The effect of polymer concentration on coaxial electrospinning of PVP/PCL core-shell nanofibers

Polimer konsantrasyonunun koaksiyel elektroeğrilmiş PVP/PCL çekirdek-kabuk nanolifleri üzerine etkisi

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Highlights

❖ *Changes in core-shell nanofiber morphology were observed depending on polymer concentration and viscosity.*

❖ *The changes in the hydrophilic properties of the surfaces were investigated according to the differences in the shell and core polymer concentrations.*

Graphical Abstract

In the study, nanofiber structures were produced in the form of PCL in shell and PVP in core by using coaxial electrospinning method. By changing the polymer concentration, the effect of polymer/solvent ratios on fiber diameter and surface hydrophilicity in coaxial electrospinning was observed.
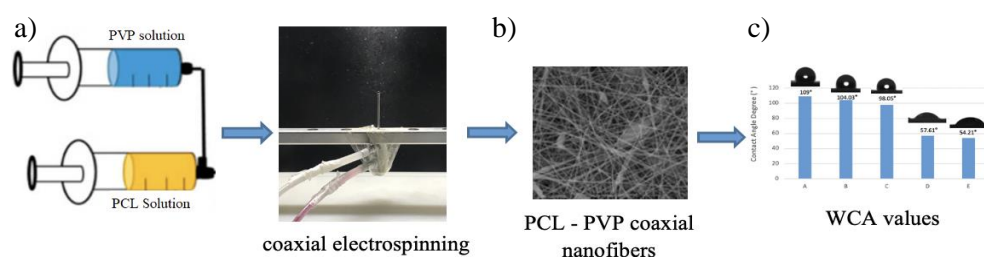

Figure. PVP/PCL core shell nanofibers production method a), SEM image of nanofiber morphology b), and water contact angle (WCA) values of nanofibrous surfaces c)

Aim

Investigation of the effect of polymer concentration on fiber diameter and surface hydrophilicity in coaxial electrospinning

Design & Methodology

By creating two different test groups, both core and shell polymer concentrations were decreased first, then the core concentration was decreased by keeping the shell concentration constant.

Originality

The literature survey resulted in no study available on the examination of the effect of polymer concentration change on surface hydrophilicity.

Findings

The contact angle decreased from 104.3° to 57.61° when 10% PVP-10% PCL was reduced to 6% PVP-6%PCL. The nanofiber diameters of 10% PVP-10% PCL, 8% PVP-8% PCL and 6% PVP- 6% PCL were 280 ± 276.26, 145 ± 66.08 and 98 ± 38.3, respectively

Conclusion

As the core polymer concentration decreased, it migrated towards the shell and carried core polymer properties (hydrophilicity) to the surface. Also nanofiber diameters decreased with decreasing viscosity.

Declaration of Ethical Standards

The author(s) of this article declare that the materials and methods used in this study do not require ethical committee permission and/or legal-special permission.

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ABSTRACT

Core-shell nanofibers are generally developed by coaxial electrospinning using different polymers in the core and the shell. In this study, nanofibers were developed using hydrophobic polycaprolactone (PCL) in the shell and hydrophilic polyvinylpyrrolidone (PVP) polymer in the core, and the effect of polymer concentrations on fiber structure and water contact angle was observed. When the SEM images of the nanofibers, which are produced by reducing the polymer concentrations from 10% to 6% in both the core and the shell, and which constitute the first group samples of the study, are evaluated it was observed that the nanofiber diameters decreased from 280 nm to 98 nm depending on the viscosity decrease. In addition, it was observed that the contact angle decreased from 104° to 57° depending on the polymer concentration. In the continuation of the study, second group of the samples were produced by keeping the concentration of PCL polymer forming the shell structure constant at 10% by weight, while changing the concentration of PVP polymer forming the core structure to 10%, 8% and 6%. It was observed that as the viscosity of the core polymer in the structure decreased, the surfaces became more hydrophilic and the contact angles decreased from 104° to 96°. Compared to the results obtained in the first group, it was observed that the decrease in the contact angles of the surfaces was less in the second group, since the shell polymer concentration was kept constant at 10%. As a result, it was observed that polymer concentration significantly affected both nanofiber morphology and hydrophilicity in the samples developed using PCL in the shell and PVP in the core in the coaxial electrospinning method.

