

Near infrared spectroscopy for the quantitative determination of mass transfer kinetic during water vapour absorption by a polymer solution

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Introduction

The immersion process has been used to fabricate polymeric membranes in industry.¹ By this method, a polymer solution is cast onto a mirror and then immersed in a coagulation bath for a few minutes. The final morphology depends on the mass transfer between solvent and non-solvent, and the process parameters (relative humidity, temperature). Although the immersion process has been used mainly in industry, the high exchange rate of mass transfer between non-solvent and solvent makes it difficult to follow water diffusion into polymer solution. Vapour induced phase separation (VIPS) is a process whereby a polymer solution is exposed to a non-solvent (water vapour) but the mass transfer between solvent and non-solvent is slower than the immersion process. The vapour absorption can be followed by using near-infrared (NIR) spectroscopy. The work to be described aimed at using NIR² to determine the water concentration in the polymer solution, as the mass transfer of solvent and non-solvent before phase separation.

Materials and methods

Preparation of polymer solutions

The polymer used in this study was polyethersulfone (PES) Ultrason E6020P provided by the BASF company. The polymer solutions were prepared by dissolving the proper amount of PES in N-Methyl-2-pyrrolidinone (NMP). NMP of anhydrous grade was supplied by Sigma-Aldrich (Germany) and used without any further purification. 12 by wt% and 25 by wt% polymer solutions

were prepared by stirring at room temperature during five days in a glove box, where the relative humidity (RH) was kept below 7%. The dope solutions obtained were used within a week after being prepared.

Experimental procedure involved to determine kinetics of water absorption by the polymer solutions

The water absorption by polymer solutions was determined both by gravimetric and spectrometric measurements. Figure 1 shows the schematic diagram of the experimental set-up.

The polymer solution was first introduced into a 10 mm spectroscopy rectangular quartz cell. The depth of polymer solution was 18 mm. Experiments were carried out in a static mode, i.e. without any air circulation. The open cell was placed in a closed vessel at $40 \pm 1^\circ\text{C}$, with an atmosphere at a fixed RH controlled by a saturated salt solution (NaCl for 75%RH). Fourier transform near infrared (NIR) spectroscopy in transmission mode was used to measure the transfer of vapour water within an elementary volume of polymer solution. NIR spectra were recorded every 30 minutes using a Perkin Elmer Spectrum One NTS equipped with tungsten-halogen lamp having a quartz envelope as the light source and a deuterated triglycine sulphate (DTGS) detector. The instrument was driven by the Spectrum V3.02 software from Perkin Elmer for data scanning and processing. Four scans were averaged at 4 cm^{-1} resolution in the range of $9100\text{--}5950\text{ cm}^{-1}$. The size of the light spot was set equal to 2.5 mm diameter, and the analyses were performed at 7 nm, 11 nm and 15 mm under an air solution interface. Chemometric analysis was achieved using

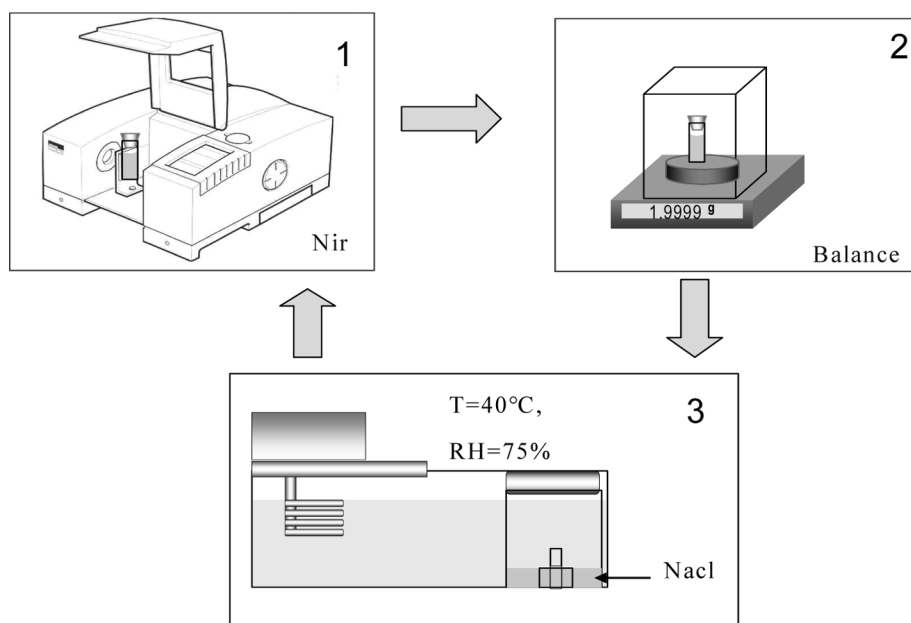


Figure 1. Experimental set-up designed to follow water absorption kinetics under controlled RH and T.

the statistical spectrum Quant+ v4.51 software from Perkin Elmer. A set of 38 standard solutions with well-defined composition of PES (from 12 to 26 wt%–), NMP (from 69 to 88 wt%–), and water (from 0.1 to 10 wt%–) was then prepared and two spectra were obtained for each sample. This collection of 76 spectra was used to build the calibration model. The calibration model was then validated by full cross validation.

Results and discussion

The NIR transmission spectra are shown in Figure 2.

