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Electrospun polyvinylpyrrolidone / graphite composite nanofiber mats: Effect of the filler on the morphology and wettability

Elektroeğirilmiş polivinilpirolidon / grafit kompozit nanofiber keçeler: Katkının morfoloji ve ıslanabilirlik üzerine etkisi

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Abstract

The aim of this study is to investigate the effect of graphite (GR) content on the morphology and wettability of polyvinylpyrrolidone (PVP) / GR composite nanofibers. For this purpose, PVP and PVP/GR composite nanofiber mats of various filler contents (0.6%, 1.2%, 1.8%, 2.4%, 3%, 3.6% and 4.2 % of GR (wt.% of PVP)) were fabricated by electrospinning. The morphology and diameters of the nanofibers were characterized by SEM. Average diameters of 218 nm for unfilled PVP nanofibers and between 170 nm and 203 nm for composite nanofibers were observed. The water wettability of the nanofiber mats was also characterized by contact angle measurements. Contrary to expectations, the results reveal an increase in the water wettability of composite PVP nanofiber mats with increasing graphite content. This evolution seems to be based on the mild hydrophilicity of graphite discovered in recent years. The relationship with nanofibers' electrical conductivity was also examined.

Keywords: Electrospinning, Polyvinylpyrrolidone, Graphite, Nanofibers, Wettability

Özet

Bu çalışmanın amacı grafit (GR) oranının grafit katkılı polivinilpirolidon (PVP) kompozit nanoliflerin morfolojisi ve ıslanabilirlik özellikleri üzerindeki etkisini araştırmaktır. Bu bağlamda, elektroeğirme yöntemi kullanılarak, PVP nanolif keçeler ile birlikte farklı oranlarda (%0,6, %1,2, %1,8, %2,4, %3, %3,6 ve %4,2 GR oranlarında (% PVP)) katkı içeren PVP/GR kompozit nanolif keçeleri üretilmiştir. Nanoliflerin morfolojileri ve çapları taramalı elektron mikroskobu (SEM) ile belirlenmiştir. Üretilen katkısız nanoliflerin ortalama çapı 218 nm olarak saptanmış iken, kompozit nanoliflerin çapları 170 nm ile 203 nm arasında değişmektedir. Keçelerin ıslanabilirliğini incelemek amacı ile temas açısı ölçümleri gerçekleştirimiştir. Beklentilerin aksine, grafit oranı arttıkça ıslanabilirliğin arttığı gözlemlenmiştir. Burada, grafitin son yıllarda keşfedilen hafif düzeyde hidrofilik özelliğinin etkili olduğu düşünülmektedir. Ayrıca, bu bulguların nanoliflerin elektriksel iletkenlikleri ile ilişkileri de incelenmiştir.

Anahtar kelimeler: Elektroeğirme, Polivinilpirolidon, Grafit, Nanolifler, Islanabilirlik

1 Introduction

Due to their high surface area-to-volume ratio and high porosity, polymer nanofibers are attractive materials for a wide range of applications spanning from energy storage to biomedical applications [1]. A straightforward and cost-effective process available for the production of polymer nanofibers is electrospinning. This method allows a large-scale production of continuous nanofibers from different types of polymers [2]. The principle of this technique is quite easy. It requires a high voltage power supply, a syringe pump, a metallic collector and a polymer solution. Basically, the polymer solution is introduced into a syringe equipped with a metallic needle and pumped through a grounded metallic collector. When a high voltage is applied to the needle, a jet is ejected through the collector. The jet follows a short straight trajectory and then evolves by whipping until the collector. As the solvent evaporates during the evolution of the jet, solid continuous polymer nanofibers are deposited on the collector.

Studies on the electrospinning of various polymers exist in the literature. Among those polymers, polyvinylpyrrolidone (PVP) catches more and more attention. PVP is a non-toxic, biocompatible material with outstanding physical and chemical properties. Due to its versatility, this polymer is especially used in biomedical applications but also in other fields such as adhesives, coatings or electrical applications [3].

