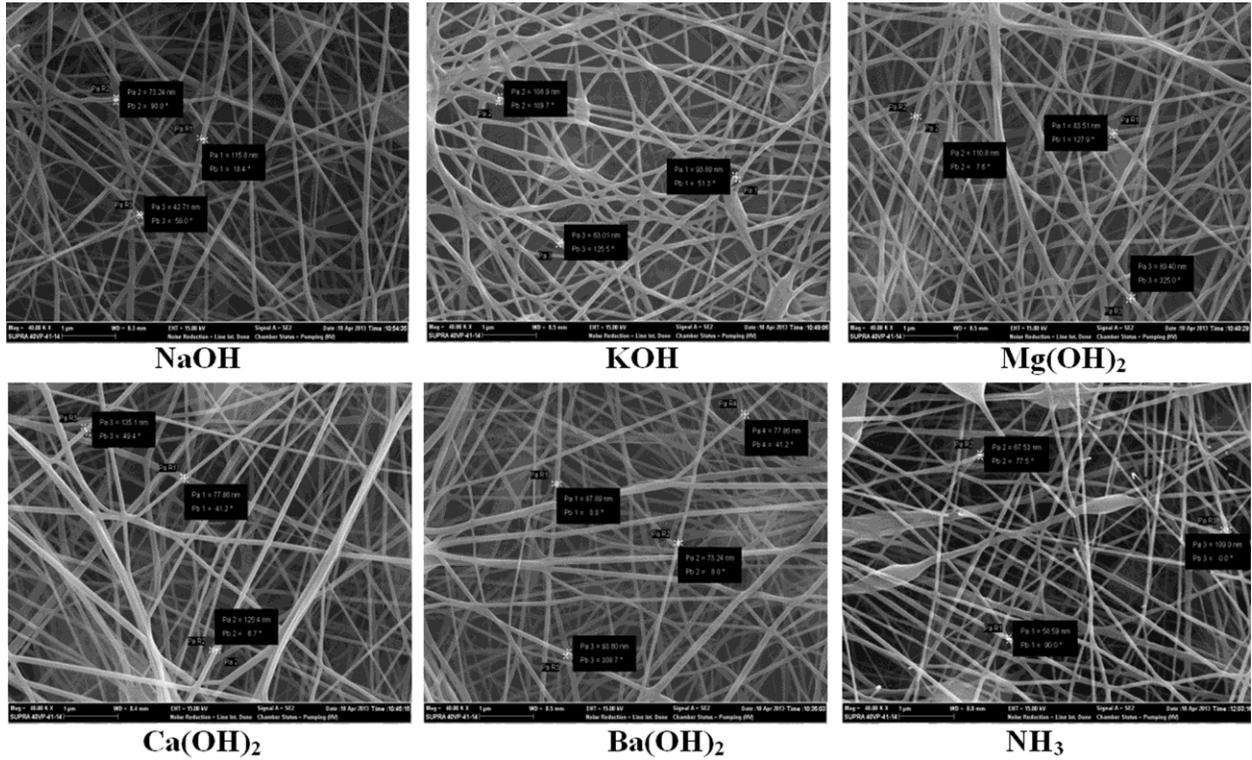


Fig. 3 — SEM images of PU nanofibres doped with different bases

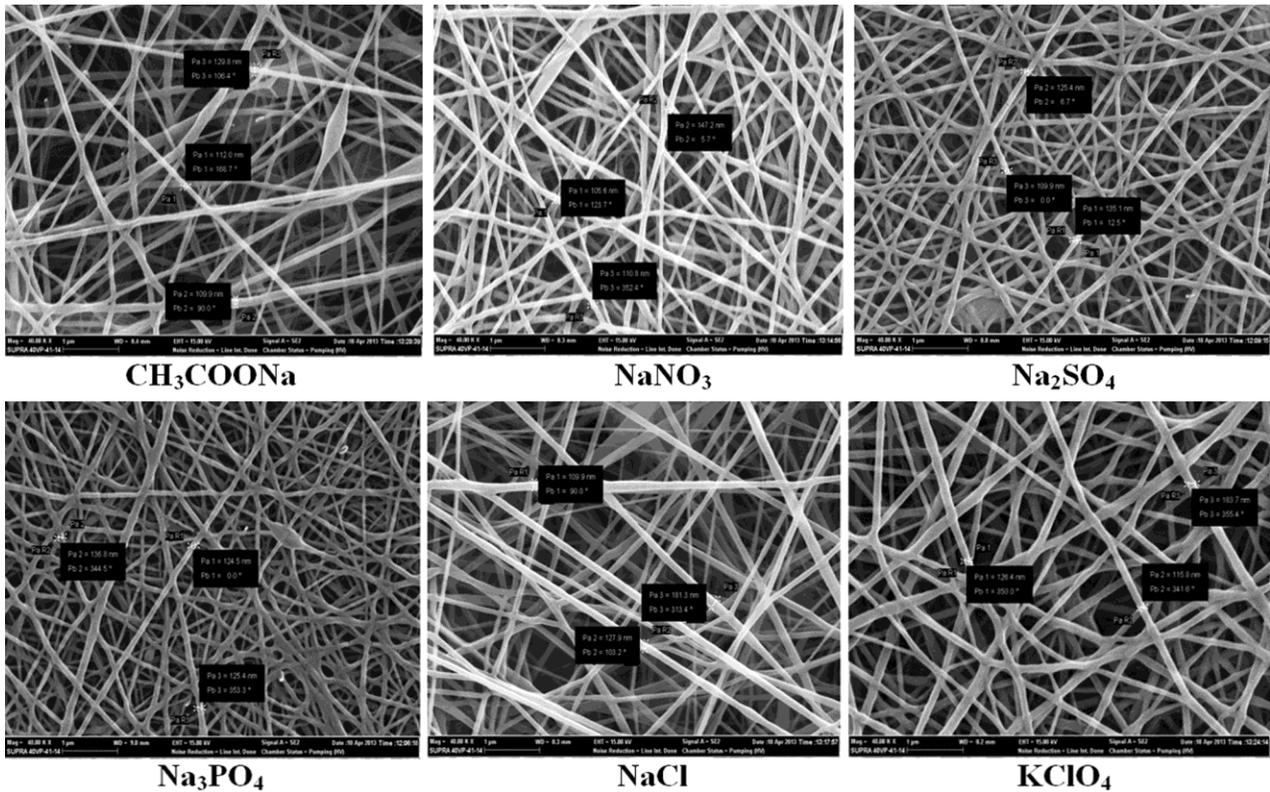


Fig. 4 — SEM images of PU nanofibres