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Poly(ether imide) Membrane Formation by Water Vapour Induced Phase Inversion

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Summary: The film formation by the phase inversion process induced by humidified air was investigated at 40°C from a 16 wt-% poly(ether imide)/*N*-methyl-2-pyrrolidinone solution. Weight measurements of the film forming system and video recording of the phase separation were performed in-situ to get a deep insight of the mass transfer and of the mechanism of the structure formation. Films with a cellular morphology were produced for a processing relative humidity higher than 30% and dense homogeneous films below this value. The influence of the relative humidity on the film morphology (dense or cellular, cell size, anisotropy) was discussed in terms of thermodynamic (ternary phase diagram) and kinetic aspects of the phase separation. On this basis, we propose a phenomenological model to explain what happens during the film formation.

Introduction

Polymeric membranes have been developed in recent years for a wide range of industrial applications using porous and non-porous materials. The intrinsic properties of a material stem from its chemical structure. Such structural factors determine, among others, intrinsic mechanical properties, chemical resistance and permeability. The processing also affects in a certain way the properties because the morphology of the material obtained is related to the process by which the polymer is transformed. Therefore, there is a strong interdependence on the final properties between the polymer structure and the elaboration conditions.

The majority of the polymeric membranes are produced using a phase inversion process. [1,2] The first stage consists to prepare a homogeneous polymer solution, which is cast or spun according to the desired geometry for the membrane. Thereafter, depending on the process conditions, various membrane materials featured by completely different morphology can be prepared that is, for example, a dense

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homogeneous film by solvent evaporation of the polymer solution and an asymmetric membrane with a greater or lesser porous structure by immersion in a coagulation bath.[3,4] In the latter case, diffusion of non-solvent in and of solvent out the formed layer induces a phase separation yielding the formation of pores.

This paper reports on an intermediate process which consists in supplying the non-solvent from the vapour phase, so-called "non-solvent vapour induced phase separation" (VIPS).[5-6] The milder conditions of the phase inversion taking place in this technique result in an easier possibility of understanding how the microstructure is formed in the material, which can afford a better control of the properties of the membranes obtained.

Poly(ether imide) (PEI) was chosen as a model polymer because of the large range of polyimide film applications. The phase inversion was initiated from 1-methyl-2-pyrrolidinone (NMP) solutions using water vapour as the non-solvent. After casting, the polymer liquid film was dried under a gas stream at a given relative humidity (RH). Water induces in the film a phase separation, via the nucleation and growth of a polymer-lean phase dispersed in a polymer-rich phase. Depending on the processing parameters (temperature, RH and gas flux), the membrane materials obtained can present a dense or a cellular structure, composed of cells of various shape and size.

This study dealt with the influence of RH during the solvent evaporation stage on the morphology of the PEI film produced. A physico-chemical analysis of the polymer solution was first conducted to determine the different domains in the ternary diagram PEI/NMP/water and the conformation of polymer chains just before the phase separation. On the basis of this information and that gained from the in-situ mass transfer determination and from scanning electron microscopy (SEM) performed on the dried films, a phenomenological model was proposed accounting for the morphology formation of PEI films obtained by the VIPS process.

Experimental Part

Materials: PEI (Aldrich) was dried for 24 hours at 170°C under before use. Anhydrous NMP (Aldrich) was taken under a nitrogen atmosphere without any further purification. Polymer solutions were prepared at room temperature by stirring PEI in NMP during 5 days under nitrogen. The obtained solutions were used within a week.

Phase diagram: The binodal is the composition curve from which starting with a homogeneous solution the phase separation occurs yielding a turbid system. This cloud point was visually determined at 40°C through the addition of 18 MΩ water/NMP mixture (10/90 - 40/60 wt-%) into PEI solutions (1 - 30 wt-%). When this point was reached, the solution was kept at 40°C for 12hr. In the case where the mixture became homogeneous, a small amount of 18 MΩ water/NMP was added and the procedure started again until a stable cloud point was observed. The mixture was finally centrifuged at 40°C to separate the two phases. The tie lines were determined using a FTIR spectroscopic titration[7] of the polymer-lean phase. The FTIR spectra (Nicolet 710 spectrophotometer) were recorded using an attenuated total reflectance system. Multivariate Partial Least Square (PLS) regression[8] was used as the calibration technique with the PLSplus grams32 software to established a cross validation calibration. The calibration was carried out with 11 samples whose the composition in water and NMP was known.

