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Kinetics of mass transfer during vapour-induced phase separation (VIPS) process and its influence on poly-(vinylidene fluoride) (PVDF) membrane structure and surface morphology

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ABSTRACT

The aim of our researches is to study the interplay between membrane morphology and elaboration parameters during non-solvent induced phase separation (NIPS) processes. The present investigation is to correlate the solvent-nonsolvent mass transfer kinetics with the structural morphology and properties of polymeric membranes obtained via water vapour induced phase separation (VIPS) process. For the first time, we have monitored and quantified mass transfer kinetics during VIPS process on homogeneous solution of poly-(vinylidene fluoride) (PVDF) dissolved at two different temperatures in NMP, using near IR spectroscopy (NIR) with chemometric model. A significant change in mass transfer rate (i.e., water penetration) has been observed much earlier than the liquid demixing of the polymer solution occurs for two studied dissolution temperatures. Consecutively to the water penetration, modifications in the physical state (gelation) of the polymer started to occur prior to reaching demixing process. This phenomenon was discussed in terms of macromolecular organization of PVDF caused by the decrease of the solvency power. It is assumed that this physical evolution of the polymer solution influences the phase separation mechanisms and thus the obtained surface and structural morphology of the PVDF membranes.

Keywords: Mass transfer; Nonsolvent; Water; Vapor-induced phase separation (VIPS); Poly-(vinylidene fluoride) (PVDF); Membranes; Crystallization; Morphology; Near IR spectroscopy

1. Introduction

Poly(vinylidene difluoride) (PVDF) can be used to fabricate wide variety of membranes as it is semi-crystalline polymer whose crystalline phase provides good thermal stability while the amorphous phase adds some flexibility to the membrane. Their crystallization process and crystallinity can be controlled by experimental parameters. This allows us to tune the surface and structural morphologies depending on the applications, for example, microfiltration and membrane distillation require membranes with larger surface pores. Besides microfiltration, microporous PVDF membranes are used in biology for immuno-blotting techniques [1], and have a high potential as a separator in lithium batteries [2] in membrane contactors [3] Membrane distillation can desalinate seawater using low-grade heat energy or solar heat, but it has limited

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mass fluxes and membrane fouling issues. To overcome these issues, hydrophobic membranes which exhibit better antifouling ability and higher flux than those of existing polymer membranes can be used even at high salt concentration, owing to their high chemical and thermal stabilities and water-repelling ability [4].

Majority of the polymeric membranes have been prepared by phase inversion/separation process in which, homogeneous polymer solution becomes thermodynamically unstable due to external forces and phase separates [5,6]. It can be induced of any or combination of the following driving forces i.e., temperature [7], nonsolvent [8], chemical reactions [9], and shear stress [10]. Among them, the non-solvent induced phase separation has been a versatile method for controlling the structural morphology, surface energy, crystallization, porosity, and performance of the membranes. Membrane formation of semi-crystalline polymer is typically affected by crystallization and liquid-liquid (l-l) demixing. Depending on the thermodynamic and kinetic parameters, the demixing process of the homogeneous polymer solution dramatically influences the morphology of the final material. When a non-solvent in liquid phase i.e., wet/immersion process, comes in contact with polymer solution, mass exchanges between the polymer solution and coagulation bath is very rapid. However, this process is generally associated with the formation of macrovoid in the membranes which can limit their many industrial applications [11]. To overcome or slow down the mass exchanges, the vapour phase of nonsolvent is used to induced phase separation i.e., vapour induced phase separation (VIPS). Mostly, water vapour is used, as the phase inversion can be strongly influenced by relative humidity. In the last decade, VIPS process has gained increasing interest from industries and academia, because of its advantages esp. control over mass exchange and variety of surface and structural morphologies. Recently VIPS process has been adopted to develop drug delivery and coating devices [12], self-cleaning superhydrophobic membranes [13].