All spectra were processed with a predictive model based on PCR, using the range 9100–5950 cm^{-1} because in this area of the NIR spectrum separate absorption bands can be attributed to each compound. The absorption bands corresponding to the compounds mixed in the solution were found at 7000 cm^{-1} , 6900 cm^{-1} and 6450 cm^{-1} for water, 8800 cm^{-1} and 6000 cm^{-1} for PES and 8516 cm^{-1} , 8307 cm^{-1} and 7300 cm^{-1} for NMP. In NIR spectroscopy, it is difficult to attribute bands to a single molecular structure because of the overlapping of the absorption bands corresponding to the different chemical bonds. The absorption maximum located at 6900 cm^{-1} is assigned to the first overtone of the OH-stretching band of the water molecule. The strong absorption band at 6000 cm^{-1} was assigned to the first overtone of the aromatic group found in PES molecules.³ NIR spectra are mainly composed of overtone and combination bands due to the hydrogen stretching vibration. The complex nature of the NIR spectra requires data interpretation through mathematical

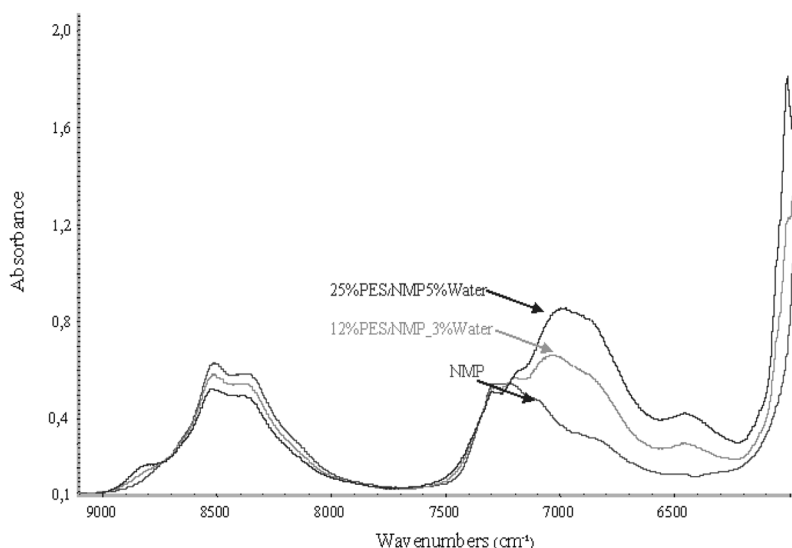


Figure 2. NIR transmission spectra of pure NMP, 12%PES/NMP3%Water, and 25%PES/NMP/5%water solutions.

Table 1. Calibration results of the model developed to predict the composition of the PES/NMP/Water solutions (cross-validation)

Range (cm ⁻¹)	Property	SEC (wt-%)	SECV (wt-%)	SEC/SECV
9100 to 5950	Water	0.066	0.069	0.959
9100 to 5950	NMP	0.153	0.158	0.968
9100 to 5950	PES	0.212	0.218	0.971

and statistical approaches. Quantitative determinations were realized to obtain the composition of the solution. The calibration results of the model are presented in Table 1.

The low values obtained for *SEC* and *SECV* indicated that the mass fraction of the three compounds could be reliably predicted by NIR with a PCR algorithm. The ratio *SEC/SECV* is very close to 1. This means that the accuracy obtained in calibrations on the composition of the solution deduced by NIR spectroscopy are acceptable. The variation of the water mass fraction within a 12 and 25 wt-% PES/NMP solution at 40°C and 75%RH is shown in Figure 3.

For both concentrations, a slight difference of water concentration gradient occurred between points 1,2 and 3, which is increasing with time. Moreover, the comparison between a low and high concentration solutions showed evidence of the influence of the polymer concentration on the water diffusion rate. For 25% PES/NMP, at 7 mm, a modified water transportation was found in the polymer solution before phase separation.

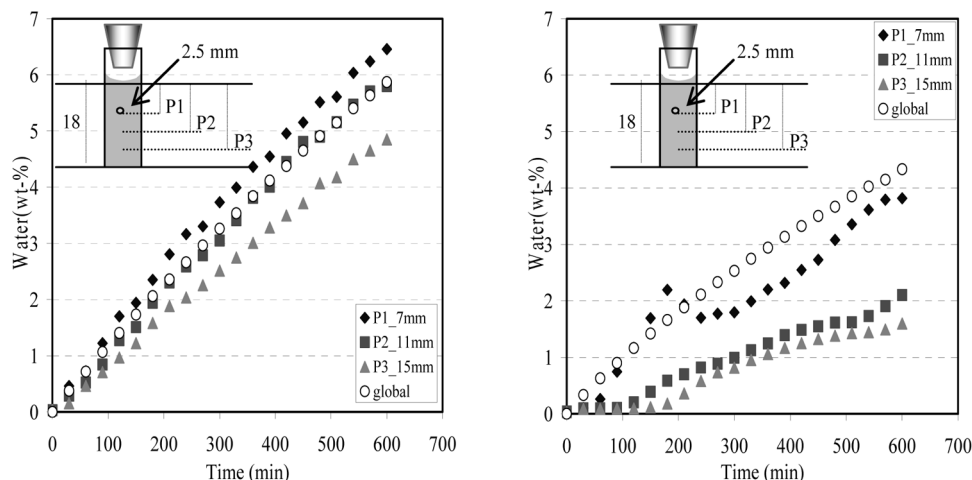


Figure 3. Variation of the water mass fraction within a 12 and 25 wt-% PES/NMP solution at 40°C and 75% RH.

Conclusions

The experimental NIRS setup for following the vapor water/polymer solution relationships, combined with the PCR method can be employed to predict the profile of water concentration before phase separation. Polymer concentrations have a strong influence on the water vapour transfer in the polymer solution.

References

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