

Investigation into the Rheological Properties of PES/NMP/Nonsolvent Membrane-Forming Systems

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ABSTRACT: From the perspective of a polymer solution, the rheological properties of the popular polyethersulfone (PES)/*N*-methyl-2-pyrrolidone (NMP)/nonsolvent (NS) membrane-forming system were investigated thoroughly with a controlled stress rheometer (HAAKE RS75, Germany). The scope of the study included measurements of the controlled-stress flow curve, creep recovery, and dynamic oscillation. H₂O, 1-butanol, ethylene glycol, and diethylene glycol were used as NS additives. The effects of the polymer concentration and the quality of the solvent mixture, as characterized by the approaching ratio, on the rheological behavior of the dopes were studied. Up to 38 wt % PES and extremely adjacent to the phase separation (i.e., the approaching ratio of the dope was 0.95), the viscous property dominated all the dopes, which behaved as Newtonian fluids. Moreover, all the membrane-forming dopes investigated were in the crossover regime in the semidilute region, in which the chains were overlapping but unentangled. © 2001 John Wiley & Sons, Inc. *J Appl Polym Sci* 82: 283–291, 2001

Key words: polyethersulfone; membrane-forming systems; rheological properties; solvent quality

INTRODUCTION

The phase-inversion process is a common method for preparing asymmetric polymeric membranes for a wide range of applications in gas separation, the food and dairy industry, the pharmaceutical and biochemical industry, water treatment, and so on.^{1–3} Different membrane structures are expected for various applications. Many investigations have been carried out concerning the mechanism of the phase-inversion process to understand its nature, information which would be helpful for preparing membranes with perfect structures and high performance for particular membrane processes. The properties of the result-

ant membranes are determined by the thermodynamic state of the casting solution (i.e., the dope) and the nonsolvent (NS)–solvent exchange during coagulation. The thermodynamics of the dope can be described satisfactorily with a triangle phase diagram.^{4–6} The NS–solvent exchange and the composition path after immersion can be measured with various techniques^{7–11} or simulated by mass-transfer models.^{12–15}

However, the mechanism is not yet thoroughly understood. The thermodynamic and kinetic factors are somewhat isolated in the reasoning of the membrane-formation mechanism. Additives such as NSs, inorganic salts, and surfactants are always used to tailor the membrane properties. The presence of the additives in the dope not only changes the thermodynamic state of the dope but also influences the conformation and dynamics of the polymer, which affects the kinetics of phase

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separation in turn. However, the latter is seldom mentioned in the literature. Nevertheless, the rheological properties of multicomponent polymer systems do relate closely to the interaction between the components and the phase configuration; the rheological response can reflect a change in the conformation of macromolecules exactly.^{16,17} In a membrane-forming system, rheological properties are significantly affected by the quality of the solvent mixture, which is usually degraded by additives. A change in the rheological properties of the dope, including a change in the viscosity of the dope, influences the NS–solvent exchange, the velocity of phase separation, and the gelation dynamics. To some extent, the competition between the three dynamic processes determines the structure and performance of the resultant membrane. Therefore, rheology is likely to be a powerful tool for an investigation into the mechanism of membrane formation.

Unfortunately, only a few studies on the rheological behavior of dopes limited to viscosity have been reported in the literature, even though viscosity is an important aspect during membrane preparation.^{18–22} Furthermore, most of the investigations focused on the relation between the rheological conditions during the fiber-spinning process and the properties of the membrane.^{23–27} There are hardly any reports on the understanding of the dope on the molecular level via a rheological perspective. The membrane performance can be affected by the dope viscosity. An increase in the viscosity of the dope will decrease the tendency for macrovoid formation.² Okuno et al.²⁰ reported preparing poly(vinyl chloride) (PVC) membranes with different morphologies from casting solutions with different additives. The physical structures of the PVC membranes were significantly influenced by the conformations of the polymer in the casting solutions, which were evaluated via the relative viscosity. Torrestiana-Sanchez et al.²¹ measured the primary normal stress difference (N_1), the elasticity of the dope, yet it cannot be used to explain the difference in membrane structure and performance. To our knowledge, there are only a few published investigations on dope viscoelasticity (e.g., compliance and complex module), which can reflect the conformation of the dope.

In addition, because the dope is in nature a multicomponent and polydisperse polymer solution, modern theory on polymer solutions can be applied to an investigation of the phase-inversion

process. Only after the regime is set in which the dope is can we depict the behavior of macromolecules during the phase-inversion process via practical theory and to interpret the membrane formation.