Recently we have employed VIPS method to prepare PVDF membranes by varying temperature of dissolution (T_d), time of exposure to the water vapor before immersion in water bath [14]. We found that these variations have significantly affected the surface and structural morphologies and so the performance of the membranes. The existence of a critical dissolution temperature (T_{cri}) was also found to be ~40°C. With the solution of lower T_d (32°C) ($<T_{cri}$) the membranes with lacy (bicontinuous) structure were obtained. With solution of higher T_d (60°C), the obtained membranes were composed of polymer nodules. Still it has been unclear that how the solvent-nonsolvent exchange kinetics affect the membrane formation during VIPS process with varying T_d. Thus, the analysis of mass transfer associated with VIPS becomes very important for determining the composition path on the phase diagram and better understanding on the membrane morphology building.

In the present study, we employed near infrared (NIR) spectroscopy as a non-destructive technique for following on-line kinetics of water penetration/absorption during VIPS, for the first time with PVDF. As we obtained two different morphologies with the solutions dissolved at different T_d, we have investigated the kinetics with solutions of T_d below and above T_{cri}. Then, the kinetics has been further correlated to the structural and surface morphologies of PVDF membranes obtained.

2. Experimental

2.1. Materials

Poly(vinylidene fluoride) (PVDF) (Kynar 760, M_n: 4,44,000) as pellets was purchased from Elf Atochem. The solvent, N-methyl pyrollidone (NMP) as anhydrous grade was obtained from Fluka chemicals and used without any further purification.

2.2. Polymer solutions

Initially, PVDF (0–25 wt.%) was dissolved in an aprotic polar solvent N-methyl pyrollidone (NMP) at 58 ± 2°C for 2 h. Solutions were cooled and degassed by allowing to standby for 15–20 h at room temperature. Binary solutions of i) water in NMP which was dissolved at room temperatures and ii) PVDF in NMP were mixed to obtain ternary (PVDF, water in NMP) standard solutions. The possible number of standards is limited by the domain of polymer solubility. The demixing takes place as soon as the binodal curve in the ternary phase diagram of the given system is reached (i.e., <9 wt.% of water). These solutions were used for further analysis within a week after preparation.

2.3. Near infrared spectroscopic analysis

The solvent and a range of both binary and ternary standard solutions were analyzed using Perkin Elmer ONE NTS near IR spectrophotometer at room temperature for developing a chemo-metric quantification method.

2.4. Mass transfer analysis

Mass transfer analysis was performed with two solutions dissolved at 32°C for 5 d and 60°C for 2 h. Both the solutions are homogeneous and transparent.

The polymer solution was first introduced into a 10 mm rectangular cuvette specific to near infrared (NIR) measurements. The depth of the polymer solution was 15 mm. The ratio surface area/volume was calculated to be ca 0.066 mm^{-1}. Experiments were carried out in static mode, by exposing the open cuvette to atmospheric relative humidity about 97.6 ± 0.6%, in a thermostatic (22 ± 1°C) vessel containing saturated aqueous solutions of potassium sulphate (K_2SO_4). Water absorption was monitored by performing NIR spectral analysis at 3 different positions of cuvette with a preset 2.5 mm diameter of NIR light beam. Keeping the dimensionless position (z) as 1 at air/solution interface, the analysis was performed at $z = 0.92$, 0.66, 0.40 in one case, and $z = 0.87$, 0.62, 0.38 in another. The cell was repetitively taken out the vessel at regular given times and closed with a PTFE lid to prevent atmospheric water vapor absorption. In addition, the overall mass evolution was determined with time by weighting it on a precision balance. The cell was then placed again in the closed vessel. These operations were conducted as quickly as possible to not disturb the water absorption experiments. The overall mass variation of the polymer solution i.e., overall mass (wt.%), was calculated from gravimetric data using Eq. (1);

$$\text{Overall mass (wt.\%)} = \frac{m_t - m_i}{m_i} \times 100 \qquad (1)$$

where m_t is the mass of polymer solution (polymer, solvent and absorbed water) at a given time t and m_i the initial mass of the polymer solution.