Keyword: **Nanofiber, Coaxial Electrospinning, Polycaprolactone, Polyvinylpyrrolidone**

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ÖZ

Çekirdek-kabuk nanolifleri, çekirdekte ve kabukta genellikle farklı polimerler kullanılarak koaksiyel elektroeğirme yöntemi ile geliştirilmektedir. Bu çalışmada, kabukta hidrofobik polikaprolakton (PCL) ve çekirdekte hidrofilik polivinilpirolidon (PVP) polimeri kullanılarak nanolifler geliştirilmiş ve polimer konsantrasyonlarının lif yapısı ile su temas açısı üzerindeki etkisi gözlemlenmiştir. Polimer konsantrasyonlarının hem çekirdek hem de kabukta %10'dan %6'ya düşürülmesiyle üretilen ve çalışmanın ilk grup numunelerini oluşturan nanoliflerin SEM görüntüleri değerlendirildiğinde, vizkozite düşüşüne bağlı olarak nanolif çaplarının 280 nm'den 98 nm'ye düştüğü gözlenmiştir. Bunun yanı sıra, polimer konsantrasyonuna bağlı olarak temas açısı 104°'den 57°'ye düşmüştür. Çalışmanın devamında, kabuk yapısını oluşturan PCL polimeri konsantrasyonu ağırlıkça %10 olarak sabit tutulurken, çekirdek yapısını oluşturan PVP polimeri konsantrasyonu %10, %8 ve %6 şeklinde değiştirilerek ikinci grup numuneler üretilmiştir. Yapıdaki çekirdek polimerinin viskozitesi azaldıkça yüzeylerin daha hidrofilik hale geldiği ve temas açılarının 104°'den 96°'ye düştüğü gözlenmiştir. Birinci grup ile kıyaslandığında ikinci grupta kabuk polimer konsantrasyonu %10 olarak sabit tutulduğu için yüzeylerin temas açılarındaki düşüşün daha az olduğu gözlenmiştir. Sonuç olarak, koaksiyel elektoeğirme yönteminde kabukta PCL ve çekirdekte PVP kullanılarak geliştirilen numunelerde, polimer konsantrasyonunun hem nanolif morfolojisini hem de hidrofilite değerlerini belirgin olarak etkilediği görülmüştür.

Anahtar Kelimeler: Nanolif, Eşeksenli Elektroeğirme, Polikaprolakton, Polivinilpirolidon

1. INTRODUCTION

Electrospinning is one of the widely preferred production methods to produce nanofibers [1]. Electrospun nanofibers are used in many different fields due to their high surface-to-volume ratio, high porosity, flexibility and good mechanical properties [2]. Fields such as medical, filtration, energy storage, sensors and composites are some of the areas where electrospun nanofiber studies are carried out intensively [3-7].

The morphologies of nanofibers can be altered according to their intended applications through differentiation of production methods, modification of production method parameters, or selection of materials. In the

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electrospinning method, several parameters significantly influence nanofiber structure. Some of these parameters are the feed rate of the polymer solution, applied voltage, distance between the collector and needle tip, nozzle diameter, nozzle shape, humidity, and temperature [8,9]. Modifying these parameters according to the desired nanofiber structure facilitates the achievement of desired properties in the final product.