doped with different salts

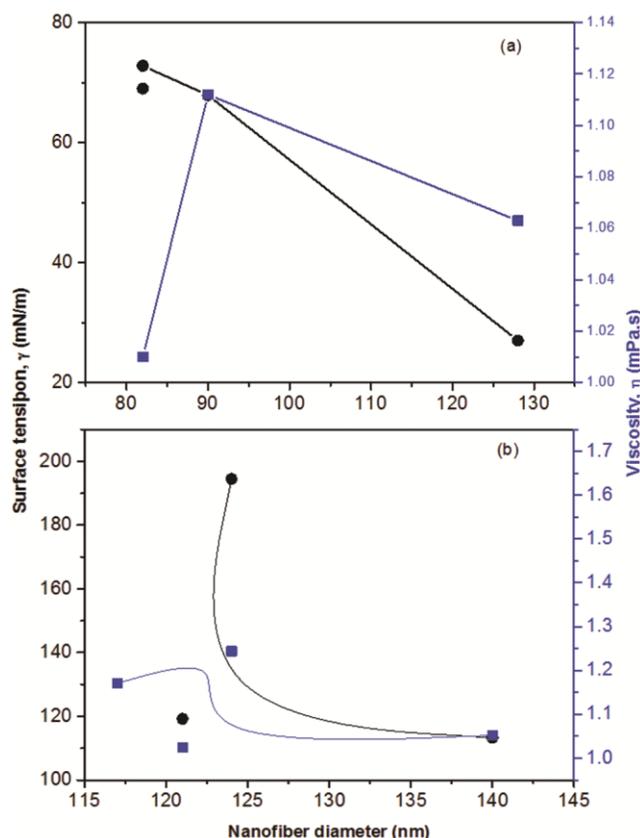


Fig. 5 — Change in diameter of nanofibres with surface tension and viscosities of (a) acids and (b) salts