Many studies on the improvement of the properties of polymer nanofibers by the incorporation of fillers exist in the literature. One of the cost-effective and interesting filler for composite nanofibers is graphite. This allotrope of carbon is a natural mineral that seems to present suitability for biomedical applications. Nag et al. [4] fabricated graphite/PDMS sensors for biomedical applications. Hsin et al. [5] investigated the use of PVP-modified graphite nanofibers as catalyst supports in direct methanol fuel cells. Therefore, graphite is a good filler candidate for PVP for biomedical applications.

According to Kurusu and Demarquette [6], the wettability of PVP nanofibers is an important parameter for tissue engineering and scaffold applications.

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Therefore, the aim of this study is to investigate the effect of graphite content on the morphology and wettability of PVP/GR composite nanofibers. For this purpose, PVP and PVP/GR composite nanofiber mats of various filler contents (0.6%, 1.2%, 1.8%, 2.4%, 3%, 3.6% and 4.2 % of GR (wt.% of PVP)) were fabricated by electrospinning. The morphology and diameters of the nanofibers were characterized by scanning electron microscopy (SEM). The thermal properties of the nanofibers were investigated by differential scanning calorimetry (DSC). Then, the water wettability was examined via contact angle measurements. Finally, for a deeper understanding, the relationship of these properties with the electrical conductivity was also questioned.

2 Materials and methods

2.1 Materials

A high molecular weight polyvinylpyrrolidone with an average molecular weight of 1300 kg/mol (K85-95) was supplied from Acros Organics. Ethanol was supplied from Aytaş, Turkey (96% purity). Graphite powder (99 % purity) was supplied from Nanokar (D50 <1µm).

2.2 Preparation of PVP and PVP/GR solutions

The electrospinning solutions were prepared by dissolving PVP powder in ethanol under magnetic stirring for several hours. Solutions of PVP in ethanol of 7% (w/w) were prepared.

For the electrospinning of composite nanofiber mats, solutions of 7 wt. % of PVP in ethanol with various contents of graphite (0.6%, 1.2%, 2.4%, 3%, 3.6%, 4.2% (wt.% of PVP) were prepared. After its addition to the polymer solution, the graphite powder was dispersed using an ultrasonic homogenizer (MSK-USP-12N).

2.3 Fabrication of nanofiber mats by electrospinning

Nanofiber mats were fabricated by electrospinning of PVP and PVP/GR solutions with an in-house electrospinning device. The optimized processing conditions are given in Table 1. For each case, the polymer solution was first introduced into a 10 mL syringe equipped with a metallic needle having outer and inner diameters of 0.813mm and 0.495mm, respectively. The optimum tip-to-collector distance was fixed. Then, the polymer solution was pumped at a constant feed rate. A high voltage was applied on the metallic needle and the nanofibers were electrospun on a grounded metallic collector wrapped with aluminum foil.

Table 1. Optimal electrospinning conditions

Voltage (kV)	Tip-to-collector distance (cm)	Feed rate (mL/h)
17.5	14	1.25

2.4 Characterization

The morphology of electrospun fiber mats was characterized by Scanning Electron Microscopy (SEM) using a HITACHI Flex1000 microscope at 15 kV. SEM micrographs were used in order to determine the diameters of the nanofibers from 100 nanofibers using the method described elsewhere [7] with IMAGE J software (v.1.52i, National Institute of Health, USA).

Differential Scanning Calorimetry measurements were performed with DSC 25 (TA Instruments) calorimeter.

In order to characterize the wettability of the mats, contact angle measurements were performed using a Bohlin Scientific – Theta Flex optical tensiometer with water.

To investigate the chemical structure of PVP/GR composite nanofibers, Fourier Transform Infra-Red (FTIR) spectroscopy measurements were realized with a ThermoFisher Nicolet IS50 device equipped with an Attenuated Total Reflection (ATR) element within a range of 4000-400 cm^{-1}.

Electrical resistivity measurements were performed to characterize the electrical conductivity of the nanofiber mats using a Keithley 6517-B multimeter equipped with an 8009 resistivity test fixture. The measurements were repeated on three replicates.