Electrospun nanofibers made from a variety of biocompatible and biodegradable polymers have shown a great potential for usage as efficient biomedical applications such as wound dressings and tissue engineering [10]. Due to their outstanding electrospinning capabilities and biocompatibility, poly(e-caprolactone) (PCL) and polyvinylpyrrolidone (PVP) are frequently utilized as tissue-engineered scaffolds and controlled drug delivery systems [11,12]. PCL is a semi-crystalline polyester that is simple to work with, has strong mechanical qualities, and is very compatible with many different kinds of polymers. However, its hydrophobic feature restricts its use as a scaffold in tissue engineering since it may influence cell adhesion [13]. By combining PCL with the proper hydrophilic polymer such as PVP, it is possible to modify its hydrophobicity [14]. PVP is a biocompatible, water-soluble synthetic polymer that is generally used as a drug dissolution enhancer. The rapid dissolution of PVP can be slowed down by mixing with other polymers [15]. In the literature, there are different studies in which PCL and PVP polymer are used in core-shell nanofiber production. Kaviannasah et al. tested the fiber structures, strength and degradation differences by using PCL and PVP polymers in different combinations in both the core and the shell in coaxial nanofiber production. According to the results, the increasing use of PVP in both the core and the shell increased the viscosity of the solution and the fiber diameters, while causing a decrease in the strength. It was also observed that PCL degraded more slowly than PVP [16]. Suganya et al. defined the role of polymers in the structure in their study that produced herbal medicine-added PCL/PVP dressings. In the study, while PVP polymer acts as a drug carrier medium, the contribution of PCL polymer to the strength of the structure is mentioned [17]. The combination of strength and degradation properties of polymers was also utilized in which drug-loaded PCL and PVP coaxial nanofibers were produced for bone regeneration. In another study [18], it was shown that coaxial PCL/PVP fibers have lower strength and elongation values compared to PCL fibers. This is because the inclusion of PVP makes the fibers more flexible and deformable. The fluid retention or swelling capacity of the biomaterial composite is a crucial property for facilitating nutrient circulation and drug release. The hydrophilic nature of PVP increased the swelling ability of the system compared to PCL fibers alone. Thus, the inclusion of hydrophilic polymers increased surface protein interactions through the formation of a hydration layer, which in turn increased

protein adsorption, making the nanofibers more biocompatible [18].

Coaxial electrospinning method has been developed in order to minimize the burst release in blend electrospinning and to load some sensitive additives such as proteins, growth hormones, drugs etc. that are negatively affected by organic solvents into the fiber without being damaged [19]. In core-shell nanofibers, the core swells over time and dissolves, forming pores in the shell. In drug delivery systems, while drugs are loaded into the core, the shell phase forms a protective layer. The coaxial electrospinning method can also be used to eliminate drug-polymer mismatch. For example, hydrophilic drugs in the core phase and hydrophobic polymers in the shell phase can be combined. Thus, the shell phase can degrade slowly and act as a physical barrier that provides sustained release [20]. Cheng et al. used coaxial electrospinning to load platelet-rich plasmas into PCL/PVA (polyvinylalcohol)/silk fibroin core-shell nanofibers. In the study where the release profiles were examined, it was observed that the coaxial nanofibers sustained released plasma for 30 days [21]. In the coaxial electrospinning method, two polymer solutions are fed through with special nozzle with two needles, one of which is in the center of the other, to form the shell and core. Existing studies show that the spinnability of the core fluid is not as important as the shell fluid. But fiber formation problems arise when the viscosity of the core fluid is too low. Therefore, the core fluid must have a certain minimum viscosity if it is to be entrained continuously without breaking [22].

In this study, it was aimed to produce nanofiber structures in the form of PCL in shell and PVP in core by using coaxial electrospinning method. Studies in the literature show that the morphology, viscosity, strength and degradation behavior of PVP/PCL core-shell nanofibers can be significantly affected by polymer concentration. However, no other study has been found on how the hydrophilicity of the nanofiber structure varies, as well as the fiber diameters, when the concentration of PVP in the core and PCL in the shell changes during coaxial electrospinning. In this study, PCL and PVP polymer concentrations were changed by weight and the effects on nanofiber morphology and hydrophilicity of nanofiber surfaces were investigated.