In this work, the rheological properties of dopes with different additives were studied. The polyethersulfone (PES)/*N*-methyl-2-pyrrolidone (NMP) membrane-forming system, popular in industry and academia, was used as the model system. Water and typical aliphatic alcohols [1-butanol, ethylene glycol (EgOH), and diethylene glycol (DegOH)] were selected as NS additives. Adding these NSs to the dope can change the quality of the solvent mixture, which is described by the approaching ratio (α).²⁸

$$\alpha = \frac{m_{\text{nonsolvent}}/m_{\text{solvent}}}{(m_{\text{nonsolvent}}/m_{\text{solvent}})_{\text{cloud point}}} \quad (1)$$

where the numerator is the mass ratio of the NS and solvent in the casting solution and the denominator is the mass ratio of the NS and solvent in the corresponding system at the cloud point.

A controlled-stress rheometer (HAAKE RS75, Germany) was used to complete the flow curve, creep-recovery, and oscillatory tests, which gave the rheological properties of the dopes. The purpose of this study was to perform a variety of rheological tests and investigate the effects of concentration and solvent quality (α) on the rheological behavior of the dope. Moreover, a rudimentary explanation for the experimental phenomena is given from the perspective of a polymer solution.

EXPERIMENTAL

Materials

PES [Ultrason® E 6020P; weight-average molecular weight (M_w) = 58,000, weight-average molecular weight/number-average molecular weight (M_w/M_n) = 3.6], kindly donated by BASF (Germany), was used as the polymer. The polymer was dried at 150°C *in vacuo* for 12 h. The water was deionized and filtered with an ultrafiltration membrane. NMP, 1-butanol, EgOH, and DegOH were analytical-grade reagents and were dehydrated with 5-Å molecular sieves dried at 500°C for 4 h.

General Measurements

All solvent mixtures were prepared by mass with an analytical balance (LIBROR AEL-160, Japan) with a precision of ± 0.1 mg.

The densities of pure solvents and their mixtures were determined with a 10-cm³ pycnometer at $25 \pm 0.005^\circ\text{C}$. The pycnometer was calibrated with exceptionally high-purity water from a Double D-Ionstill (Jencons Scientific, Ltd., USA), and its density was 0.99705 g cm^{-3} at 25°C .

The viscosities of the solvent mixtures were measured at $25 \pm 0.005^\circ\text{C}$ with dilution Ubbelohde viscometers calibrated with pure NMP. Viscometers with different capillary sizes were used to ensure that the efflux times were all in excess of 100 s so that the kinetic energy correction could be neglected.

Solution Preparation

Because polymer concentrations are usually between 10 and 38 wt % in membrane preparations, PES/NMP binary systems the PES/NMP/H₂O ternary systems ($\alpha = 0.79$ and 0.95 , respectively) with concentrations of 1–38 wt % were prepared. In addition, 15 wt % PES/NMP/NS systems with various α values were also prepared to elucidate the effect of the quality of the solvent mixtures on the dope properties. The cloud-point data for PES/NMP/H₂O, PES/NMP/1-butanol, PES/NMP/EgOH, and PES/NMP/DegOH can be found elsewhere.^{29,30}

To obtain clear and homogeneous polymer solutions, we mixed PES and solvent mixtures with various values of α bottles and kept them at room temperature for 24 h; then, we electromagnetically stirred them at 45°C for 24 h. All samples were sealed and kept in a desiccator for 2 months before rheological measurements.

Rheological Measurements

Rheological properties were measured with a HAAKE RS75 rheometer at 25°C . A DG41 Al double-gap sensor system, a Z41 Al coaxial cylindrical sensor system, a C60/1° cone-plate sensor system, or a C35/1° cone-plate sensor system was selected according to the viscous behavior of the sample. For cone-plate sensor systems, a solvent trap was used to prevent solvent volatilization for stable and reproducible tests. For each solution, a flow curve was first created with increased shear stress (τ) according to regular steps. The shear

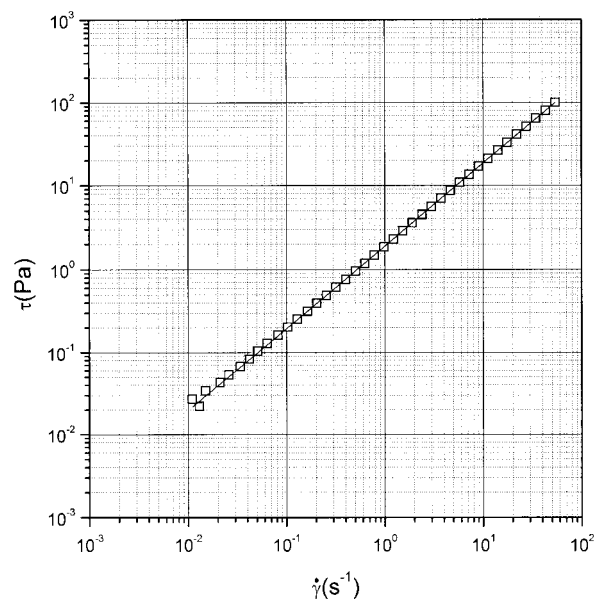


Figure 1 CS flow curve of 20 wt % PES/NMP: (□) data from the CS flow-curve measurement and (—) the curve fitted from the Ostwald power-law equation.

