Role of Specific Interactions on Fiber Formation in the Electrospinning of Poly(vinyl phenol)/Poly(vinyl pyrrolidone) Blend Solutions

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ABSTRACT: The minimum concentration (C_i) required for electrospinning polymeric fibers from solutions of mixtures of poly(vinyl phenol) and poly(vinyl pyrrolidone) has been experimentally determined for different blend compositions. This minimum concentration C_i has its lowest value when the polymers are mixed in a 1/1 molar ratio. This article shows different results that seem to indicate that the strong hydrogen bonding interactions between the two polymers and the corresponding higher apparent molecular weight cause the reduction of the C_i value. © 2009 Wiley Periodicals, Inc. J Appl Polym Sci 114: 2922–2928, 2009

Key words: electrospinning; hydrogen bonding; fiber formation

INTRODUCTION

The electrospinning[1,2] process employs an electrostatic potential to form uniform fibers with diameters on the order of 100 nm–10 μm. The resulting fibrous mats with high-specific surface area and submicron degree of porosity have a wide range of potential applications, including filtration devices, membranes, vascular grafts, protective clothing, molecular templates, and tissue scaffolds.

Electrospinning occurs when a charged-polymer solution or melt emits a charged-fluid jet in the presence of an electric field.[3,4] The jet follows a chaotic trajectory of stretching and splaying until it reaches a grounded target, thereby completing the circuit. A jet of low-molecular-weight fluid breaks up into small droplets, giving rise to the phenomenon termed as electrospraying.[5] However, polymer fibers can be obtained using a solution with sufficient chain overlapping and entanglements. For fiber formation to occur, a minimum polymer concentration (C_i) is required. Above the critical concentration, a combination of beads and fibers is observed and, when the concentration is sufficiently high (C_f), only fibers are produced. Nevertheless, fiber quality depends also on the drying conditions.

Several investigators[6,7] have tried to establish the optimum concentration range that assures stable fiber formation. From a rheological strategy, a new critical concentration appears, the so-called entanglement concentration (C_{en}). Fibers and beads are obtained when a related parameter, the solution entanglement number $(\eta_e)_{soln}$, is close to 2 (one entanglement per chain), whereas a value of 3.5 is necessary for obtaining whole fibers.

This approach is only valid when the polymer is in a good solvent. In systems where strong interactions are present, such as hydrogen bonding,[8,9] polymer–polymer interactions cannot be disregarded. Increased interchain interactions may serve to stabilize the physical entanglements by forming additional junction points, which may facilitate fiber formation at concentrations lower than predicted. Recently, Long and coworkers[10,11] has demonstrated that sufficiently strong intermolecular interactions can act as chain entanglements.

In this work, the effect of the specific interactions in the electrospinnability of a polymer blend with strong intermolecular hydrogen bonding ability has been studied. It is well known[12] that blends of poly(vinyl phenol) and poly(vinyl pyrrolidone) (PVPh/PVP) give rise to strong hydrogen bonding interassociation. The minimum concentration required for electrospinning (C_i) has been experimentally determined for different (PVPh/PVP) blend compositions.

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EXPERIMENTAL

Materials

All polymers and solvents were used without further purification. Poly(vinyl phenol) (PVPh) ($M_w = 15{,}000$), poly(vinyl pirrolidone) (PVP) ($M_w = 1{,}300{,}000$), and dimethyl sulfoxide (ACS reagent) (DMSO) were purchased from Sigma Aldrich (Madrid, Spain).

Electrospinning

Different compositions of PVPh and PVP were electrospun after being dissolved in DMSO. All the experiments were performed three times. The electrospinning set-up used in this study included a syringe mounted in a syringe pump (Cole-Parmer), a 18-gage blunt-end needle, a ground electrode, and a Spellman CZE1000R high-voltage supply (0–30 kV CZE1000R; Spellman High Voltage Electronics Corp.) with a low-current output (limited to a few μA). The positive lead of a high-voltage power supply was connected to the syringe needle via an alligator clip. A ground (stainless steel sheet on a screen) was placed 30 cm from the needle tip. The syringe pump delivered the polymer blend solution at a controlled flow rate, which ranged from 0.07 to 0.5 mL/h, whereas the voltage was varied from 5 to 8 kV. The resulting fibers were collected on the screen to produce a sheet of nonwoven fabric.