2. MATERIAL AND METHOD

For the study, Polyvinylpyrrolidone (PVP) (Mw: 360.000 g/mol) and Polycaprolactone (PCL) (Mw: 80.000 g/mol) were obtained from Sigma-Aldrich. Formic acid (100%), glacial acetic acid (100%) and ethanol were purchased from Merck. Distilled water was used as one of the solvents. PCL polymer solutions were prepared by dissolving PCL at different polymer concentrations (10, 8, 6 % wt.) in acetic acid/formic acid (1:2 w/w) under magnetic stirring for 3 hours at room temperature. To prepare the PVP solutions, PVP (10, 8, 6 % wt.) was

dissolved in distilled water/ethanol (1:1 w/w) solvent ixture for 12 hours at room temperature.

To produce nanofibers, NanoSpinner NE300 model electrospinning device was used. Inovenso IPS-14 double syringe pump was used to feed the polymer solutions that will form the shell and core structures at different feed rates. The coaxial nozzle has an outer syringe diameter of 2 mm and an inner syringe diameter of 1.15 mm. Changing the nozzle diameter affects the morphology of core-shell nanofibrous structures by changing the electric field distribution. The electric field envelope increases with increasing diameter of the core and shell nozzles, increasing the jet whipping angle [23]. Thus, it provides the production of stable core-shell nanofibers. For this reason, these diameters were preferred instead of smaller diameter core and shell needles. Optimum electrospinning parameters were adjusted as in Table 1 by making changes in the parameters during production and the same production parameters were used for all samples. In Table 2, the polymer concentration of coaxial electrospun nanofiber samples were given.

ZEISS EVO 40 Scanning Electron Microscope (SEM) was used for image analysis of nanofiber morphologies. Fibre diameters were measured with the ImageJ software by selecting 100 different fibres from SEM images at 10.000 magnification. To determine the water contact angle (WCA) of the samples, the contact angle measuring system – KSV – CAM 101 was employed. Deionized water was dropped on the nanofiber surfaces and the mean contact angles of the samples were measured. All measurements were repeated three times for reliability. Viscosities of all polymer solutions were measured with Brookfield DV-E Viscometer in order to examine the effect of polymer concentration and viscosities on fiber morphology.

Table 2. Polymer ratios of nanofiber surfaces fabricated by coaxial electrospinning

	PCL Concentration (wt.%) (Shell)	PVP Concentration (wt.%) (Core)
PCL10-PVP10	10	10
PCL8-PVP8	8	8
PCL6-PVP6	6	6
PCL10-PVP8	10	8
PCL10-PVP6	10	6
PCL8-PVP6	8	6

Table 1. Electrospinning production parameters of PVP/PCL coaxial nanofibers.

	Polymer concentration (%)	Feed Rate (mL/h)	Voltage (kV)	Distance (cm)	Collector Drum Speed (rpm)
PCL	10 8 6	0.8	24	20	200
PVP	10 8 6	0.2	24	20	200

3. RESULTS AND DISCUSSION

3.1 Fiber Morphology

In Figure 1, SEM images and fiber diameter distribution graphs of coaxial nanofibers were given. When the SEM images and graph of PCL10-PVP10, PCL8-PVP8, and PCL6-PVP6 (Figure 1. A, B, C) are examined, it is clearly seen that there was a decrease in fiber diameters as the concentration decreased in both the shell and core polymer. The average fiber diameters are 280, 145 and 98 nm, respectively. The reason for the changes in fiber diameters can be explained by the decrease in the viscosity of the polymer solutions with the decrease in concentration. Since there were problems in jet formation during the production of PCL10-PVP10, the diameter distribution was not homogeneous and the standard deviation was high, as can be seen from the fiber diameter distribution graph. In addition, high concentration causes high standard deviations in fiber diameter distributions. In the study of Nasim et al., while the silk fibroin concentration was 10%, the nanofiber diameters ranged between 60 and 140 nm, while at 14% concentration, the nanofiber diameters varied between 140 and 440 nm [24]. The viscosities of polymer solutions are also given in Table 3. As it can be seen, 2% increase in polymer concentration caused solution viscosities to increase approximately twofold. The relationship between solution viscosity and polymer concentration can be attributed to the power-law relationship and is largely dependent on the nature of the polymer, such as polymer structure, molecular weight, and polydispersity. As the polymer concentration increases, the viscosity gradually increases until the concentration reaches a certain value [25]. According to the literature, viscosity of the solution is a parameter that has an effect on the morphological structure and average diameter of the nanofibers [26]. When the SEM images of PCL10-PVP8, PCL10-PVP6, and PCL8-PVP6 (Figure 1. D, E, F) were examined, it was observed that the bead formation in the fibers increased as the PVP concentration in the core decreased. This is because the viscosity values of the shell and core structures are different from each other [27].