3. Results and discussion

3.1. Quantification method

The near IR spectroscopy is effectively used to analyze the changes in chemical species, using their combination and overtone regions in vibrational spectrum. Perkin Elmer software 'Spectrum Quant + v4.51' was used to process the standard spectra and quantify the concentration of water, PVDF and solvent (NMP). A quantitative model were developed using PLS regression [15] the studied properties being the water, the solvent and the polymer weight fraction in the ternary systems. A set of standard solutions with determined water weight fraction was prepared for different PVDF concentrations. The calibration models were validated by full cross validation. They allowed us to predict the kinetics of water absorption and the evolution of the composition of the polymer solutions. The prediction accuracy of the calibration models was evaluated by considering the Standard Error of Calibration (SEC) and the Standard Error of Cross Validation (SECV). SEC gives an indication of the fit quality of the regression and is described as the square root of the residual variance divided by the number of degrees of freedom (Eq. 2).

$$\text{SEC} = \sqrt{\frac{\sum_{i=1}^{n_s}\left(\hat{y}_i - y_i\right)^2}{n_s - n_f - 1}} \qquad (2)$$

where $\hat{y}_i$ denotes the predicted property value for the ith standard; y_i is the property value for the ith standard; n_s is the number of standards and n_f is the number of factors. SECV gives an estimate for the standard error of prediction (SEP), that is, the magnitude of the error expected when independent samples are predicted using the model. In the cross-validation calibration, one standard is removed at a time from the calibration and the PLS model is built using the n_s–1 standards. The removed standard is then predicted using this model. This is done for each standard in the calibration set. The SECV is calculated from the following equation (Eq. 3):

$$\text{SECV} = \sqrt{\frac{\sum_{i=1}^{n_s}\left(\hat{y}_i^{(i)} - y_i\right)^2}{n_s - 1}} \qquad (3)$$

where $\hat{y}_i^{(i)}$ denotes the predicted property value for the ith standard when it was dropped from the PLS. This formula provides a very fast way for estimating the error to be found in the property values when predicting them. SEC gives an indication of the accuracy of the calibration and of the quality of the data fitting between the property of the standard samples and the predicted property value. Therefore, SEC should be either as close as possible to zero, or in the same order of magnitude as the error of the reference method, in this study the gravimetric absolute error (Table 1).

SECV evaluates the accuracy of the model to predict unknown sample. It should be also as low as possible. In that context, a SEC/SECV ratio close to unity means that the model is as good in calibration as in validation.

NIR spectra were analyzed at dimensionless position 0.92 ($z = 1$ interface), during the VIPS. Upon time,

Table 1
Calibration method results from PLS model

Properties	No. of latent variables (LV)	SEC (wt.%)	SEP (wt.%)
Water	4	0.14	0.15
PVDF	5	0.30	0.32
NMP	5	0.35	0.36

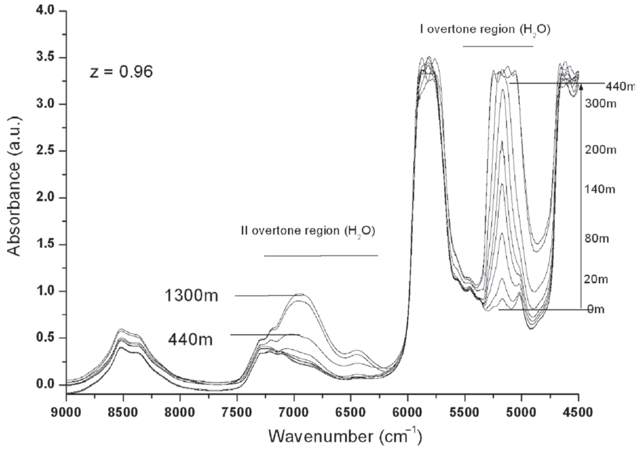


Fig. 1. Near IR spectra of PVDF (20%, T_d 60°C) solution obtained at different time (min.) during VIPS at dimensionless position $z=0.92$ (where $z=1$ is interface).