T_g: D.S.C measurements were carried out at a heating rate of 10°C.min^{-1} using a TA Instruments DSC 2920 Modulated. Samples were cooling thanks to flowing nitrogen. The Tg values were determined at the onset of the transition region of the heating curves.

Viscosity: Rheological measurements were performed at constant strain (100 Pa) in the linear viscoelastic range and at 40 °C using a cone-plan Physica UDS 200 rheometer equipped with a Peltier temperature control.

Film preparation: The PEI solution (16 wt-%) was cast on a glass plate in a chamber at 25°C under an atmosphere with a RH value less than 7%. The thickness of the liquid film was 250μm. The plate is then rapidly introduced in the evaporating chamber (40°C ± 0.5°C) and brought into contact with a constant laminar air flux (2 L.min^{-1}). RH of the atmosphere in the evaporating chamber was adjusted to the desired value by bubbling the air through a water column at a controlled temperature in a way as RH can be varied from 0 to 90 % with an error range of ± 2 %. Films were finally immersed in a water bath at 70°C to peel off the film from the plate and extract NMP.

Mass transfer: In-situ mass measurements were carried out by weighting the film forming system every 10 seconds until such time as no significant variation was observed meaning that the evaporating process was completed. Error on mass measurement was lesser than 0.005g for a sample weight of about 0.4g.

Microscopy: The cross-sectional morphology of films was investigated using SEM (Hitachi S-4500). The phase separation was observed in situ with an optical microscope (Nikon) equipped with a digital camera (Microvision Kappa, Archimed™ software).

Film characterisation: Film thickness (±0,5 µm) was determined by a series of measurements in different places using a digital length gauge (Heidenhain, Subway MT12-VRZ 405).

Results and Discussion

1. The ternary system PEI/NMP/H_2O

The process of phase inversion is initiated by the diffusion of a non-solvent into a homogeneous polymer solution. It is now well documented that the demixing properties and thereby the morphology of the membrane obtained by immersion phase separation vary in a large extent depending on the respective quality of the solvent(s) and of the non-solvent(s) for the polymer.[9] Therefore, we investigated first the properties of the ternary system PEI/NMP/H_2O. The binodal delimiting the demixing area in the ternary phase diagram was determined at 40°C in the range of PEI concentrations 1 – 30 wt-% (figure 1). It can be seen that the solubility domain is limited to water concentrations less than 5 wt-% meaning that only small amount of non-solvent is required to generate a phase separation. Moreover, the fact that the critical point occurs at very low PEI concentration (1.25 wt-%) involves a nucleation by the polymer lean phase (the polymer concentration used to yield membranes is generally higher than 10 wt-%).

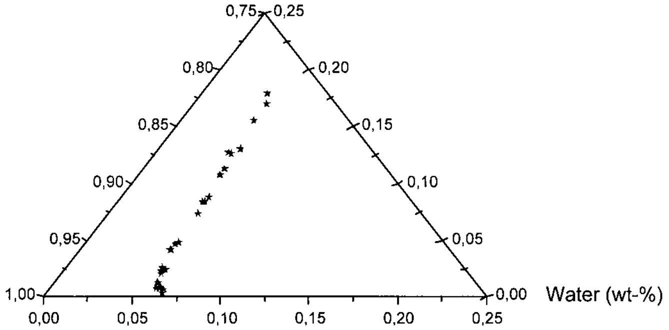

Figure 1. Binodal for the PEI/NMP/H_2O system at 40°C.

FTIR analysis of the polymer-lean phases was carried out to get information on the tie lines in the ternary phase diagram. As an example, figure 2 shows the calibration curves for the NMP and water content with 11 binary mixtures (NMP/H_2O). The excellent agreement between the experimental and the predicted values results in the possible quantitative determination of the polymer-lean phase composition. The PEI content was inferred from the NMP and H_2O concentrations given by the FTIR titration (table 1). The tie lines were then drawn from both the compositions of the starting mixture and of the polymer-lean phase (figure 6).

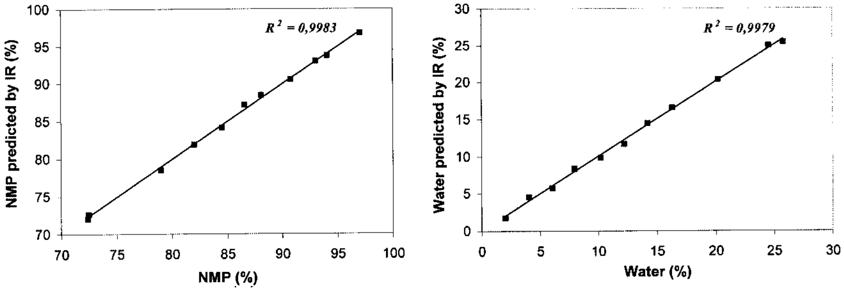

Figure 2. Calibration curves for NMP and water in binary mixtures.