3 Results and discussions

3.1 Effect of graphite content on fiber diameter and fiber morphology

The effect of filler content on fiber diameters is represented in Figure 1.

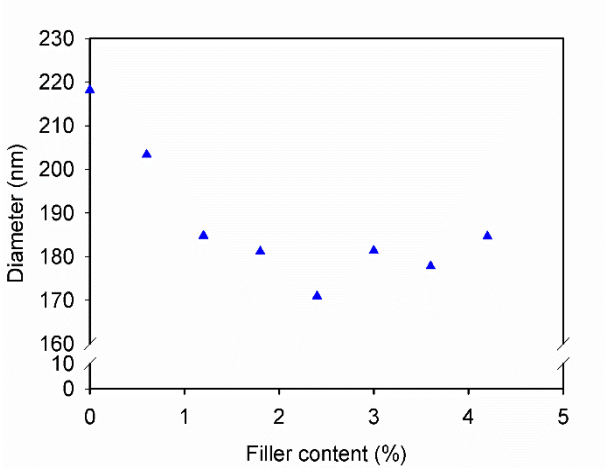

Figure 1. Effect of filler content on mean nanofiber diameter.

The unfilled PVP fibers have an average diameter of approximately 218 nm. A decrease of fiber diameter is observed with increasing GR content until approximately 170 nm for 2.4% of GR content and it stabilizes around 180 nm for higher filler contents. This evolution of the diameter of the nanofibers is in correlation with the literature. Similarly, Huang et al. [8] observed a decrease of PVP/cellulose nanocrystals/silver nanoparticle containing hybrid composite nanofibers with increasing filler content. The authors attributed this evolution to an increase of the

