

COMPATIBILITY STUDY ON NANOCELLULOSE AND
POLYETHERSULFONE BASED BLENDS

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The compatibility of a nanocellulose/polyethersulfone blend system was studied by viscometric methods, scanning electron microscopy (SEM), polarized optical microscopy (POM) and Fourier transform infrared spectroscopy (FTIR). The viscometric methods and polarized optical microscopy results were obtained for the blended solution with the weight fraction of polyethersulfone in the range of 0-1.0. Meanwhile, the scanning electron microscopy, infrared spectroscopy and differential scanning calorimetry results were obtained for the transparent films cast from the blended solutions that contained a 0.04 weight fraction of NCC and a 0.18 weight fraction of polyethersulfone. The results demonstrated that partial compatibility existed in the blend system, which may result from the strong hydrogen-bonding interaction between the hydroxyl group of NCC and the sulfonyl group of polyethersulfone.

Keywords: nanocellulose, polyethersulfone, blend system, hydrogen-bonding, compatibility

INTRODUCTION

Membrane separation processes represent an efficient separation technology, which meets the demand of energy saving, high productivity and environmental protection for modern industry.¹ Polymer blends can be effective for expanding the scope of membrane materials, by endowing the blend membranes with a variety of polymer properties. Thus, a polymer blend can make up for the lack of certain material properties, and improve the properties of ultrafiltration membrane.²

Polyethersulfone (PES) has excellent overall properties and is often used to prepare polymer membrane materials.³ It possesses excellent membrane-forming properties and high thermal/chemical stability, with the disadvantage of its high cost.⁴ Another major limitation is its hydrophobicity, which causes easy adsorption of hydrophobic particles in the liquid on the surface of PES membrane materials, leading to membrane fouling. Cellulose is a renewable, biodegradable and the most abundant organic raw material in the world, which has become widely used at an industrial level.⁵ It is very likely that cellulose

will be a major chemical resource in the future.⁶ The good hydrophilicity and specific surface area of nanocellulose can make up for the hydrophobicity of polyethersulfone membranes and improve their pore structure. To achieve this, finding suitable solvent systems that would both dissolve nanocellulose and provide a feasible reaction environment is a prerequisite.

To the best of our knowledge, most studies available in the literature on this topic are mainly focused on the preparation of NCC/PES membranes, while rarely discussing the compatibility of NCC with PES. This investigation aims to provide theoretical basis for membrane preparation. Also, the research into new solvents of nanocellulose in the past decades, has pointed out that a good solvent should allow better control of the substitution degree, a more uniform distribution of substituents along the polymer chain, and a higher conversion yield. As a result, N,N-dimethylacetamide (DMAc)⁷ has been investigated for this purpose, due to its high thermal stability, strong resistance to hydrolysis and low corrosiveness. It is one of the most

efficient solvent systems for nanocellulose, its dissolving capacity could reach 13 wt%,⁸ but it can also dissolve PES.

This study deals with the compatibility between nanocellulose and polyethersulfone in blends. The membranes were prepared from blends of nanocellulose and polyethersulfone *via* the phase inversion method induced by immersion precipitation. The miscibility of the nanocellulose/polyethersulfone blend system was studied by determining absolute viscosity and by analyzing its structure during phase separation. The structure of the membrane was investigated by scanning electron microscopy (SEM), Fourier transform infrared spectroscopy (FTIR) and differential scanning calorimetry (DSC). Blending nanocellulose and polyethersulfone can result in an interesting system, which might find broader applications.

EXPERIMENTAL

Materials

Nanocellulose (laboratory-made, average dimensions of $40 \pm 16 \times 327 \pm 120$ nm), N,N-dimethylacetamide (DMAc) and polyethersulfone (PES) were supplied by Changchun Jilin University Special Plastic Engineering Co., Ltd. (China). All the other reagents were of analytical grade and used as received.

Preparation of blend membranes

Blend membranes were prepared by mixing two separate homogeneous solutions. Firstly, the homogeneous solution of nanocellulose (4 wt%) was prepared by using DMAc as solvent. Secondly, the homogeneous solution of PES (18 wt%) was prepared by using DMAc as solvent as well. Then, the casting solution was prepared by uniformly mixing together the two solutions in the required ratios and stirred at 90 °C for one hour. The casting solution was cast on a glass plate using a doctor blade and the blade height was 0.12 mm. The blend membranes were prepared by the phase inversion technique.⁹ After 10 seconds, the glass plate was immersed in a water bath. The membrane sheets were stored in deionized water for 48 h to remove the residual DMAc completely and obtain the membrane. Because of their high influence on the performance of the membranes, the thermodynamic conditions were maintained constant throughout the process.¹⁰

Viscometric method

Viscosity measurements of the casting solutions were made in a glass constant temperature water bath at 25 ± 0.1 °C, using an Ubbelohde dilution viscometer. Every value was measured three times and then averaged.