rate ($\dot{\gamma}$) was 0.001 – 3000 s^{-1} , depending on the viscometric behavior of the sample. After that, a stress sweep test in the oscillatory mode was performed to define the linear viscoelastic region. A stress that was in the linear viscoelastic region and large enough was applied to the solution to complete a creep-recovery test in the controlled stress mode and a frequency sweep test in the oscillatory mode. Dynamic measurements were made with frequencies of 0.015 – 10 Hz (i.e., 0.092 – 62.832 rad s^{-1}).

RESULTS AND DISCUSSION

General

The 20 wt % PES/NMP system was selected as the model system to illustrate the rheological behavior of the samples tested in this work. As shown in Figure 1, the controlled stress (CS) flow curve of 20 wt % PES/NMP over 4 orders of magnitude of $\dot{\gamma}$ (0.01 – 100 s^{-1}) was accurately fitted by the Ostwald power-law equation $\tau = K\dot{\gamma}^n$. The exponent n , representing the deviation from Newtonian behavior, was 0.9999 .

In the linear viscoelastic range defined by the stress sweep at 1 Hz , a creep-recovery test was carried out for the model system, and the data are

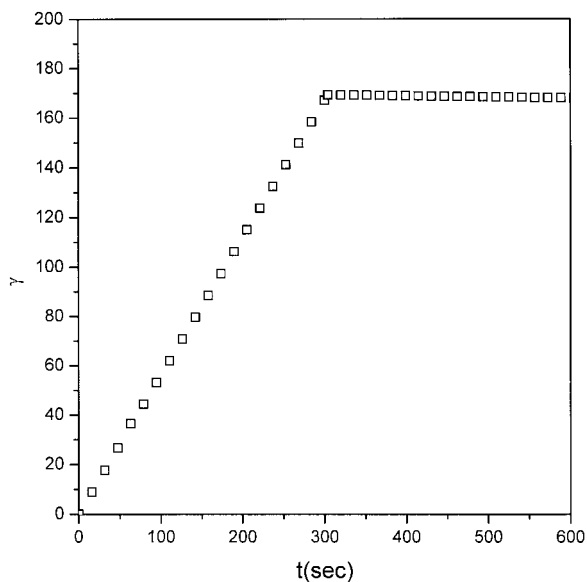


Figure 2 Creep-recovery test of 20 wt % PES/NMP.

given in Figure 2. The strain–time curve has good linearity; that is, the absolute value of the correlation coefficient (r) is 0.99, which implies that the model system was a typical Newtonian fluid. At least no elasticity was detected. Furthermore, the zero shear viscosity ($\eta_{0(C-R)}$), calculated from the creep-recovery data, was in agreement with the value from the CS flow curve given in Table I.

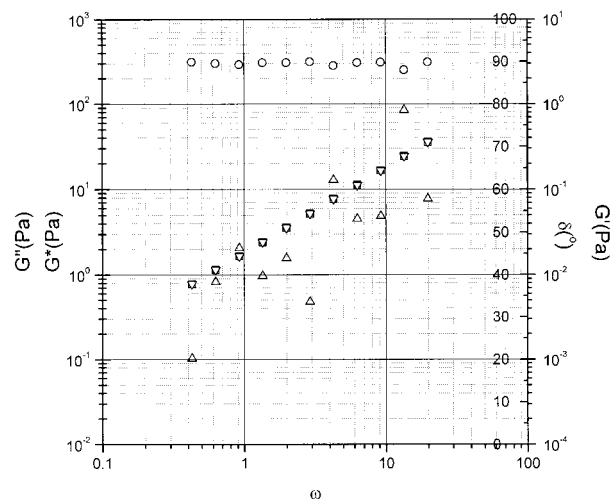


Figure 3 Dynamic oscillation test of 20 wt % PES/NMP: (□) G^* , (▽) G' , (△) G'' , and (○) δ .