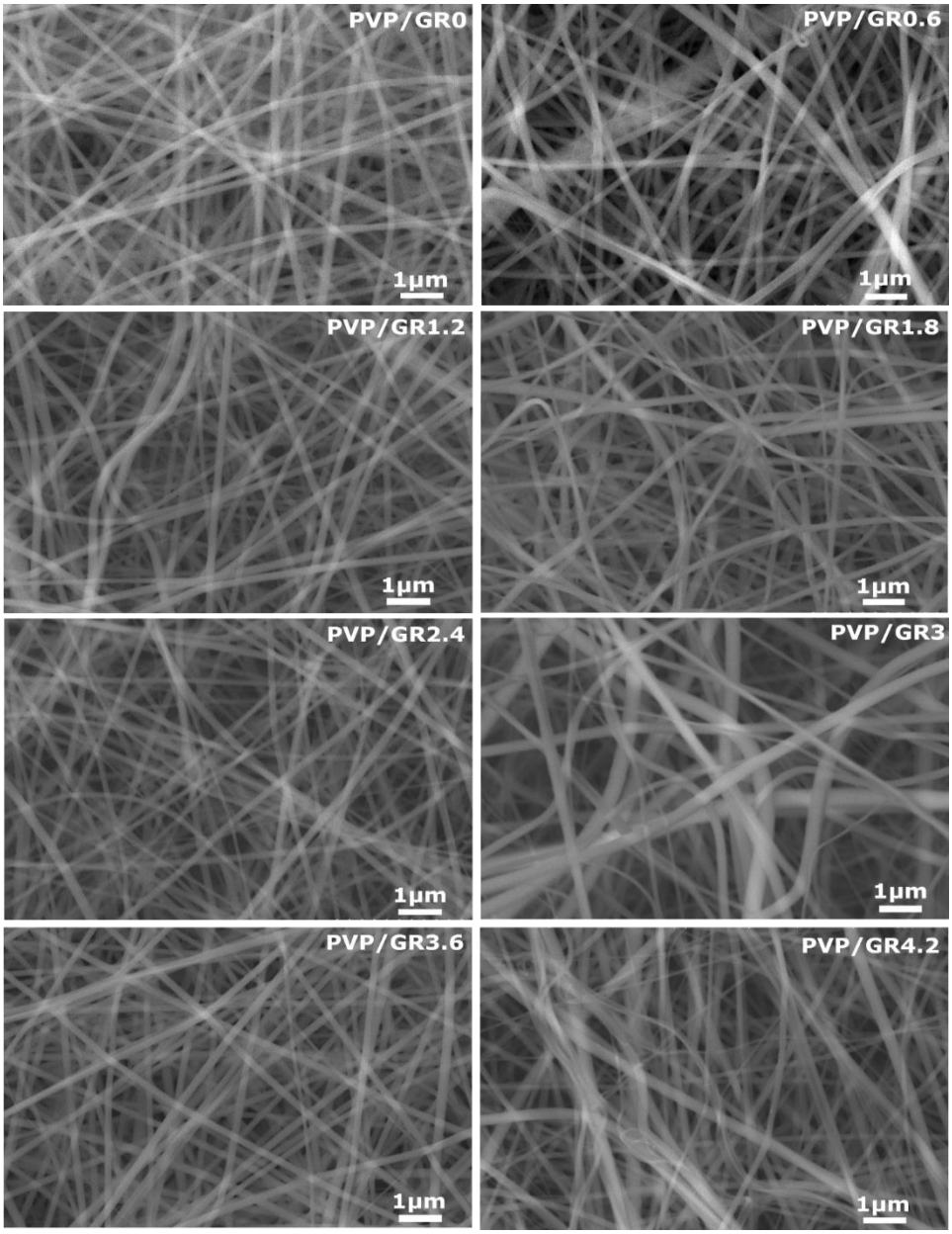

Figure 2. SEM micrographs of PVP nanofiber mat and PVP/GR composite mats with different filler contents.

surface charge of the polymer jet due to the electrical conductivity of silver nanoparticles. Therefore, strong extensional forces are applied on the polymer jet which results in thinner nanofibers when the filler content increases. This interpretation seems also valid for the composite nanofibers produced in this study as graphite increases the electrical conductivity of PVP nanofibers.

The morphology of the electrospun nanofibers was examined by Scanning Electron Microscopy. The SEM micrographs of the PVP nanofiber mat and PVP/GR composite mats with different filler contents are presented in Figure 2. In the case of PVP nanofibers (PVP/GR0), homogeneous and cylindrical nanofibers were obtained.

However, composite nanofibers mats present extra webs of very thin nanofibers with increasing graphite content. Moreover, a closer look at the PVP/GR4.2 sample shows that above 3.6%, some nanofibers have a flat ribbon morphology.

The nanofibers diameter distributions are given in Figure 3. According to these results, a narrower distribution is observed for unfilled PVP nanofibers. This result is in correlation with the morphology of the nanofibers observed in SEM micrographs presented in Figure 2. Indeed, the PVP/GR0 sample is composed of homogeneous cylindrical nanofibers. A broad distribution is observed for almost all the other samples which can be explained by the presence of extra webs of thinner fibers as shown in Figure 2. However, the fiber diameter distribution is narrower for fibers with 3.6% of GR. This result is in correlation with SEM micrograph of this sample where nanofibers with an approximately homogeneous diameter are observed. Besides, lesser extra webs are present in that case.