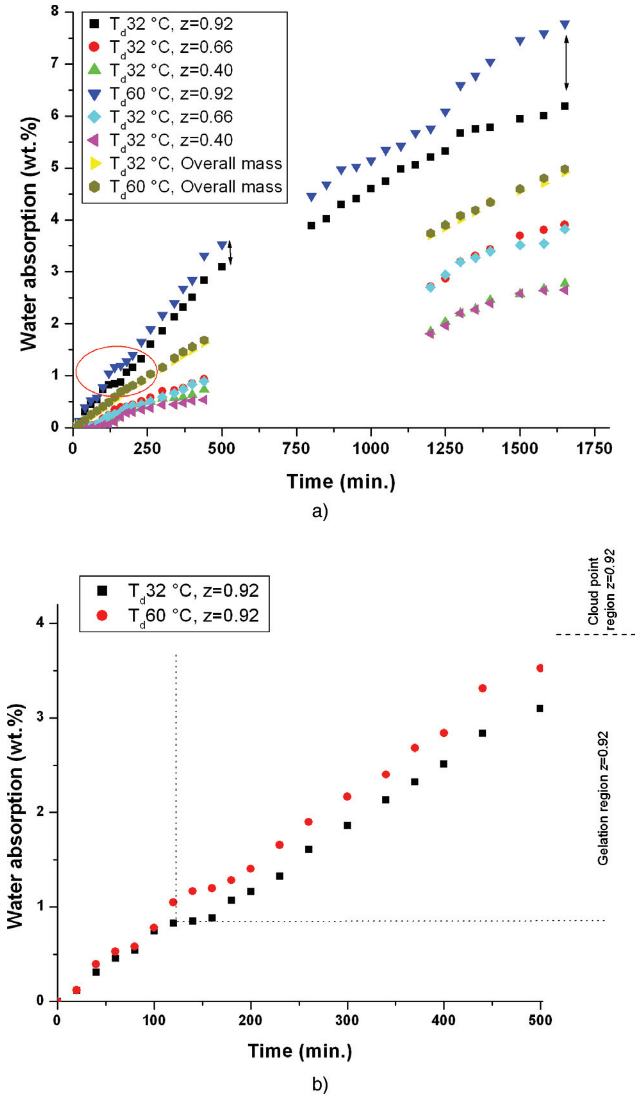
an increase in absorbance can be observed in Fig. 1 at 5000–5400 cm^{-1} and later at 6500–7250 cm^{-1} with a maximum peak 5170 cm^{-1} and 6990 cm^{-1}, respectively, which are assignable for inclusion of water.

Because of variation in diffusion rate upon depth, there may be a possibility of gradient in the concentration of water, within 2.5 mm spot of analysis. However, the quantified values are still valid, as the trend will not be much affected by this gradient.

3.2. Water absorption

The quantified water concentrations in polymer solutions upon time of exposure to the VIPS conditions are shown in Fig. 2. It can be observed in Fig. 2a that overall mass of the solution linearly increases with increasing time for both the dissolution temperatures.

However, a careful examination, the increase in water mass fraction at different depths in the solution, shows the existence of water concentration gradient. Near the interface, after 200 min, there is a significant variation in the rate of absorption. The water absorption is relatively higher after 700 min, for the solution of higher T_d (60°C) than that of lower T_d (32°C). In Fig. 2b, it can be seen that there is plateau or reduced rate of absorption around 140–200 min and thereafter the rate is slightly increased, for the spot just below the interface ($z=0.92$). This plateau is repeatedly observed even with other (amorphous) polymers (e.g., polyethersulfone (PES), polyetherimide (PEI)) also esp. when the polymer concentration is higher than 15 wt.% [16]. The initial time and duration of this plateau with those polymers depend on their solvency in presence of water. This implies that there may be a slight modification in macromolecular organization from its mother solution. During the plateau level at $z=0.92$, the observed water concentrations are 0.83 ± 0.2 and 1.16 ± 0.2 wt.% for the solution dissolved at 32°C and 60°C respectively. We assume that this concentration of water can be a minimum/threshold concentration of water to cause any physical modification of polymer chains in the solution and/or change in rate of absorption. It should be mentioned that during and after the plateau level, translucent behavior at interface layer of the solution was observed. This peculiar behavior associated with the plateau in water absorption kinetics can be attributed to the formation of gel by which physical modification of polymer chains occurs much earlier than the liquid-liquid demixing during the phase separation process.



a)

b)

Fig. 2. Water absorption kinetics during VIPS in PVDF solutions at different depths a) Overall water absorption and b) water absorption near the interface ($z=92$) for shorter period (upto 500 min).