Instrumentation

FTIR spectra were performed in a Nicolet spectrometer (Magna 560). Ten scans were signal averaged at a resolution of 2 cm^{-1}. Samples were prepared by casting onto KBr windows. DMSO was totally removed after maintaining the samples in a vacuum oven at 100°C for a minimum period of 15 days.

Rheological measurements of the polymer solutions were performed in a TA instruments ARG2 stress–controlled rotational viscoelastometer at 25 ± 2°C using a cone-plate geometry ($\varphi = 40$ mm, $\alpha = 2°$). The measurements were performed at least three times, obtaining less than 2% error.

Electrospun fiber morphology was analyzed using a Hitachi S-2700 field emission scanning electron microscope (FESEM) at 15 kV accelerating voltage. Fibers for FESEM analysis were mounted on a SEM disk and sputter-coated with an 8 nm Pt/Au layer to reduce electron charging effects. Different measurements on random fibers for each electrospinning condition were performed.

RESULTS AND DISCUSSION

Electrospinning process

After dissolving the adequate amounts of poly(vinyl phenol) and poly(vinyl pyrrolidone) in dimethyl sulphoxide (DMSO), to have solutions with different concentrations and different molar ratios, the obtained solutions were electrospun. As an example, Figure 1 shows the SEM micrographs of the structures formed from different concentrations of solutions of the 1/1 (PVP/PVPh) monomer molar ratio blend.

As Figure 1 shows, at 6 wt % polymer concentration, polymer droplets were observed, indicating insufficient chain overlap. However, at 9.2 wt % polymer concentration, fiber formation occurred in the form of thin fibers that were connected by polymer droplets ("beaded fiber morphology"). As the concentration was further increased (13.8 wt %) the fiber diameter increased and the bead number decreased. In this blend composition, the 9.2 wt % was considered as the minimum concentration to electrospinning (C_i), because this was the minimum concentration where the majority of the beads were included in the fibers. As an example, of visual reference, Figure 2 shows the photographs obtained for pure components and for the 1/1 molar relation blend at C_i.

Using the same methodology, the minimum concentration required to electrospin (C_i) was measured for blends with different molar compositions. The obtained results are summarized in Table I.

As shown in Table I, the minimum concentration is clearly lower in PVP[13] than in PVPh.[14] It is well established in Ref. 15 that this concentration is

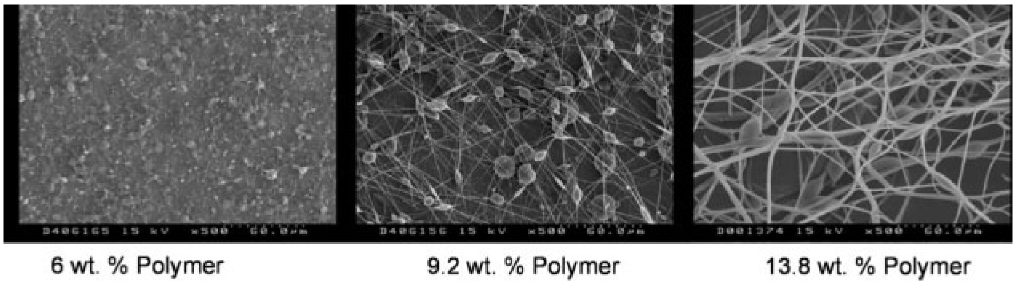
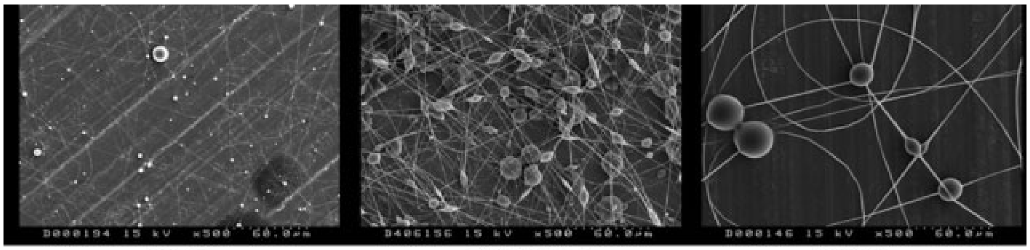


Figure 1 Photographs showing the structures that can be produced for the 1/1 molar relation blend as the concentration is increased.