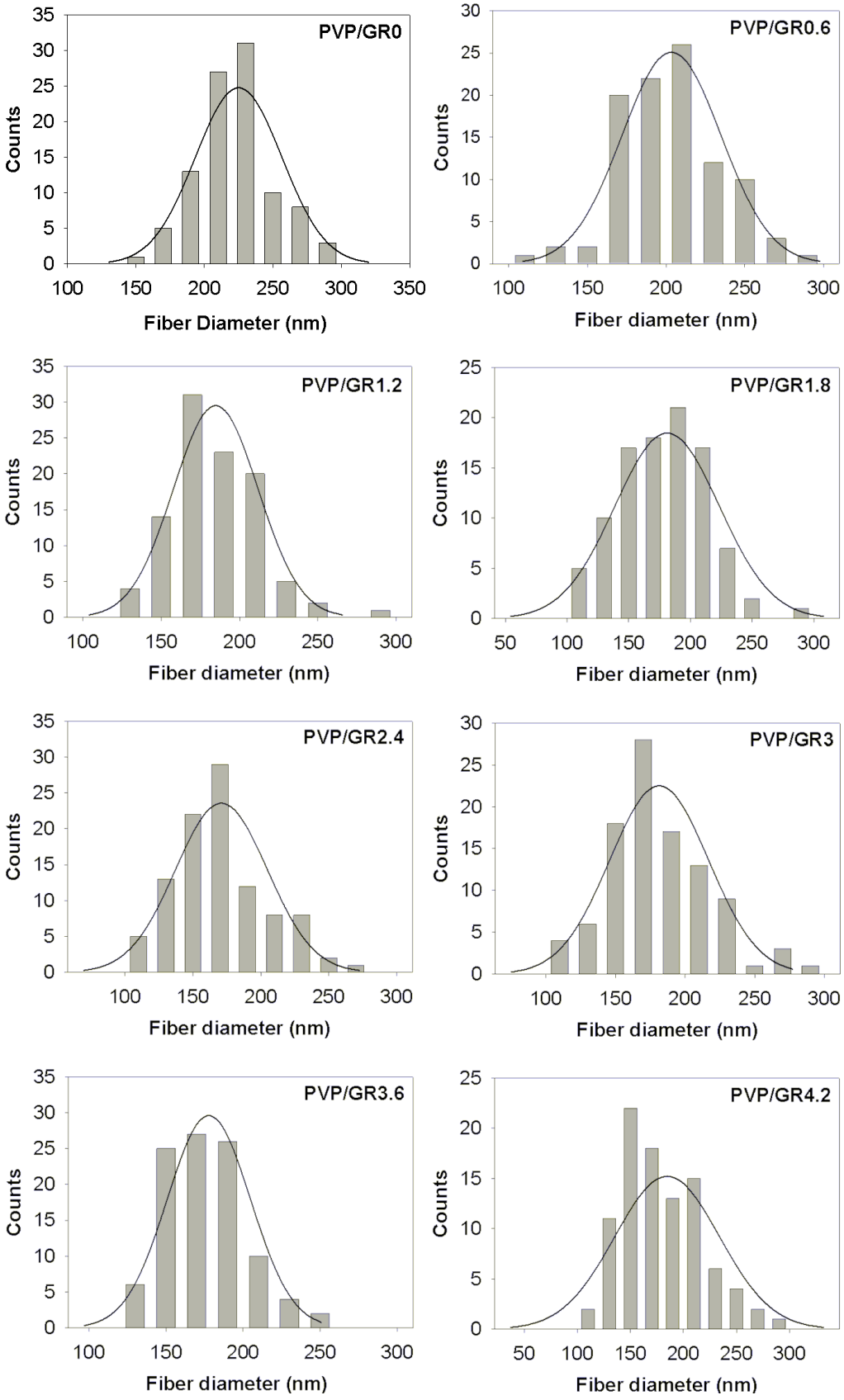

Figure 3. Nanofiber diameter distribution of PVP nanofiber mat and PVP/GR nanofiber mats with different filler contents.

3.2 FTIR analysis of PVP and PVP/GR composite nanofibers

Figure 4 presents the FTIR spectra of PVP nanofibers and PVP/GR composite nanofibers. It can be seen that all the spectra show the characteristic peaks of PVP. As there is no chemical bonding between the filler particles and the polymer, the presence of graphite has no effect on the FTIR spectra of the composite nanofibers. Especially, the characteristic PVP peak observed at 1675 cm^{-1} (carbonyl stretching (C=O)) appears at approximately the same wavenumbers for all samples. This observation is also valid for the broad absorption band around 3450 cm^{-1} corresponding to the hydroxyl stretching (-OH) which are associated with the presence of free hydroxyl group that form hydrogen bonds with residual water [9].