and hence its concentration must be optimal. Figures 5 (a) and (b) indicate how the nanofiber diameter changes with the solution's viscosity. Diameters of nanofibres obtained from acid- and salt-doped PU solutions do not follow a general pattern of change depending on viscosity. Only two of the preselected acids yield smooth nanofibres. Comparing them, diameters of the nanofibres obtained by adding H_3PO_4 (high viscosity) to the PU solution are relatively larger than those obtained with the addition of CH_3COOH . This is due to the likely increase in the solution's viscosity caused by the H_3PO_4 . This finding supports the general descriptions reported by the relevant literature²⁰. It is detected that there is no proper correlation between the viscosity values of salts in the solutions having the same concentration and nanofiber diameters obtained from salt-doped PU solutions.

In the final step, the effect of divalent metal cation size on the nanofiber diameter has been studied, subject to the same anion type and base-doped solution concentration. Such a study has not been found in the literature to the best of our knowledge. The results are found quite interesting. It is observed

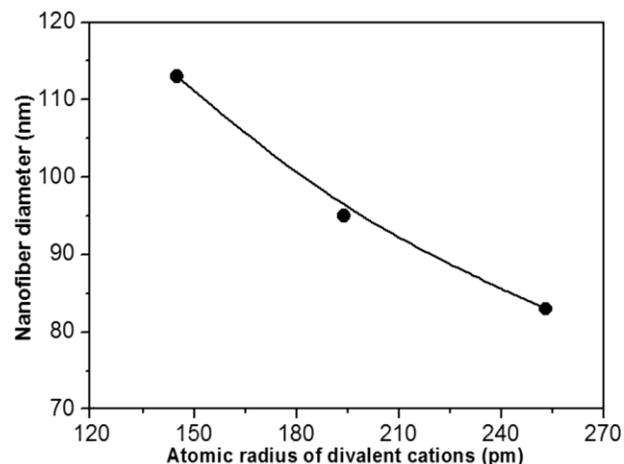


Fig. 6 — Effect of size of divalent metal cation on the diameter of nanofibres

that the diameters of nanofibres obtained from the PU solutions doped with 0.1 M of $\text{Mg}(\text{OH})_2$, $\text{Ca}(\text{OH})_2$ and $\text{Ba}(\text{OH})_2$ decrease as the metal cation's charge increase (Fig. 6). Mg^{2+} (*a.r.* 145 pm) yields thick nanofibres, whereas Ba^{2+} (*a.r.* 253 pm) yields finer ones. These are strong bases and exhibit complete ionization. Therefore, when they are added to the PU solutions, large cation reduces the surface tension, resulting in a reduced diameter of the nanofiber. Previous studies on the relationship between surface tension and divalent cations are not contrary to such an interpretation²¹.

4 Conclusion

Electrospinning has been carried out with a 13% (weight ratio, in DMF-ethylacetate solvent mixture) PU solution by adding different types of acids, bases, and salts prepared with 0.1 M concentration. Then, the effects of acids, bases, and salts on the nanofiber diameter and its morphology are investigated. Acid-doped PU nanofiber morphology exhibit a higher deterioration in comparison to the base- and salt-doped ones. Homogeneous, fine and smooth nanofibres are obtained from salt-doped PU solutions. The differences observed in the nanofiber morphology and diameter with respect to the acidity, surface tension, viscosity, and electrical conductivity properties of the additives have been evaluated. In conclusion, acids, bases, and salts are added to the medium as a requirement of the objective and targeted application in order to obtain a longer and finer fibre structure. This addition is found highly effective on the nanofiber structure. It is possible to modify the diameter, length and

geometry of nanofibres as desired and make them ready for the area of application as required. In recent years, studies involving electrospun nanofibres and the increase in the diversity of application areas of nanofibres have made it necessary to examine in detail the factors affecting fibre geometry and diameter. This study will be more useful in the application areas, such as biotechnology, defense, food and environment.

Acknowledgement

The authors gratefully acknowledge the support provided by the HU Scientific Research Foundation through the project no. HU-BAB-011D10601001.

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