PVP 1/1 Blend PVPh

Figure 2 Photographs of the fibers obtained at C_i for pure PVP, 1/1 molar ratio blend and pure PVPh.

directly related to the solution viscosity and, therefore, to the polymer molecular weight. Taking in mind that the molecular weights of the PVPh and PVP are 15,000 and 1,300,000, respectively, the lower critical concentration required in the case of PVP can be attributed to this factor. On the basis of an exclusive consideration of the effects mentioned earlier, the blends would have C_i values between those obtained in the pure components (12–50%). However, this is not the case for blends with 4/1, 2/1 and 1/1 molar ratios, because they show C_i values lower than those obtained with the pure polymers.

The diameter of the fibers and the electrical conductivity of the solutions are also shown in Table I. It is generally accepted that for a pure polymer, the diameter of the fiber increases with the concentration and decreases with the electrical conductivity. As we have previously stated, the minimum concentration for obtaining fibers from the 2/1 and 1/1 PVP/PVPh molar ratio blends is lower than the obtained in pure PVP. However, in these blends, the obtained fiber diameter is higher than the obtained in pure PVP. Although the changes in the electrical conductivity could explain this behavior, in Ref. 10, it has been shown that the hydrogen bonding association can also give rise to larger fiber diameter.

Rheological measurements

In an attempt to explain these results, the viscosity of the solutions at the precise C_i concentration was measured at different shear rates. In all cases, viscosity showed a linear behavior in the range of the shear rates used in this work, allowing a newtonian (η_0) to be determined. The obtained results are shown in Table I.

According to the results shown in Table I, the newtonian viscosity of the solutions at the minimum electrospinning concentration has different value, being the viscosity of the 1/1 blend clearly lower. Although the solution viscosity depends on the investigated concentration and this parameter has the lowest value in the 1/1 molar ratio blend, it must be emphasized that this blend has a high ability to form fibers, generally ascribed to a high viscosity. These results suggest that the solution viscosity is not the main (or, at least, the only) factor that is affecting the ability of fiber formation in this system.

Several authors[6,15] have shown that the minimum concentration required for fiber formation (C_i) is near the entanglement concentration (C_{en}), at which chain entanglements in the solution become significant.

To calculate the entanglement concentration[16] (C_{en}), the newtonian viscosity of each blend was measured at different DMSO concentrations. The obtained results are shown in Figure 3. As can be seen, for each blend, the viscosity shows a change in the slope at the entanglement concentration (C_{en}).

According to the results shown in Figure 3, the entanglement concentration (C_{en}) in the blends is

TABLE I
Minimum Concentration for Electrospinning, Entanglement Concentration, Newtonian Viscosity Values at C_i, Fiber Diameter at C_i, and Conductivity Values at C_i, for Different Blends

Molar composition (PVP/PVPh)	1/0	4/1	2/1	1/1	1/2	1/9	0/1
C_i (wt %)	12.0	11	10.1	9.2	12.8	29	50.0
C_{en} (wt %)	4.3	7.6	7.2	6.1	10.3	[a]	[a]
η_0 (Pa.s)	0.39	0.36	0.31	0.14	0.34	3.87	122
Diameter (μm)	0.5	[a]	1.4	1.0	1.5	[a]	1.6
σ (S/m)10^{-4}	17.7	[a]	15.2	8.7	8.8	[a]	[a]

[a] Not measured data.

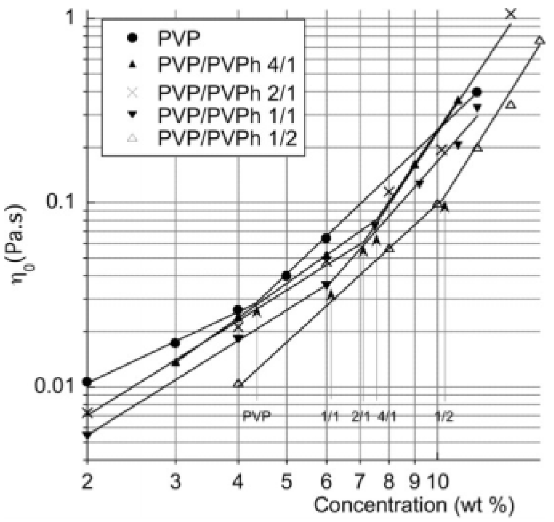
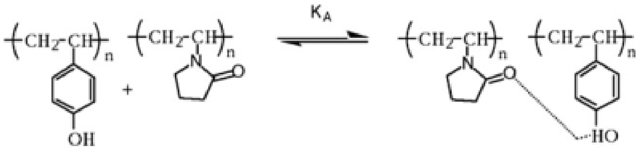