Table 1. Composition of the PEI-lean phase as a function of the starting ternary system.

	Initial Point			**PEI lean phase**		
	PEI (wt-%)	**NMP** (wt-%)	**Water** (wt-%)	**PEI** (wt-%)	**NMP** (wt-%)	**Water** (wt-%)
4 (40°C)	4.54	86.52	8.93	1.32	89.64	9.04
5 (40°C)	8.3	84.46	7.24	1.11	91.8	7.09

Gelation occurs when the polymer concentration becomes high enough to produce strong physical interactions connecting the macromolecules in a three-dimensional network. This phase transition is featured by a dramatic increase of viscosity. Figure 3 shows that the gelation took place for a PEI content of 32 wt-% in a NMP solution. In ternary systems, the presence of water gives rise to reinforcement of the macromolecular interactions as evidenced by the increase of viscosity with the water content exhibited on figure 4. These results indicate that water generates aggregation of PEI macromolecules far below the phase separation. Light scattering experiments confirmed that finding (results not shown). Furthermore, it can be assumed that the gelation occurs at lower PEI concentrations in ternary systems.

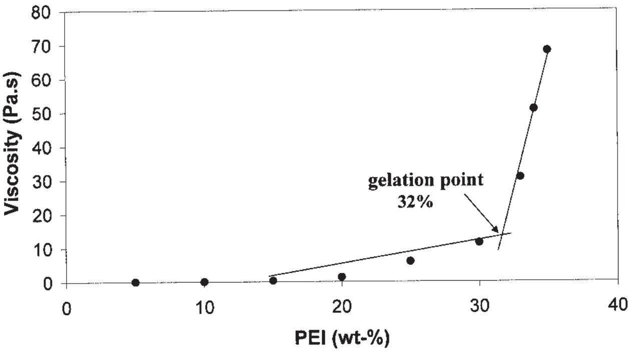

Figure 3. Viscosity at 40°C of PEI/NMP solutions as a function of the PEI content.

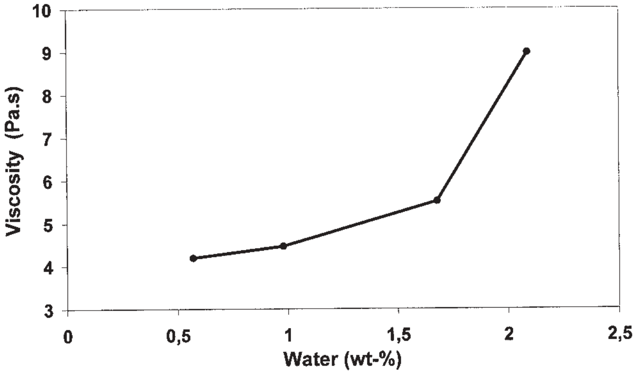

Figure 4. Viscosity at 40°C of PEI 25 wt-% ternary solutions vs the water content.

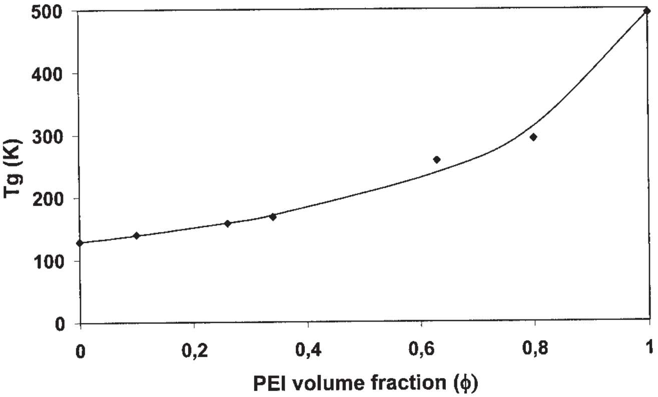

Figure 5. Variation of T_g versus the PEI volume fraction (ϕ) in PEI-NMP solutions.

By increasing the polymer concentration, the mixture finally solidifies when T_g passes below the temperature of the experiment. Figure 5 shows the variation of Tg as a function of the volume fraction of PEI (ϕ) for PEI/NMP systems.