Polarized optical microscopy (POM)

Polarized optical microscopy analysis (POM) of the NCC/PES blend solution was carried out on an Olympus polarizing microscope at 200x magnification, at room temperature.

Scanning electron microscopy (SEM)

SEM is an important tool for determining the morphology of the membranes. The morphology of the membranes can be used to ascertain the structure of pores and subsequently would be helpful in identifying the mechanism of the formation of pores.¹¹⁻¹³ SEM images were taken on a JSM-6700F scanning microscope. The sample was coated with a thin layer of gold in vacuum before examination.

Differential scanning calorimetry (DSC)

One of the most commonly used methods to estimate the compatibility of polymer blends is to determine the glass transition temperature (T_g) and compare it to those of the component polymers. NCC, PES and the membranes were scanned with a Netzsch STA2500 at a heating rate of 10 °C min⁻¹ in nitrogen atmosphere from room temperature to 250 °C.

Fourier transform Infrared Spectrophotometric analysis (FTIR)

KBr disk infrared (IR) spectra were recorded using a TENSOR27 FTIR spectrometer in the range of 4000-500 cm⁻¹, after the samples were dried.

RESULTS AND DISCUSSION

Viscosity method

The blends of NCC and PES were prepared in DMAc with different PES dosages, of 0, 20%, 40%, 60%, 80%, 100%. The solution viscosity can represent the compatibility of a polymer blend solution. It has been reported that the plots for compatible blends are linear, otherwise the plots are s-type.¹⁴ The plots of relative viscosity *versus* concentration were non-linear, as shown in Figure 1, suggesting that the two components of the blend were partially compatible. Upon the addition of PES, the viscosity of the solution increased, as a function of the increasing amount of the components in the system. The increase in viscosity may be also explained by the association between the two components *via* hydrogen bonding of the hydroxyl-sulfonyl functional groups. Then, when the PES dosage was above 80%, there was a sharp decrease in the relative viscosity. This phenomenon may occur because of an excessive amount of PES. In the present study, the viscosities were calculated by Eqs. (1)-(3):

$$\eta_r = t / t_0 \quad (1)$$

where t and t_0 are the flow time of the sample solution and DMAc, which is 1 mol/L, respectively.

$$\eta_{sp} = \eta_r - 1 \quad (2)$$

$$[\eta] = \sqrt{2(\eta_{sp} - \ln \eta_r)} / C \quad (3)$$

Polarized optical microscopy (POM)

The changes that the casting solutions underwent in morphology were studied with a view to understanding the effects of hydrogen bonding. When the two phases were compatible, a homogenous transparent solution could be observed. Otherwise, separate phase boundaries

would be noticed. According to the mechanical properties of the membranes and pure water flux we tested in an earlier study,⁴ we confirmed that the most suitable blending ratio for PES and NCC was 18:1. Polarized optical microscopy was performed at room temperature. The micrographs shown in Figure 2 (from a to d) represent the different reaction stages. The system was homogenous and transparent as the reaction progressed. No phase separation was observed after the membrane was allowed to stand for 7 days. Therefore, it could be concluded that NCC and PES are compatible or, at least, partially compatible.

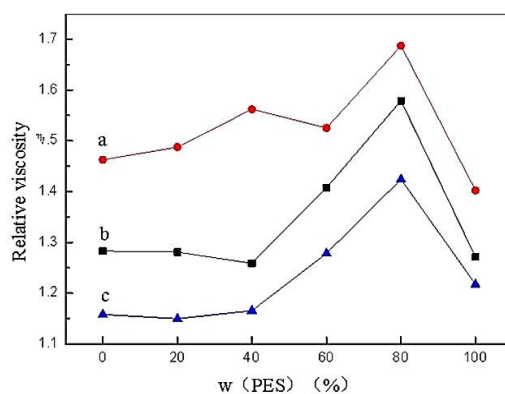


Figure 1: Dependence of relative viscosity on the composition of NCC/PES blends; the curves represent various solution concentrations: (a) 0.62 g/100 mL; (b) 0.32 g/100 mL; (c) 0.16 g/100 mL