Figure 3 The η_0 dependence on concentration for different molar ratio blends.

higher than the value obtained in pure PVP. This result can be explained on the basis of the molecular weight of the PVP used in this work, much higher than that of the PVPh (M_w PVP = 1,300,000; M_w PVPh = 15,000). It is well known that the number of entanglements increases with polymer chain length or molecular weight, so C_{en} should decrease when the molecular weight increases. In the case of the blends, we can suppose that the average molecular weight will decrease when the PVPh fraction increases. Consequently, the C_{en} will increase when the PVPh concentration increases. However, the C_{en} value in the 1/1 blend is lower than the obtained in the 4/1 and 2/1 blends, although according to the mentioned hypothesis this value should be higher.

As it has been stated in Ref. 6, the entanglement concentration can be related to the fiber formation ability. Table I shows the values obtained for the entanglement concentration and the minimum fiber formation concentration obtained by electrospinning the different blends.

According to the data presented in Table I, the minimum concentration for electrospinning is always higher than the entanglement concentration. Nevertheless, if focus our attention on the difference between the two concentrations, it is clearly apparent that the values of these concentrations in the blends are closer than in pure PVP. This result shows that the spinnability of the blends is more favorable than that of pure PVP. Moreover, in comparing the values of the different blends, it is remarkable that in the case of the 1/1 molar ratio, both the entanglement concentration and minimum fiber formation concentration show their lowest values.



Scheme 1 Hydrogen bonding interassociation between PVP and PVPh.

Hydrogen bonding interaction

The poly(vinyl phenol)/poly(vinyl pyrrolidone) blends present important specific interactions via hydrogen bonding association that could be related to the fiber formation ability.[12,17] The carbonyl group of PVP gives rise to strong hydrogen bonding interactions with the hydroxyl of PVPh.[18,19] This equilibrium can be described by a constant, named K_A that is depicted in scheme 1.

Two equilibrium constants are required to describe phenolic self-association; one describing the formation of dimers, K_2, and another describing the formation of higher multimers, K_B ("chains" of hydrogen-bonded hydroxyl groups).[20]

Different PVP/PVPh blends were prepared and their infrared spectra were recorded. Figure 4 shows the infrared spectra obtained for different blends in the 1750–1550 cm^{-1} region.

In the spectra shown in Figure 4, the broad band near 1680 cm^{-1} is assigned to the carbonyl stretching vibration, whereas the two other bands at 1610 and 1590 cm^{-1} are related to the phenolic ring stretching vibrations. In the carbonyl region, the spectra show two different spectral contributions. The first one,

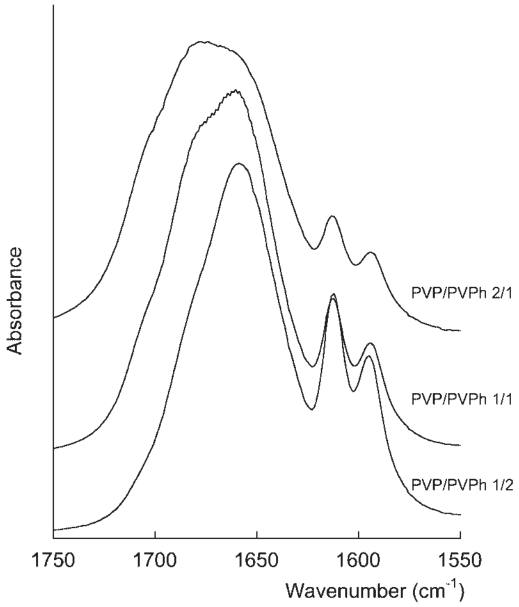


Figure 4 Scale expanded infrared spectra for PVP/PVPh blends at different molar ratios.