3.3. Nonsolvent induced gelation

It is well reported that liquid-liquid demixing is responsible for the initiation and growth of the pores in membrane in nonsolvent induced phase separation method. However, the gelation is also reported to play an important role in fixing the pore structure and skin formation of the membranes. Gelation is typically defined as formation of three-dimensional network that contains predominantly liquid. During gelation, the connecting elements occur in the initial liquid and provide mechanical strength to the gel to be self-supporting. These connections can be either chemical bonding or physical association. In our system, it is not chemical bonding to occur but physical organization which is initiated by nonsolvent i.e., water penetration. Recently, Sukitpaneet et.al [17] reported with simulations that smaller amount of water is required relatively than that of other weaker nonsolvents to collapse the PVDF chains. According to the molecular dynamic simulations, radius of gyration of PVDF chain is 24.98 Å and 18.91 Å in NMP and Water/NMP mixture. Thus, when the water is absorbed by the polymer solution in which macromolecular chains are extended or uncoiled, those chains will try to collapse themselves to reduce. However, in comparison of immersion, in VIPS process, water absorption is slower. The delayed time allows the polymer chains to crystallize during collapsing. Thus, the gelation can be attributed to the formation of crystalline phases in the solution near the interface ($z = 0.92$) as shown in the Fig. 3. The difference observed in the membrane morphology may be correlated to the influence of the dissolution temperature on the size and number of crystalline nuclei as on the distance and/or interconnections between them (Fig. 3a). The formation of crystalline aggregates in polymer/solvent/nonsolvent ternary mixtures was observed earlier with of cellulose acetate [18], polypropyleneoxide (PPO) [19] and PVDF [20]. Thus, gelation occurs before L-L demixing, because of formation of crystalline domains, predominantly in case of lower T_d. This gelation could significantly influence the further mass transfer kinetics by reducing the rate of water penetration near the interface and ultimately the phase separation process to result in different structural morphologies (Fig. 3b and 3c).

3.4. Composition paths on ternary phase diagram

Fig. 4 shows the composition paths observed during VIPS compared with simulated ternary phase diagram for PVDF, NMP, and water system. In comparison, it can be observed that composition observed at interface layer shows the lower polymer concentration for the solution of higher T_d (60°C). In this solution, the precipitation was visually observed after the VIPS process.

In comparison with kinetic data, the water absorption in the solution of higher T_d is higher and faster. The solution with lower T_d ($<T_{cri}$) may contain many pre-nuclei embryos for crystallization throughout the solution. Unlike the solution with higher T_d ($>T_{cri}$) which may contain very less quantity of pre-nuclei embryos, as the water concentration increases, the solution with lower T_d may form network of crystalline domains. Such a network formation may prevent the polymer chains to contract completely. However, in the solution of higher T_d,