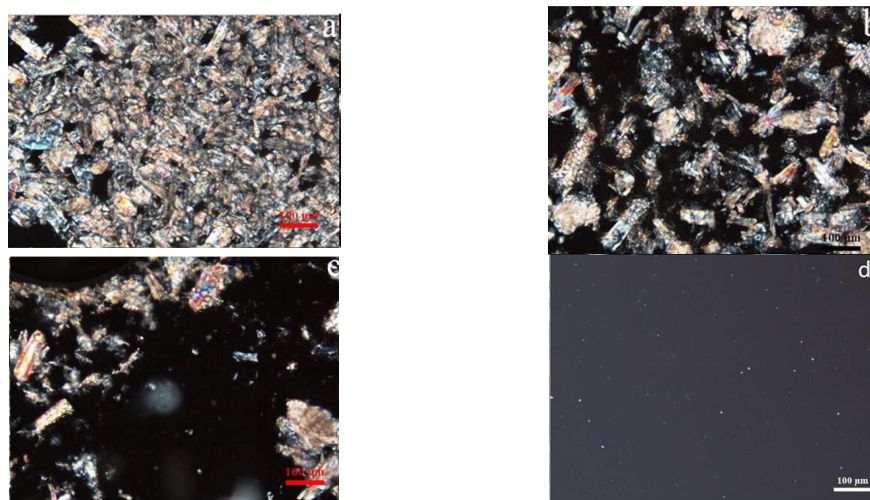


Figure 2: POM micrographs for different reaction stages of the NCC/PES blend system: (a) 1h; (b) 1.5h; (c) 2h; and (d) 3h

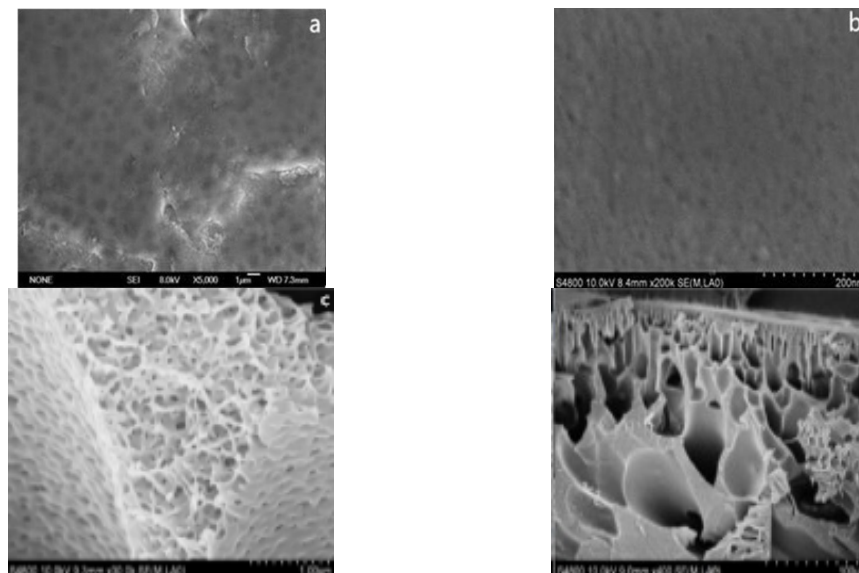


Figure 3: SEM images of the distribution of (a, c) pure PES membrane, (b, d) NCC/PES composite membrane (c, d – cross-section)

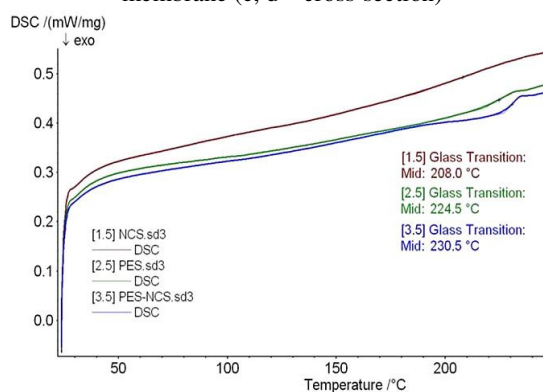


Figure 4: DSC curves of PES, NCC and composite membrane

Scanning electron microscopy (SEM)

SEM images of both the pure PES membrane and of the NCC/PES composite membrane are presented in Figure 3. As may be noted in Figure 3, the morphology of the pure PES and NCC/PES membranes is homogeneous. No obvious phase separation is visible upon the addition of PES to NCC. Interestingly, the images reveal that the surface roughness of the blend films increased, which indicates that the polymers are partially compatible.