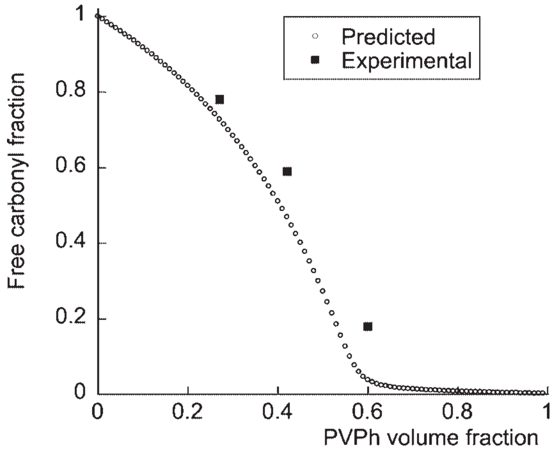


Figure 5 Predicted and experimental free carbonyl fraction as a function of the blend composition.

localized at higher wavenumber can be assigned to the free carbonyl of the PVP (1680 cm^{-1}) and the second one centered at 1660 cm^{-1} is assigned to the PVP carbonyl associated with the phenolic hydroxyl groups.[18]

Keeping in mind these assignments, it can be observed that the relative area of the hydrogen-bonded species increases when the PVPh concentration in the blend increases, the PVP/PVPh 1/2 molar ratio blend showing the highest association level in the carbonyl stretching vibration.

Considering now the PVP/PVPh 1/1 and 2/1 molar ratio blends, the infrared spectra show that the carbonyl association is lower, but in these blends, the excess of phenolic groups must be also lower than the obtained in the 1/1 blend. In fact, if the measurements had been done in the hydroxyl region, the blends with lower poly(vinyl phenol) percentage would have shown the highest level of interassociation. Unfortunately, the OH stretching region is not amenable to the analysis of the hydrogen bonding. Nevertheless, an adequate analysis based on FTIR measurements will allow an estimation of the free and associated-hydroxyl fractions.

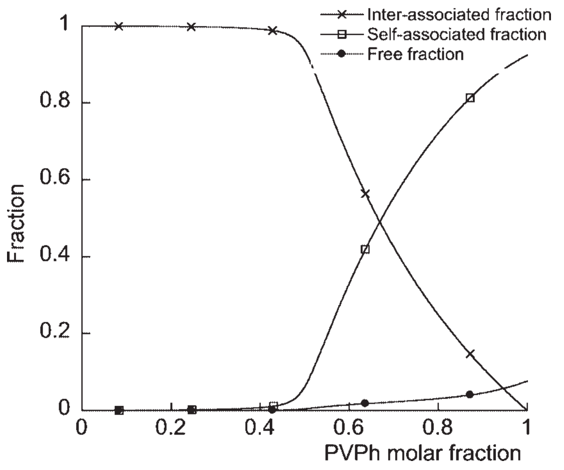


Figure 6 Prediction of the free, self-associated and interassociated hydroxyl fractions as a function of the blend composition.

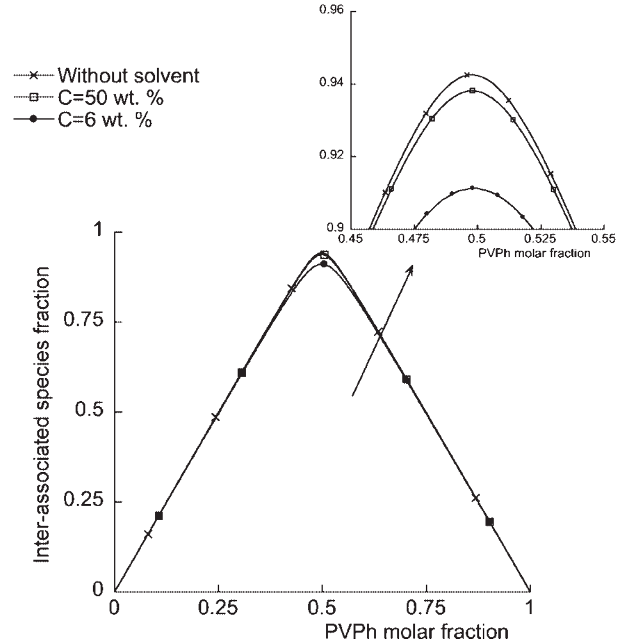


Figure 7 Calculation of the fraction of interassociated species as a function of the blend composition for samples without solvent and for 6 and 50 wt % in DMSO.