Figure 3 depicts the complex modulus (G^*), storage modulus (G'), loss modulus (G''), and phase angle (δ) from dynamic oscillation experiments. δ at all frequencies was nearly 90° . G^* nearly coincided with G'' . The discrete values of G' were about 2 orders of magnitude less than those of G'' at the same frequency (ω). These phenomena demonstrated that the viscous part dominated the model system. The zero shear viscosity was deduced as follows:¹⁷

Table I Rheological Properties of PES/NMP Systems

Concentration (wt %)	C (g/dl)	n	$\eta_{0(F-C)}$ (Pa s)	$\eta_{0(C-R)}$ (Pa s)	$\eta_{0(OSC)}$ (Pa s)
1.87	1.93	0.9721	0.004660	0.004520	0.004600
3.01	3.12	0.9897	0.007270	0.007060	0.007180
4.73	4.94	1.0160	0.01599	0.01502	0.01540
6.03	6.31	0.9954	0.02281	0.02176	0.02246
8.02	8.44	0.9875	0.04379	0.04356	0.04495
9.05	9.54	0.9894	0.06000	0.05876	0.06269
10.24	10.83	0.9972	0.09212	0.08788	0.08790
12.08	12.84	1.0068	0.1562	0.1549	0.1690
14.98	16.04	0.9550	0.4009	0.3777	0.3737
17.01	18.31	0.9975	0.7417	0.7162	0.7069
20.08	21.78	0.9999	1.472	1.483	1.470
22.62	24.70	0.9894	2.967	2.957	2.863
25.11	27.60	0.9982	6.315	6.250	6.845
27.21	30.07	0.9999	10.98	10.01	11.24
30.09	33.51	1.0014	24.31	23.75	23.70
34.93	39.42	0.9899	79.48	76.96	78.56
38.00	43.24	1.0080	362.5	338.0	364.2

Table II Rheological Properties of $\alpha = 0.79$ PES/NMP/H₂O Systems

Concentration (wt %)	<i>C</i> (g/dl)	<i>n</i>	$\eta_{0(F-C)}$ (Pa s)	$\eta_{0(C-R)}$ (Pa s)	$\eta_{0(OSC)}$ (Pa s)
3.13	3.29	0.9227	0.01241	0.01180	0.01180
8.06	8.56	0.9864	0.08471	0.08447	0.08440
14.99	16.21	0.9998	1.126	1.055	1.062
17.00	18.46	0.9993	2.149	2.021	2.044
20.00	21.89	1.0200	5.726	5.470	5.500
30.00	33.68	1.0370	113.4	105.4	116.4
37.99	43.55	0.9909	931.4	967.4	948.4

$$\eta_{0(OSC)} = \lim_{\omega \rightarrow 0} (G''/\omega) \quad (2)$$

Similarly, $\eta_{0(OSC)}$ from the dynamic oscillation test agreed with that from the CS flow curve, as shown in Table I.

Obviously, all the flow curves, creep-recovery, and dynamic oscillation tests showed that the membrane-forming system of 20 wt % PES/NMP was a Newtonian fluid. Moreover, the viscous component dominated the rheological property of the system in a wide range of the shear rate and frequency (i.e., $\dot{\gamma} = 0.01$ – 100 s^{-1} , $\omega = 0.4$ – 20 s^{-1}).

The rheological properties of PES/NMP systems with various polymer concentrations are listed in Table I. The results of PES/NMP/H₂O systems with $\alpha = 0.79$ and 0.95 are listed in Tables II and III, respectively. With H₂O, 1-butanol, EgOH, and DegOH as additives, the rheological results of the 15 wt % PES/NMP/NS ternary membrane-forming systems are shown in Table IV. As can be seen from Tables I–IV, in a wide range of polymer concentrations, from very dilute concentrations to 38 wt % (which covers the usual polymer concentrations for membrane preparations, 10–38 wt %), the PES/NMP systems be-

haved as Newtonian fluids. Neither the addition of different NSs nor increases in α changed the Newtonian property of the dopes, although the quality of the mixed solvents deteriorated. The dopes with α equal to 0.95 were extremely adjacent to the phase separation. Under the experimental conditions, the PES/NMP/NS membrane-forming systems were mainly controlled by the viscous component, and the elastic component was weak. Perhaps this was a result of the PES used in this study. The M_w and polydispersity of the PES were 58,000 and 3.6, respectively. The M_w was likely to be less than the entanglement molecular weight. However, the PES studied herein was a commercial product popular in industry and academia. Up to 38 wt %, the upper limit of the usual membrane-forming systems, PES/NMP showed Newtonian behavior. In other words, there was no chain entanglement or the chain entanglement was very weak in these dopes. Thus, not all membrane-forming systems are non-Newtonian liquids; they are dependent on the molecular weight of the polymer and the solvent selected. The PES/NMP membrane-forming systems were Newtonian fluids according to our experiments.