Differential scanning calorimetry (DSC)

The compatibility of the major components of the blend membrane is important when considering its possible applications, and one of

the most commonly used methods to estimate the compatibility of polymer blends is by determining the glass transition temperature (T_g) of the blend, in comparison with those of the component polymers. For this reason, DSC thermograms of NCC, PES and their blends were recorded and shown in Figure 4. If there is no molecular interaction or repulsion in a compatible system, a miscible polymer blend would exhibit a single glass transition temperature (T_g) between the T_g s of their components. On the opposite, incompatible blends would show two T_g s.¹⁵ Figure 4 reveals that the NCC/PES blends exhibited a single T_g , with an intermediate value between the T_g s of the initial polymers, NCC and PES, indicating the compatibility of the blends.

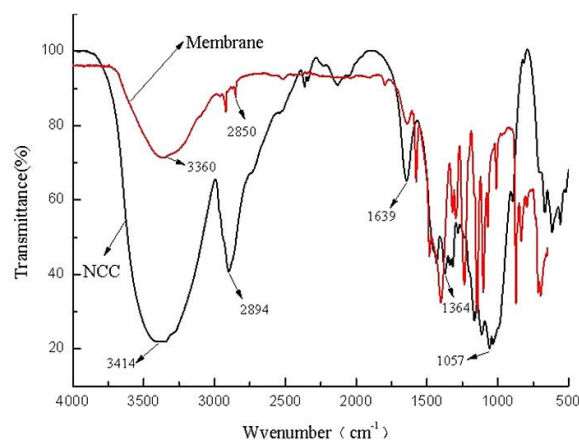


Figure 5: FTIR spectra of NCC and NCC/PES blend membrane

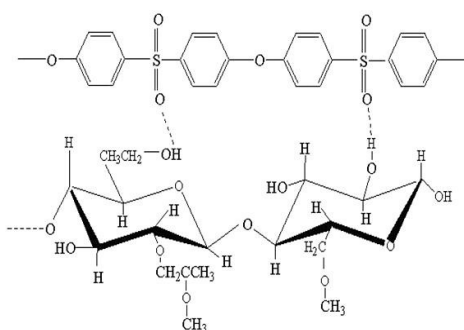


Figure 6: Schematic representation of hydrogen bonding between NCC and PES

Fourier transform infrared spectroscopy analysis (FTIR)

The liquid blends were cast on clean glass plates, and as NCC and PES blended, they were subjected to FTIR analysis to obtain an insight into the structural changes that occurred. Figure 5 presents the FTIR spectra of the NCC and NCC/PES blend membrane. As can be seen from the figure, the spectrum of NCC shows the O–H stretching vibration at 3414 cm^{-1} and the characteristic C–O absorption peak at 1057 cm^{-1} . Moreover, the spectrum also exhibits characteristic peaks of nanocellulose at 2894 cm^{-1} , 1639 cm^{-1} and 1364 cm^{-1} . The presence of hydrogen bonding in the membrane could be inferred from the shape and intensity of the absorption band of the hydroxyl stretching vibrations in the FTIR spectra.¹⁶

When observing the curves in Figure 5, some difference may be noted between them: a shift of the peaks at $3750\text{--}3000\text{ cm}^{-1}$ occurred in the transmission band of the NCC/PES blends in comparison with that of pure NCC. This shift suggests that relatively little interaction takes place between the polymers. The hydroxyl

stretching vibration band shifted to a lower wavenumber upon the addition of PES. Thus, the bands of hydroxyl stretching vibration had a 54 cm^{-1} red shift relative to a free hydroxyl, while they varied markedly with the hydrogen bonding interactions between the –OH belonging to NCC and the S=O belonging to PES. A schematic hydrogen bond between NCC and PES is shown in Figure 6.

CONCLUSION

Considering the methods used in this investigation, it appears that the viscosity method was the most simple, while accurately reflecting the changes in the system and the compatibility between the components. Based on the theoretical calculations of viscosities, we concluded that this binary blend system was partially compatible.

The compatibility results were confirmed by SEM, POM, DSC and FTIR analyses in this investigation. The compatibility of the binary system may be due to the hydrogen-bonding interactions between the hydroxyl groups and the sulfonyl groups during blending. This research indicates that the compatibility of the blending

polymers can be measured and which is of help in the search for novel filter membrane materials with desired properties.

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