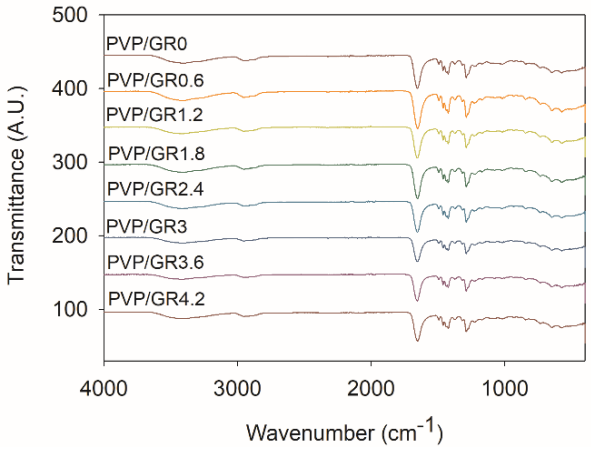

Figure 4. FTIR spectra of the nanofiber mats.

3.3 Effect of graphite content on thermal transitions

The DSC thermographs of PVP nanofiber mat and PVP/GR composite nanofiber mats with different filler contents are presented in Figure 5. For all samples, a broad endothermic peak between 50°C and 150°C is observed. The corresponding peak temperatures of the samples are gathered in Table 2. They vary between 87°C and 101°C. These results are not surprising for hygroscopic materials such as PVP and are in correlation with the literature. Adeli [10] observed the same thermal behavior for PVP (K90). The author attributed the broad endothermic peak to the dehydration of the polymer. According to the literature, it is well known in that graphite derivatives can play the role of catalysts for dehydration reactions [11]. Therefore, in the case of PVP/GR composite nanofibers, due to the presence of graphite, the dehydration of PVP occurs at relatively lower temperatures compared to unfilled PVP nanofibers.

According to La Fontaine et al. [12], PVP K90 presents a glass transition temperature of around 156°C. The authors worked with a PVP (K90 – molecular weight 1 250 000 g/mol) very similar to that one used in this study. Similar transitions are also observed with our samples.

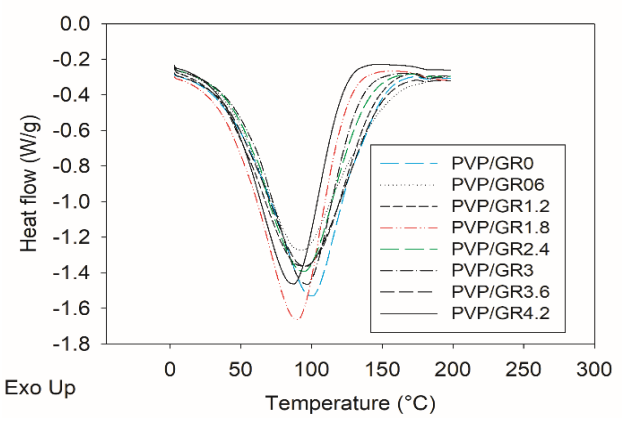

Figure 5. DSC thermographs of nanofiber mat and PVP/GR nanofiber mats with different filler contents.

Table 2. DSC thermographs of the samples.

Sample	Filler content (%)	T_{Peak}
PVP/GR0	0	100.57
PVP/GR0.6	0.6	93.26
PVP/GR1.2	1.2	94.65
PVP/GR1.8	1.8	90.58
PVP/GR2.4	2.4	94.83
PVP/GR3	3	97.17
PVP/GR3.6	3.6	96.20
PVP/GR4.2	4.2	87.50

3.4 Effect of graphite content on the wettability of PVP/graphite composite nanofiber mats

To characterize the wettability properties of the samples, contact angle measurements with water were realized at ambient temperature. The images are presented in Figure 6.

The results show that the presence of graphite filler increases the water wettability of the samples as flatter water droplets are observed for composite nanofiber mats.

The effect of filler content on contact angles is presented in Figure 7. According to this Figure, the contact angle decreases as graphite content increases until 3% and then it increases again. This evolution seems to be due to the mild hydrophilicity of graphite discovered in recent years [13].