Table 3. Viscosities of PCL and PVP polymer solutions.

Polymer Type	Polymer Concentration (%)	Viscosity (cP)
PCL	6	110
PCL	8	302
PCL	10	666
PVP	6	145
PVP	8	300
PVP	10	593

As a result, although all other production parameters were kept constant (Table 1) in the coaxial electrospinning of PCL and PVP, it was observed that the change of polymer concentrations in the shell and core changed fiber formation and nanofiber diameters.

3.2 Surface Hydrophilicity

To assess the surfaces' hydrophilicity, water contact angle (WCA) test was conducted and in order to compare the hydrophilicity values of PCL/PVP coaxial nanofibers, pristine PCL (PCL10-PCL10) and PVP (PVP10-PVP10) nanofibers were produced and their values were also measured. It has been demonstrated that the contact angle of the PCL10-PCL10, which is known to be hydrophobic, is 109°, and the contact angle of the PVP10-PVP10, which is known to be hydrophilic, is 54°. For testing WCA of the samples produced from coaxial nanofibers, two different test groups were formed such that the samples in one group had decreasing polymer concentrations in both shell and core fluids, and in the other group polymer concentrations of the core fluid was decreased while keeping the polymer ratio of the shell constant.

As may be seen in Figure 2, coaxial nanofibers with lower polymer ratios in both core and shell parts tended to display a hydrophilic characteristic and had lower WCA values where the contact angle of PCL10-PVP10 was 104° and decreased to 98° for PCL8-PVP8 and to 57° for PCL6-PVP6. As the