Table III Rheological Properties of $\alpha = 0.95$ PES/NMP/H₂O Systems

Concentration (wt %)	<i>C</i> (g/dl)	<i>n</i>	$\eta_{0(F-C)}$ (Pa s)	$\eta_{0(C-R)}$ (Pa s)	$\eta_{0(OSC)}$ (Pa s)
4.39	4.63	0.9999	0.01952	0.01936	0.01967
7.76	8.25	1.0004	0.08297	0.08407	0.08456
10.00	10.69	1.0010	0.2446	0.2475	0.2265
15.00	16.23	0.9757	1.406	1.352	1.349
20.01	21.93	0.9835	7.918	8.301	8.313
25.00	27.74	1.0090	39.07	41.36	40.96

Table IV Rheological Properties of 15 wt % PES/NMP/NS Systems

NS	α	n	$\eta_{0(F-C)}$ (Pas)	$\eta_{0(C-R)}$ (Pas)	$\eta_{0(OSC)}$ (Pas)
1-Butanol	0.00	0.9950	0.4009	0.377	0.3737
	0.30	1.0140	0.3855	0.3739	0.3788
	0.61	1.0010	0.4180	0.3376	0.3963
	0.81	0.9810	0.5013	0.4847	0.4786
	0.95	0.9553	0.6200	0.5596	0.5744
H ₂ O	0.00	0.9950	0.4009	0.3777	0.3737
	0.30	1.000	0.5394	0.5411	0.5394
	0.59	0.9941	0.8001	0.8198	0.8021
	0.79	0.9998	1.126	1.055	1.062
	0.95	0.9757	1.406	1.352	1.349
EgOH	0.00	0.9950	0.4009	0.3777	0.3737
	0.30	1.0070	0.7173	0.7821	0.6470
	0.60	0.9989	1.152	1.038	1.112
	0.80	1.0590	1.710	1.699	1.637
	0.95	1.0280	1.032	1.065	1.010
DegOH	0.00	0.9950	0.4009	0.3777	0.3737
	0.32	0.9847	0.9602	1.056	1.006
	0.64	0.9748	2.219	2.435	2.357
	0.85	0.9951	3.080	2.982	2.961
	0.95	1.000	2.146	2.096	2.075

As all the samples showed Newtonian behavior, hereafter the discussion focuses on the zero shear viscosity of the dope.

Effect of the Polymer Concentration

Polymer concentrations were converted to g dL^{-1} with the additivity of specific volumes of the polymer and solvent mixture assumed. The specific viscosity (η_{sp}) of PES/NMP and PES/NMP/H₂O with $\alpha = 0, 0.79$, and 0.95 was plotted against the polymer concentration in Figure 4. η_{sp} of polymer solutions in a good solvent was higher than that in a poor solvent in dilute solutions, whereas the reverse was true in concentrated solutions, as described elsewhere.³¹ The quality of the mixed solvents became poorer with increasing α . A plot of a system with a large value of α crossed the curve of PES/NMP at a high polymer concentration.

In addition, η_{sp} can be expressed as follows:³²

$$\eta_{\text{sp}} = C[\eta] + k_H(C[\eta])^2 + \dots + B(C[\eta])^n \quad (3)$$

where k_H is the Huggins coefficient and $[\eta]$ is the intrinsic viscosity. For PES/NMP and PES/NMP/H₂O with $\alpha = 0, 0.79$, and 0.95 , the plots of η_{sp} versus $C[\eta] + k_H(C[\eta])^2$ are shown in Figure 5–7,

respectively. At a critical concentration (C^*), the transition from the dilute regime to the semidilute regime took place. This transition is well characterized by the deviation of the plot of η_{sp} against $C[\eta] + k_H(C[\eta])^2$ from slope 1. The values

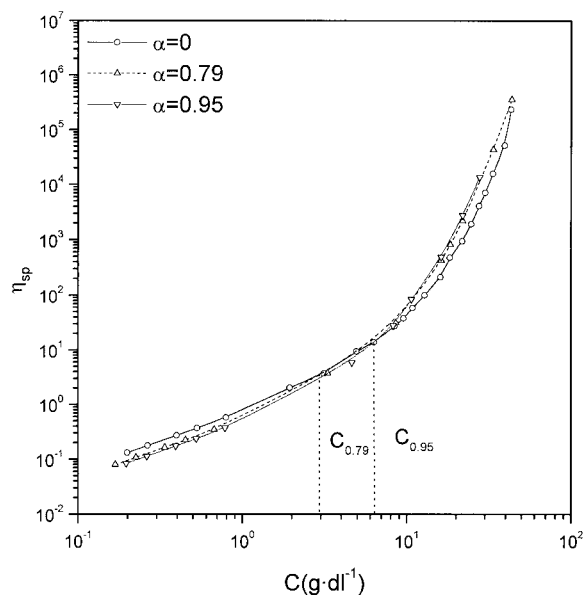


Figure 4 Plots of η_{sp} versus C for PES/NMP/H₂O systems with various values of α .