The evolution of T_g with ϕ can be fitted according to the empirical equation[10]

$$Tg = \frac{R * T_g^{NMP} * (1-\phi) + T_g^{PEI} * \phi}{R * (1-\phi) + \phi} \qquad \text{with } R = \frac{\alpha_f^{NMP}}{\alpha_f^{PEI}} \qquad (1)$$

The T_g^{NMP} value was extrapolated from the figure 5 to 129 K. The PEI T_g (T_g^{PEI}) was determined to be 493 K using DSC analysis. α_f^{NMP} and α_f^{PEI} stand for the thermal expansion coefficient of the free volume of the solvent and of the polymer, respectively. The best fitting was given using R = 3.95 as the adjustable parameter.

Thanks to the equation (1), it was found that the PEI chains are frozen in the glassy state at 40°C for a concentration of ca 82 wt-%. DSC measurements performed on ternary compositions showed a T_g decrease indicating a plasticizing action of water on the NMP/PEI system. As an example, 3 wt-% of water added to a 20 wt-% PEI solution diminished the T_g value of 7°C. This result agrees with similar effects previously reported .[11] This trend was illustrated on the complete ternary phase diagram presented on figure 6.

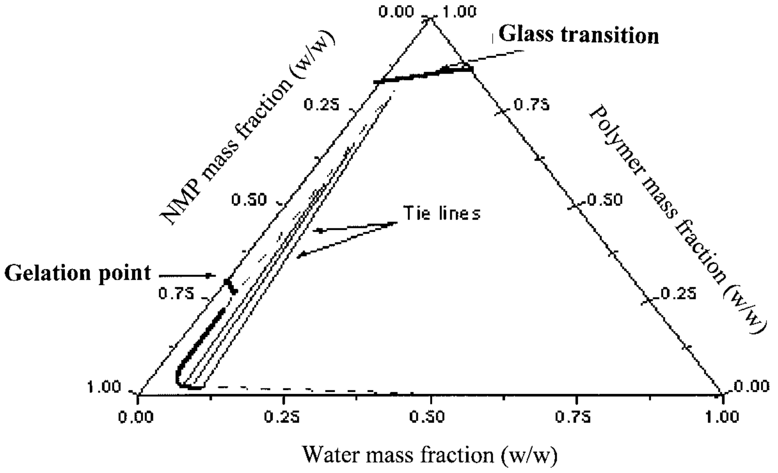

Figure 6. Ternary phase diagram for the PEI-NMP-water system.

As can be seen, the slope of the tie lines depicted on this diagram is very steep indicating that only a small amount of water absorbed into the film forming system is required to allow the polymer rich phase to enter the glassy state.

2. Water vapour induced phase separation

To get a good insight of how the morphology of the film is forming needs to know about the mass transfer taking place during the process and about the occurring of the phase separation. As above outlined, the time scale of the inversion phase process by a non-solvent vapour is much bigger than that observed by immersion in a coagulating non-solvent bath as the net inflow of non-solvent is much higher by contacting the liquid polymer film with a liquid than with a gas phase. For the purpose, we developed an in-situ analysis by determining the overall mass transfer and by video recording the membrane forming system during the phase separation.

Figure 7 displays the weight plotting when the film forming system was brought into contact with gas phases of RH varying from 0 to 70 % in the evaporating chamber at 40°C. A decreasing curve was observed under dry air describing the weight loss related to the NMP evaporation, until a plateau was reached indicating that the glass transition has been passed. At that point, the film solidified in the glassy state entrapping ca. 18 wt-% residual NMP.

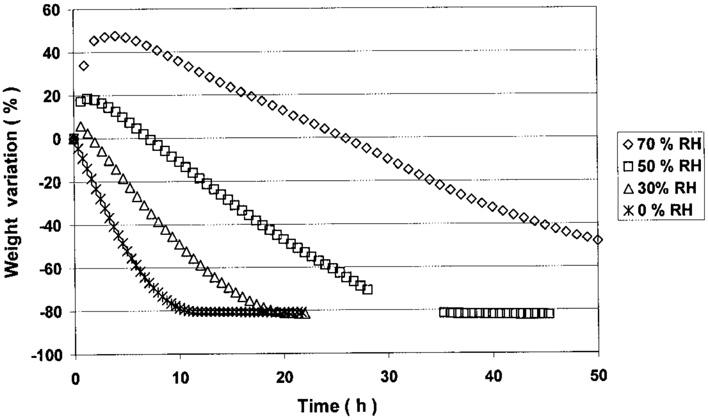

Figure 7. Weight plotting of the film forming system processed under different RHs.