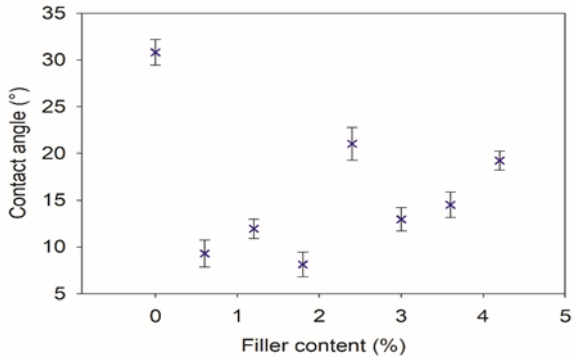

Figure 7. Effect of graphite content on water droplet contact angle on PVP mat and PVP/GR composite mats with different filler contents.

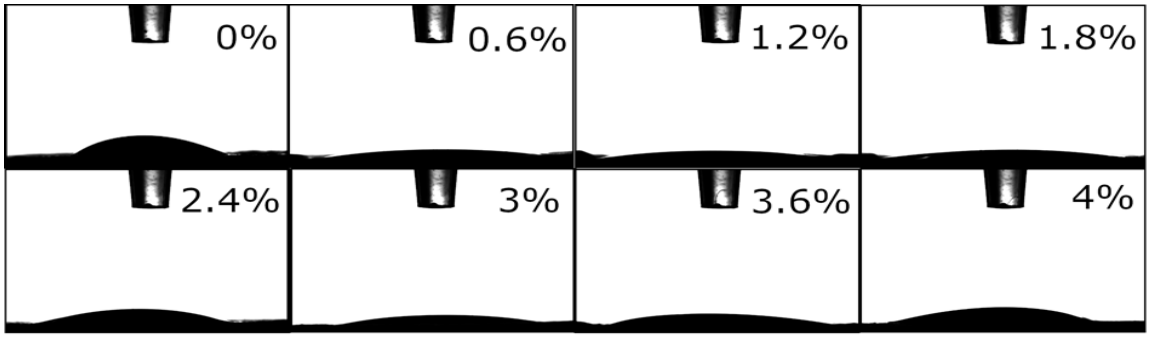

Figure 6. Contact angle images of water droplets on PVP mat and PVP/GR composite mats.

3.5 Effect of graphite content on the electrical conductivity of PVP/graphite composite nanofiber mats

For a better understanding of the wettability of the samples, the electrical conductivity of the nanofiber mats was also characterized. According to Figure 8, contact angles and electrical conductivity of the nanofiber mats have an inverse evolution: the electrical conductivity of the nanofiber mats is high when the contact angle is low. Therefore, it can be concluded that the water wettability increases when the electrical conductivity increases.

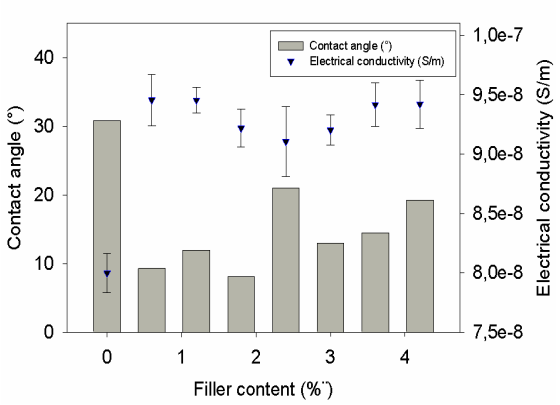

Figure 8. Graphical representation of the relationship between the evolution of the contact angles and the electrical conductivity of nanofibers with increasing GR content.

4 Conclusion

In this study, the effect of graphite content on the morphology and wettability of PVP and PVP/GR composite nanofibers with different graphite contents was investigated. Nanofibers with a PVP concentration of 7% (w/w) and graphite contents of 0.6%, 1.2%, 1.8%, 2.4%, 3%, 3.6% and 4.2 % of GR (% of PVP) were electrospun. Although homogeneous cylindrical nanofibers were obtained in the case of the unfilled PVP nanofibers, the morphology of PVP/GR composite presents extra-webs of thinner fibers or ribbon-like fibers. The water wettability of the composite nanofiber mats was higher compared to unfilled nanofiber mats. This evolution was attributed to the mild hydrophilicity of graphite.

Declaration of interests

The author declares that she has no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Similarity rate (iThenticate): %17

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