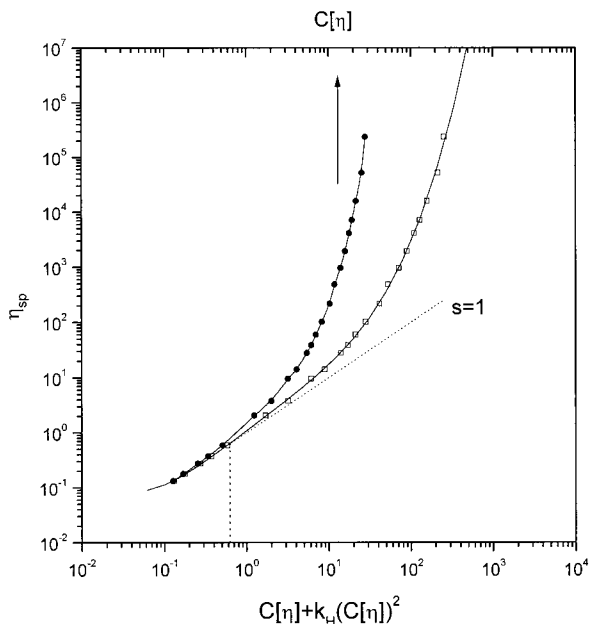


Figure 5 Dependence of η_{sp} as a function of $C[\eta]$ and $C[\eta] + k_H (C[\eta])^2$ for PES/NMP systems.

of k_H , $[\eta]$, and C^* are listed in Table V. C^* values are in the order of $[\eta]^{-1}$, as widely accepted.³³ However, the 3.4th power dependence of η_{sp} with $C[\eta]$ was not observed in the range of concentra-

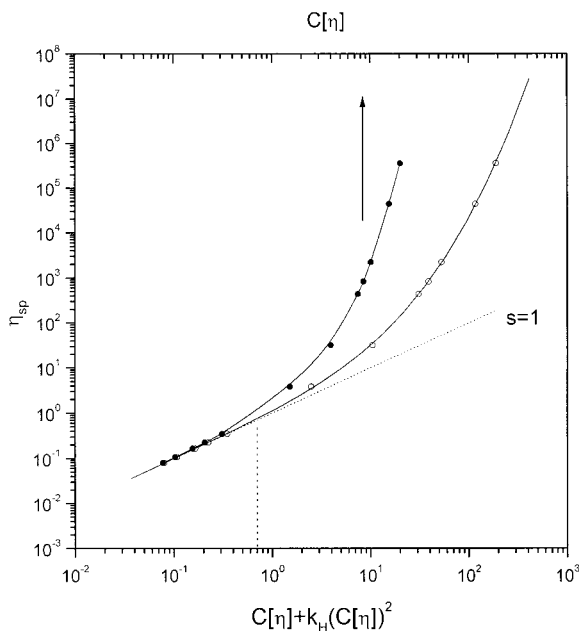


Figure 6 Dependence of η_{sp} as a function of $C[\eta]$ and $C[\eta] + k_H (C[\eta])^2$ for PES/NMP/H₂O systems with $\alpha = 0.79$.

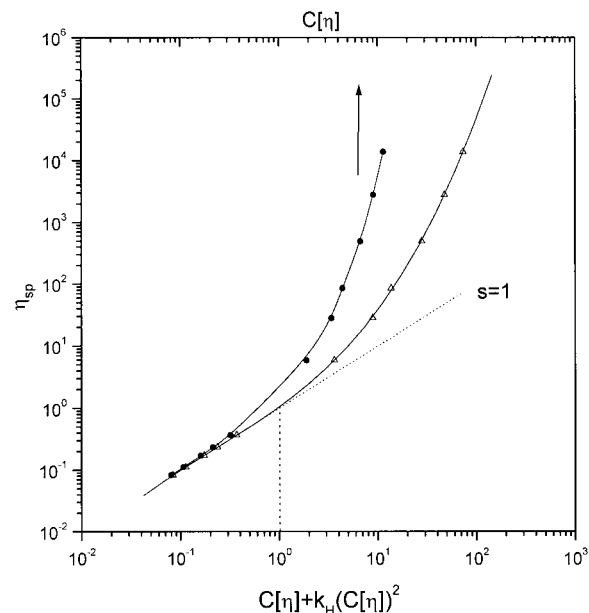


Figure 7 Dependence of η_{sp} as a function of $C[\eta]$ and $C[\eta] + k_H (C[\eta])^2$ for PES/NMP/H₂O systems with $\alpha = 0.95$.