The same experiments carried out under humidified air gave plots with a different profile featured by first an increase of the film mass. Two competitive phenomena account for this result: the water sorption mainly due to the hygroscopicity of NMP and the evaporation of the low molecular weight compounds (H_2O and NMP). At the beginning of the experiment, the chemical potential of water is assumed to be close to zero in the film so that the predominant effect is the water inflow into the liquid film resulting in a weight intake. The steady increase of the sorption rate and that of the maximum weight intake with the water activity in the gas phase related to RH support this assumption. However, it is not a direct measure of the water sorption since NMP evaporated in the same time as water diffused into the film. The diffusion rate of water slows down when the equilibrium of chemical potentials in the gas phase and in the film is approaching. At this point, the evaporation process prevailed over the water sorption thereby the film forming system reached the maximum weight. Moreover, the evaporation rate (decreasing part before the plateau) was observed to be strongly reduced by increasing RH. This effect likely originates from the high mutual affinity existing between NMP and water.

We know from the phase diagram that less than 5 wt-% water is required to induce the phase separation. The weight measurements demonstrate that this value was attained after a few minutes within the overall composition for a high water inflow (high RH) meaning that the binodal has been crossed over the entire liquid film. The film whitened for a composition very close to that determined from the thermodynamic equilibrium demonstrating that the demixing was not a surface effect and occurred almost simultaneously over the entire film. It was concluded that the rate-limiting step is the mass transfer between the gas phase and the cast film and not the diffusion within the film.

When the processing RH was in the range of 15-25 %, the liquid film whitened around the maximum intake indicating that the phase separation occurred, and then turned back homogeneous during the evaporation step. In this case, thin dense homogeneous films were obtained, whereas films with a cellular morphology were produced for higher RH. We assume from the tie lines in the phase diagram (figure 6), that the amount of water absorbed by the cast films processed in air containing less than 30 % RH was not high enough to allow the polymer rich phase to solidify in the glassy state and to fix the structure. So, the composition path crossed back the binodal to the homogeneous region. Figure 8 gathering film thickness measurements illustrates the effect of RH on the morphology.

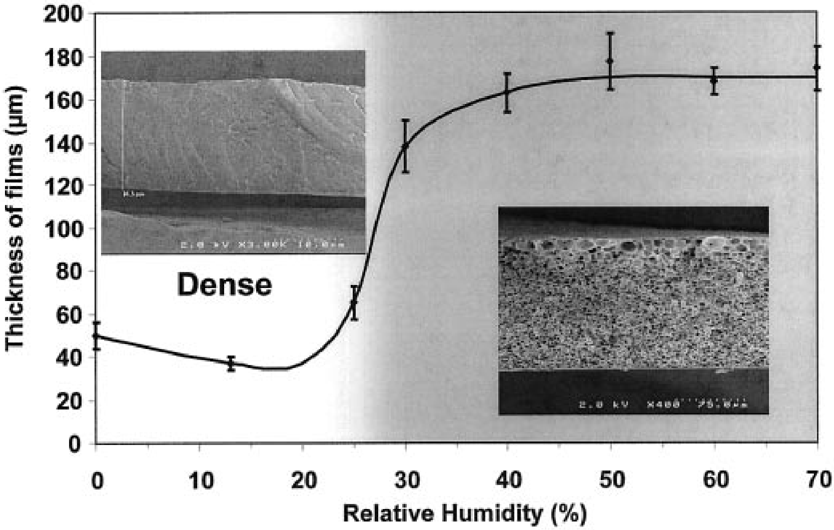

Figure 8. Effect of the processing RH on the morphology of the films obtained.

The optical microscopic observation of the phase separation at 40 % RH showed that the polymer-poor phase droplets rapidly grew and coalesced. After ca. 15 min of coarsening, no more increase in droplet size was observed. It was assumed that the polymer rich-phase forming the foam wall structure has reached the solidification concentration at this early stage setting the cellular structure. To confirm this assumption, the film forming system was quenched by immersion into a water bath at different stages of the evaporation process as described on figure 9. Quenching the liquid film before the whitening of the system (period I) gave membranes having the typical asymmetric morphology obtained by the wet phase separation process. During this period, the change of composition generated by the solvent and non-solvent exchanges between the liquid film and the gas phase cannot alter the nature of morphology and play only a role in the formation of the top layer.[9] On the other hand, cellular structures were produced if the quenching was carried out after the occurrence of the phase separation (periods II-III). We concluded that the film morphology can be then stabilised providing that the water intake is high enough to ensure the polymer rich phase to enter into the vitrification area. Depending on the ternary system polymer/solvent/non-solvent, this step will take more or less time. However, it does not need the evaporation process to be completed.