viscosity decreases with the decrease of the polymer concentration, it is easier for the hydrophilic polymer in the core to migrate towards the shell and enclosing the core polymer may not have been sufficient. In addition, PVP creates gaps and channels in the nanofiber structure, increasing the access of water into the nanofiber [28]. As the nanofiber diameters decrease with the decrease of the concentration, more contact surface has been formed between the water and the fibers [29]. In a study by Koushki et al., it was found that PCL has a water contact angle of 110° and PVA/PCL coaxial electrospun nanofibers have a water contact angle of 83°. According to the results of the study, it was observed that the addition of PVA to the PCL nanofibers reduced the hydrophobicity of the final core-shell structure. PVA is generally known to be very hydrophilic due to the presence of hydroxyl groups (O-H) and hydrogen bands; therefore, adding PVA to a hydrophobic polymer such as PCL can increase the hydrophilicity of the final structure [30]. In addition, in the study conducted by Huang et al., the WCA values of pure PCL polymer and core-shell Gelatin-PCL nanofibers were compared and it was found that the contact angle of coaxial fibers was lower [31].
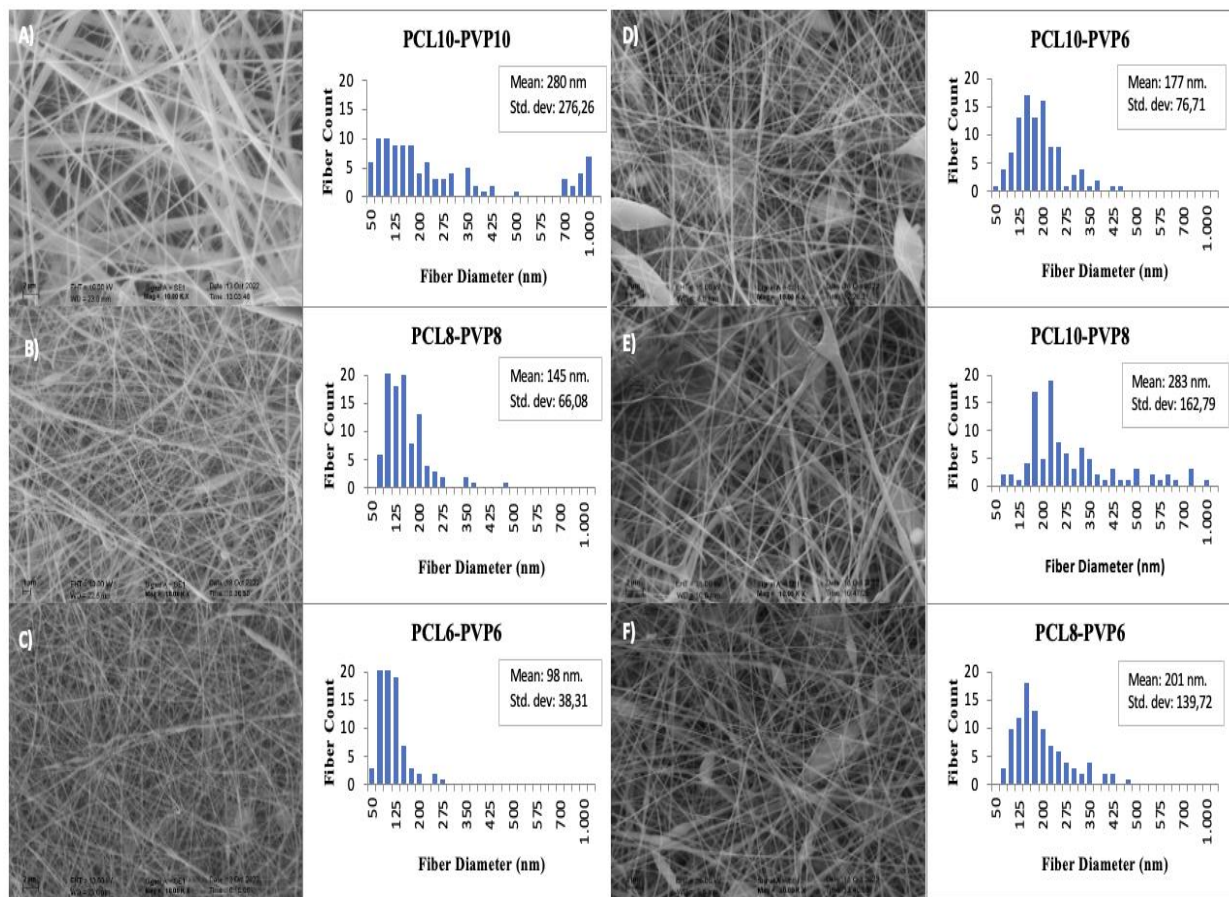
Figure 1. SEM images (at x10.000 magnifications) and fibre diameter distribution graphs of coaxial nanofibers A) PCL10–PVP10, B) PCL8–PVP8, C) PCL6–PVP6, D) PCL10–PVP6, E) PCL10–PVP8, F) PCL8–PVP6 samples, respectively.
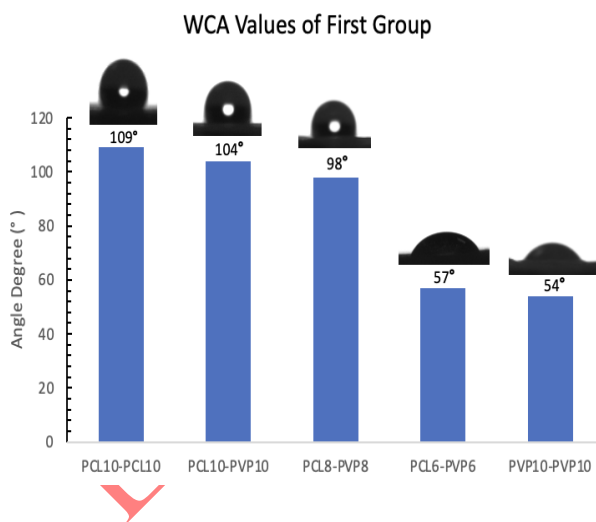