tions investigated here, which implied that $C[\eta]$ was not large enough to achieve the transition from the semidilute regime to the concentrated regime. The latter, characterized by a uniform segment density in the solution, where the free-draining behavior became predominant, behaved like a melt.^{32,34} Moreover, the absence of the power-law dependence of η_{sp} with $C[\eta]$ indicated that the membrane-forming dopes investigated herein were in the crossover regime in the semidilute region, where the chains were overlapping but unentangled.^{35,36}

Therefore, the membrane-forming dopes prepared herein were in the crossover regime where the polymer coils were not isolated, yet the degree of coil overlap was not intensive enough to form a quasiregular network, which was widespread in the concentrated solutions. This conclusion is consistent with the experimental fact that the elasticity of the dope can be negligible.

Effect of the Solvent Quality (α)

The Martin equation accurately describes the concentration dependence of the relative viscosity for polymer solutions:³⁷

$$\eta_r = 1 + C[\eta]e^{k_M C[\eta]} \quad (4)$$

Table V Characteristics of PES in the Solvent Mixture NMP/H₂O

α	$[\eta]$ (dl/g) ^a	k_H	k_M	C^a (g/dl)	C^a (wt %)
0.0	0.6418	0.2942	0.3240	1.5581	1.50
0.79	0.4604	0.4227	0.4887	2.1738	2.08
0.95	0.4103	0.4780	0.6240	2.4372	2.32

^a From Li and Jiang.²⁹

As illustrated in Figure 8, the relative viscosity for PES/NMP/H₂O systems increased with increasing α at the same polymer concentration. The obtained Martin coefficient (k_M), listed in Table V, also increased with α . This situation could be rationalized in terms of the so-called pull-along effect.^{38,39} With increasing α , the quality of the solvent mixtures deteriorated, which resulted in the preference of intersegment contacts over solvent-segment contacts. The intersegment contacts not only rendered the segment movement but also raised the effective size of the flow unit. In addition, there was no divergence from the Martin equation, which characterized the transition from the semidilute regime to a concentrated regime. The concentration of the dopes investigated here was not up to the concentrated regime.

Figure 9 depicts the effect of α on η_{sp} for 15 wt % PES/NMP/NS ternary polymer solutions. In general, η_{sp} increased as α increased. However,

η_{sp} of the dopes with polyhydric alcohols (EgOH and DegOH) dropped abnormally when α was larger than 0.80. This cannot be rationalized here. A possible explanation may lie in the large volume of NMP · nEgOH and NMP · nDegOH complexes, which could limit contact between intersegments. Further investigations are in progress.

CONCLUSIONS

The rheological properties of PES/NMP/NS membrane-forming systems were investigated. The viscous property was dominant, and PES/NMP solutions behaved as Newtonian fluids. Adding NS only degraded the quality of the solvent mixtures; PES/NMP/NS membrane-forming systems still showed Newtonian properties, although α was up to 0.95.

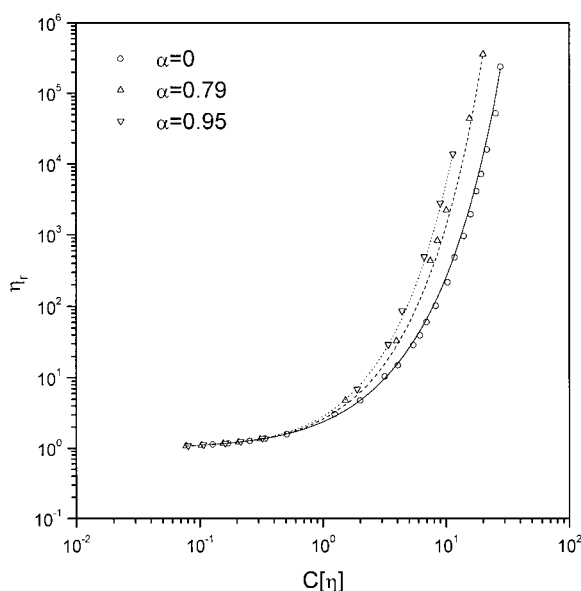


Figure 8 Fitting of the Martin equation for PES/NMP/H₂O systems with various values of α .