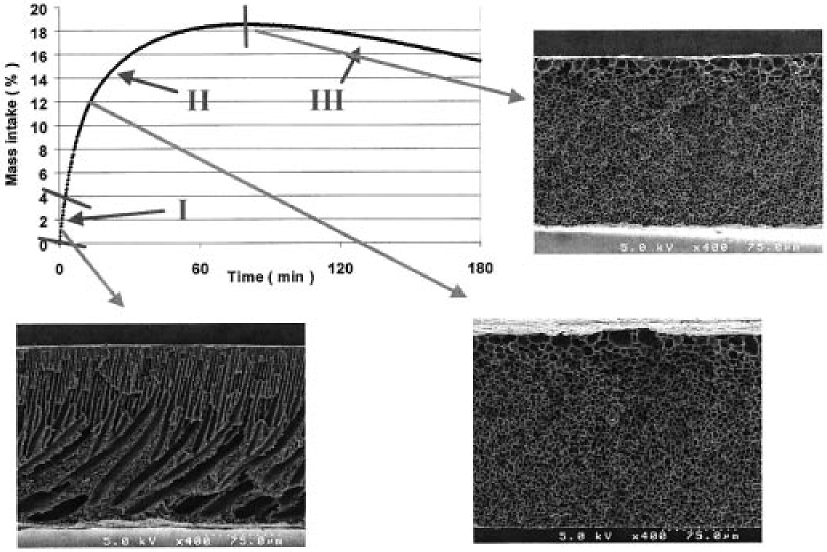

Figure 9. Quenching of the film forming system at different stages of the processing.

The SEM images of the film cross-section show an anisotropic morphology featured by the presence of a toplayer consisting in large cells and by a gradient of decreasing cell size from the air/film interface to the film/support interface. We propose the following mechanism to take into account this observation. The humidified air stream generates a water inflow and a NMP outflow first located close to the air/film interface. The local decrease of the NMP concentration entails a NMP flux from the film inner-side to the air interface, which produces a gradient of polymer concentration. In other words, the permanent supply of NMP keeps the viscosity near the air interface at a lower level than anywhere else in the film forming system. After the phase separation starts, the coarsening of droplets is hindered in the deep layers due to their higher viscosity compared to the air interface leading to the formation of the anisotropic structure.

Figure 10 exhibits the influence of RH on the average cell size expressed as the average number of cells per 100 μm^2 located in the middle of films: lower the number, larger the cells are. It was observed that the cell size decreased as RH value was higher. As above mentioned, the water intake rate is strongly enhanced by a higher water activity in the gas phase. Under these operating conditions, the polymer rich phase rapidly solidifies shortening the duration of droplet coarsening.

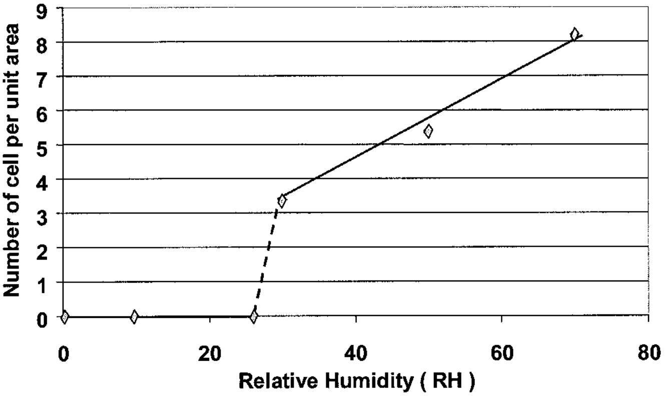

Figure 10. Influence of RH on the average cell size.

Conclusion

The non-solvent sorption from the gas phase to the cast film appears as the rate-limiting step in the phase separation process induced by air containing water vapour. The demixing proceeds by coarsening of droplets made of the polymer lean phase leading to the formation of a porous cellular morphology. It was pointed out for the system studied that the water inflow rate governs the cell size and the NMP outflow rate the extent of anisotropy. The composition path inferred from the tie lines in the phase diagram and from the mass transfer analysis showed that the solidification of the polymer rich phase could be fast enough to stabilise the structure in a few minutes. This was experimentally demonstrated by quenching the film forming system at different stages of the processing.

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