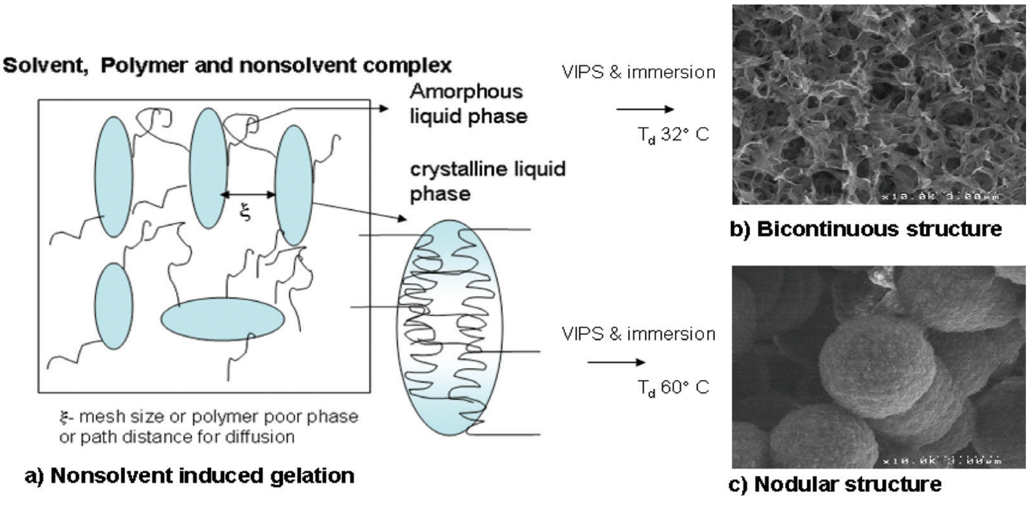
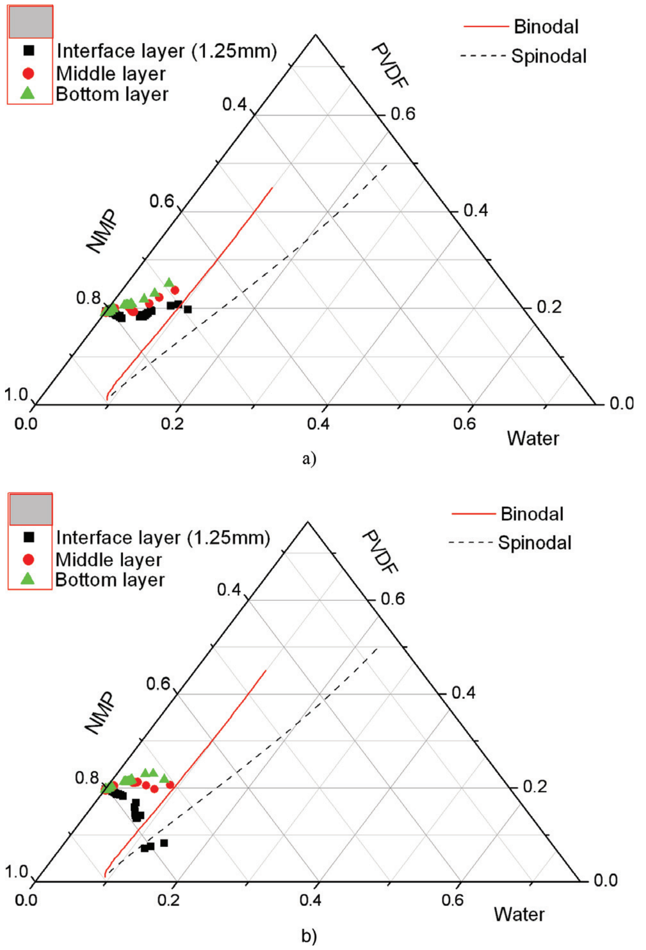


Fig. 3. a) schematic representation of nonsolvent induced gelation (via formation of crystalline domains) near ($z = 0.92$) the interface and its influence on surface morphology (b, c) of the membranes obtained from the solution of b) lower T_d (32°C) and c) higher T_d (60°C).



a)

b)

Fig. 4. Composition paths a) 32°C and b) 60°C in the ternary phase diagrams compared with simulated binodal and spinodal lines.

the contraction of polymer chains may be possible. During VIPS exposure, they contract and form self-seeded nuclei for crystallization with increasing water concentration. This leads to precipitation of polymer chains in the solution of higher T_d.

3.5. Relationship between kinetics and morphological aspects

The lower water absorption and gel formation in the solution with lower T_d can be related to the lower mobility and formation of network of polymer-rich phase. This may be related to the bicontinuous structure obtained (Fig. 3b). The higher water absorption and precipitation in the solution of higher T_d can be correlated to the higher mobility, disentanglements and slippage of the polymer chains. Further more, the mobility of polymer chains and the self-seeded nuclei for crystallization can be assigned for the formation of polymer nodules/bigger crystals on the surface of the membranes obtained (Fig. 3c).

4. Conclusions

In the present work, we have successfully developed a model for monitoring the kinetics of mass transfer during water vapor induced phase separation (VIPS) by near IR analysis. The results from water absorption kinetics indicated the possibilities of physical modification (i.e., gelation) of polymer chains in the solution very earlier than the liquid-liquid demixing. The gelation in the polymer solutions of both dissolution temperatures ($T_d < T_{cri}$ & $T_{cri} > T_d$) has been observed and it can be related to the polymer chain mobility, crystallization and explained for the corresponding structural morphologies of membranes.

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