The values of the free and associated-hydroxyl and carbonyl groups can be theoretically calculated if the values of the constants describing the hydroxyl self-association (K_2 and K_B) and the value of the phenol/pyrrolidone interassociation (K_A) are known. The values of these constants can be found in Refs. 18, 19, and from these values, the calculation of the system total association as a function of the blend composition is feasible. These calculations are based in the methodology described by Coleman et al.[21]

FTIR data obtained in this work can be used to test the validity of the interassociation constant (K_A) obtained in literature. To perform such analysis, the carbonyl stretching region was separated in its two individual bands (free and associated) using a curve resolution program (Spectra fit). The free carbonyl fraction was calculated using eq. (1).

$$f_l = \frac{A_f}{A_f + A_{\mathrm{as}}/1.31} \tag{1}$$

where A_f and A_{as} are the areas of the peaks corresponding to free and associated-carbonyl groups, respectively, and 1.31 is the ratio of the two molar extinction coefficients (taken from literature).[18]

Using the values of $K_2 = 21.6$, $K_B = 66.8$, and $K_A = 5800$, taken from Refs. 18, 19, the free carbonyl fraction can be theoretically predicted. Figure 5 compares the predicted free carbonyl fraction values with the experimentally obtained.

As can be seen in Figure 5, there is a good agreement between the experimental and predicted data. Nevertheless, the experimental free fraction is, in all cases, slightly higher than predicted. In looking for an explanation, it is necessary to point out that the free carbonyl fraction has been obtained at room temperature, where the system is clearly below the glass transition temperature, in a nonequilibrium situation. However, the theoretical predictions assume that the blend is in an equilibrium situation. This fact can be responsible of the higher free fractions observed experimentally.

Using again the equilibrium constants calculated in literature (which were proven valid in the previous section), these fractions can be theoretically predicted. The results of this calculation are shown in Figure 6.

The free hydroxyl fraction has a very low value regardless of the blend composition. On the contrary, almost all the hydroxyl groups are interassociated upto a PVPh molar fraction in the vicinity of 0.5, whereas the self-associated hydroxyl groups are prevalent when the phenol molar fraction is higher than 0.9.

The experimental- and predicted-infrared data presented in the preceding sections have been obtained for polymer blends without solvent. However, in the electrospinning process, the polymer blend is dissolved in dimethyl sulphoxide and this fact makes difficult the acquisition of good infrared data. Nevertheless, these data can be calculated using the equilibrium constants as will be shown in the next section.

First, we assumed that there is not interaction between the solvent (DMSO) and the polymers. Although this assumption could sound incorrect, the polymer/solvent association constant will be clearly lower than the associations occurring in the polymers. Keeping in mind these suppositions, the fraction of total interassociated species (hydroxyl and carbonyl) as a function of the PVPh/PVP blend compositions has been calculated for the system without a solvent and for two different polymer concentrations (6 and 50 wt % in DMSO). The obtained results are shown in Figure 7.

In the data shown in Figure 7, regardless the polymer concentration, a maximum in the interassociated species fraction is obtained in the 0.5 molar composition blend. Moreover, in the 0.5 molar ratio blend, the interassociated species fraction slightly decreases with the system dilution, but it has high values even at relatively low concentration (6%). This means that in concentrations similar to those used in the electrospinning process, the interactions between the two polymers are still relevant as a consequence of the high value of the interassociation equilibrium constant.

All the obtained results show a possible relation between the ability of hydrogen bonding and the electrospinnability of the blends. In our opinion, the hydrogen bonding interassociation between the two polymers gives rise to new species with apparent molecular weight higher than that of the pure isolated polymers. It is well established that for a given polymer an increase in the molecular weight implies a decrease in the minimum concentration for obtaining fibers so the minimum observed in the equimolecular molar ratio could be related to an apparent increase of the polymer molecular weight.

CONCLUSIONS

Blends of PVP and PVPh show an enhanced electrospinnability compared with those of the pure components due to the strong interassociation existing between the phenolic hydroxyl of PVPh and the carbonyl of PVP. In the PVP/PVPh 1/1 molar ratio blends the interactions are optimized and the minimum concentration for obtaining fibers by electrospinning is considerably lower. In general terms, it can be concluded that the formation of hydrogen bonding in polymer blends can be an effective way to reduce the minimum fiber obtaining concentration.

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