Figure 2. WCA values of PCL/PVP coaxial nanofibers with different core and shell polymer concentrations.

fact that core enclosing performance of the shell polymer did not change since the PCL concentration (and the viscosity) was kept constant as 10%. Therefore, when 10% PCL is used in the shell, it is seen that the contact angle is 96° even if the PVP ratio in the shell drops to 6% (PCL10-PVP6). In other words, PCL/PVP coaxial nanofiber still shows hydrophobic properties. On the other hand, when the PCL concentration in the shell decreased to 6% (PCL6-PVP6), it was observed that the hydrophilicity increased significantly with the effect of PVP in the core. As a result, when the polymer concentrations used in the shell and core in coaxial electrospinning are changed, it is seen that nanofiber structures with different hydrophilicity are formed.

When the results in Figure 3 are examined for the samples PCL10-PVP10, PCL10-PVP8, and PCL10-PVP6, similar to the results presented in Figure 2, decrease in the viscosity of the core polymer resulted in lower contact angle values due to the polymer migration from the core to the shell. However, decrease in the contact angles was lower than those observed for the
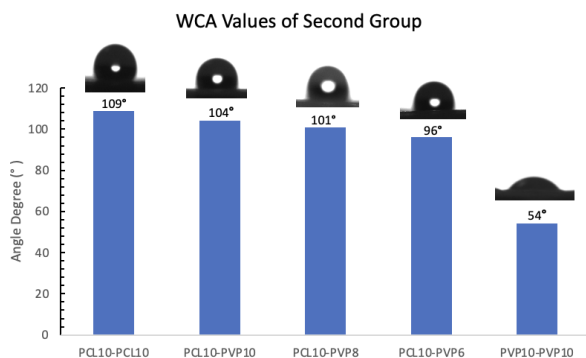
Figure 3. WCA values of PCL/PVP nanofibers and coaxial nanofibers with different core polymer concentrations of PVP in core.

4. CONCLUSION

In this study, changes in core-shell nanofiber morphology were observed depending on polymer concentration and viscosity. According to SEM images, nanofiber diameters decreased from 280 nm to 98 nm as polymer concentration decreased from 10% to 6%. In addition, beaded fiber formation was observed as the difference between the shell and core polymer concentrations increased. Besides, as the polymer concentration decreased, the contact angle of the PVP/PCL core-shell nanofibers decreased, so the structure became more hydrophilic. The contact angle decreased from 104° to 57° when PCL and PVP concentrations were reduced to 6 % wt from 10 % w. When the shell polymer concentration was kept constant at 10 % wt PCL and the PVP concentration in the core was reduced to 6 % wt, the contact angle decreased from 104° to 96°. The reason for this was thought to be the increase in the tendency of PVP in the core to migrate towards the shell with the decrease in viscosity. In conclusion, the effect of polymer concentration on the formation of core/shell fibers and surface characteristics is evident. Therefore, in order to obtain core/shell nanofibers with the required fiber diameter and hydrophilicity values, polymer concentrations must be selected appropriately. In future studies, the release behavior of drugs and similar therapeutics to be added to the core of nanofibers will be evaluated.

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DECLARATION OF ETHICAL STANDARDS

The author(s) of this article declare that the materials and methods used in this study do not require ethical committee permission and/or legal-special permission.

AUTHORS' CONTRIBUTIONS

Nursema PALA: Literature review, experimental design, data collection, data analysis and interpretation.

Nebahat ARAL: Experimental design and management, data analysis and interpretation, critical review.

Banu NERGİS: Determination and management of the conceptual design process, literature review and critical review.

CONFLICT OF INTEREST

There is no conflict of interest in this study.

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