Solution NMR Evaluation of Polyvinylpyrrolidone and Collagen Interaction

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Abstract: *Polyvinylpyrrolidone (PVP) is a water soluble polymer with a large number of commercial uses. This commercial success derives from its biological compatibility, low toxicity, film-forming and adhesive characteristics, unusual complexing ability, relatively inert behavior toward salts and acids, and its resistance to thermal degradation in solution. Because of these diverse properties, PVP finds important applications in the pharmaceutical, food, beverage, cosmetic, toiletry and photographic industries. The main purpose of this work is to evaluate the microstructure of PVP/collagen employing solution NMR, in order to better understand the blend behavior of polymer-polymer interactions. The PVP/collagen mixtures present signals from both polymers and the signals from C=C and/or aromatic C can be a source of information on polymer/polymer miscibility. Thus, other NMR measurements, such as 1D spectral simplification, attached proton test (APT) and 2D HETCOR will be part of the NMR methodology used to characterize this polymer/polymer system.*

Polyvinylpyrrolidone (PVP) is a water soluble polymer with a large number of commercial uses. This commercial success derives from its biological compatibility, low toxicity, film-forming and adhesive characteristics, unusual complexing ability, relatively inert behavior toward salts and acids, and its resistance to thermal degradation in solution.[1] Because of these diverse properties, PVP finds important applications in the pharmaceutical, food, beverage, cosmetic, toiletry, and photographic industries. Today, it has been currently used for medical purposes, especially when it is blended with a protein, and collagen is one of those that can be blended with PVP.[2] As blending in polymers occurs in the amorphous region, it is necessary to investigate such a region. We carried out this investigation using ^{13}C solution NMR.[3,4,5] The main purpose of our work is to evaluate the microstructural features employing solution NMR to better understand the blend behavior of polymer-polymer interactions.

NMR analyses were carried out in a MERCURY 300, operating at 75.4 MHz. The ^{13}C solution NMR spectra were recorded with 20% w/v (polymer/solvent) in two deuterated solvents (water–D_2O and dimethylsulfoxide-DMSO), applying 90° pulse and 1s of delay.

PVP and collagen were analyzed by ^{13}C solution NMR using two solvents, namely, D_2O and DMSO. According to the spectra, it can be seen that for PVP both solvents presented good quality in terms of solvent-polymer interaction. Therefore, the carbonyl region presented different splitting as a response of microstructure assignment. Collagen was also soluble in both solvents. However, a distinct difference in the spectral resolution was observed. The collagen water solution showed better spectral resolution. The collagen DMSO spectrum shows signals that are broader than those in water, which is attributed to the strength of polymer/solvent interaction. Also, 20 carbonyl and 5 methyl resonances were found, among other signals. Accordingly, we prepared the membrane mixtures using DMSO as solvent for both polymers, and recorded NMR analyses using D_2O to obtain good

spectral resolution.

The membrane films of PVP/collagen at different ratios (90/10, 80/20, 70/30 and 50/50) obtained by DMSO solution were first analyzed by ^{13}C solution NMR, and a range of chemical shift values for the blends investigated are listed in Table 1. It is worth pointing out that all signals are narrow, which can be evidence that some miscibility between blends components can be occurring.

Table 1. ^{13}C solution NMR assignments of membrane films of PVP/collagen

PVP/collagen	Assignments (ppm) C=O	C=C and/or aromatic	aliphatic
100/0	**176-174**	-	**50-20**
90/10	180-160	140-110	80-10
80/20	180-160	140-110	80-10
70/30	180-160	140-110	80-10
0/100	**180-160**	**140-110**	**80-10**

The carbonyl blends signals also showed distribution sequences of microstructures that can be assigned in the systems. Both the number and values of chemical shift for these microstructures did not change comparing to those of the initial polymers because the interaction process occurs with the same strength for all types of carbon, as it is an unselective process.

The mixtures present signals from both polymers and the signals from C=C and/or aromatic C can be a source of information about polymer/polymer miscibility.

Thus, other NMR measurements such as 1D spectral simplification, namely attached proton test (APT) and 2D HETCOR should be part of the NMR methodology used to characterize these polymer/polymer systems. Solid state analyses to obtain information on polymer blends miscibility can thus be conducted using relaxation times.

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