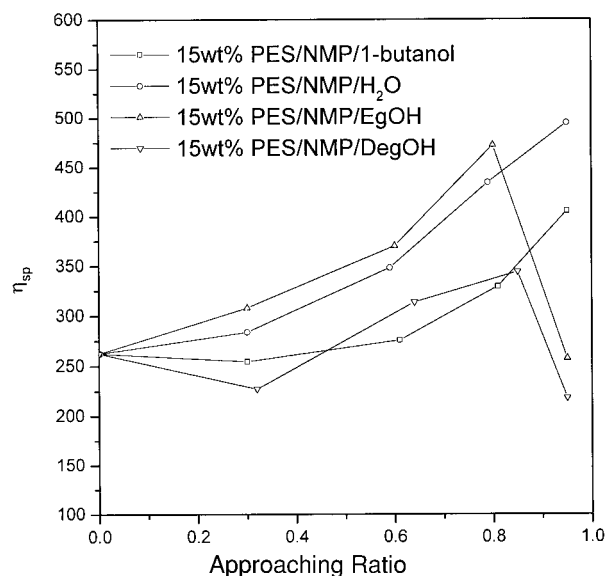


Figure 9 Effect of α on η_{sp} for the 15 wt % PES/NMP/NS system.

The investigated membrane-forming systems were in the crossover regime, where the chains were overlapping but unentangled; this was consistent with the Newtonian behavior of the dopes. The quality of the solvent mixture characterized by α was degraded by additives. Additives can influence not only the thermodynamic state of a dope but also the rheological properties of a membrane-forming system; these can be helpful for understanding the membrane-formation mechanism.

REFERENCES

- Hägg, M.-B. *Sep Purif Methods* 1998, 27, 51.
- Van de Witte, P.; Dijkstra, P. J.; Van den Berg, J. W. A.; Feijen, J. *J Membr Sci* 1996, 117, 1.
- Kesting, R. E. *J Appl Polym Sci* 1990, 41, 2739.
- Altena, F. W.; Smolders, C. A. *Macromolecules* 1982, 15, 1491.
- Yilmaz, L.; McHugh, A. J. *J Appl Polym Sci* 1986, 31, 997.
- Zeman, L.; Tkacik, G. *J Membr Sci* 1988, 36, 119.
- Strathmann, H.; Kock, K.; Baker, B. W. *Desalination* 1975, 16, 179.
- Altena, F. W.; Smid, J.; Van den Berg, J. W. A.; Wijmans, J. G.; Smolders, C. A. *Polymer* 1985, 26, 1531.
- McHugh, A. J.; Tsay, C. S. *J Appl Polym Sci* 1992, 46, 2011.
- Kim, H. J.; Tyagi, R. K.; Fouda, A. E.; Jonasson, K. *J Appl Polym Sci* 1996, 62, 621.
- Kim, H. J.; Fouda, A. E.; Jonasson, K. *J Appl Polym Sci* 2000, 75, 135.
- Reuvers, A. J.; Van den Berg, J. W. A.; Wijmans, J. G.; Smolders, C. A. *J Membr Sci* 1987, 34, 45.
- Tsay, C. S.; McHugh, A. J. *J Polym Sci Part B: Polym Phys* 1990, 28, 1327.
- Radovanovic, P.; Thiel, S. W.; Hwang, S. T. *J Membr Sci* 1992, 65, 213.
- Cheng, L.-P.; Soh, Y. S.; Dwan, A.-H.; Gryte, C. C. *J Polym Sci Part B: Polym Phys* 1994, 32, 1413.
- Zheng, Q.; Yang, B.-B.; Wu, G.; Li, L.-W. *Chem J Chin Univ* 1999, 20, 1483.
- Ferry, J. D. *Viscoelastic Properties of Polymers*; Wiley: New York, 1980.
- Strathmann, H.; Koch, K. *Desalination* 1977, 21, 241.
- Wood, H.; Wang, J.; Sourirajan, S. *Sep Sci Technol* 1993, 28, 2297.
- Okuno, H.; Renzo, K.; Uragami, T. *J Membr Sci* 1993, 83, 199.
- Torrestiana-Sanchez, B.; Ortiz-Basurto, R. I.; Fuente, E. B. L. *J Membr Sci* 1999, 152, 19.
- Maggioni, J. F.; Eich, A.; Wolf, B. A.; Nunes, S. P. *Polymer* 2000, 41, 4743.
- Aptel, P.; Abidine, N.; Ivaldi, F.; Lafaille, J. P. *J Membr Sci* 1985, 22, 199.
- Shilton, S. J.; Bell, G.; Ferguson, J. *Polymer* 1994, 24, 5327.
- Chung, T. S.; Teoh, S. K.; Lau, W. W. Y.; Srinivasan, M. P. *Ind Eng Chem Res* 1998, 37, 3930.
- Qin, J. J.; Chung, T. S. *J Membr Sci* 1999, 157, 35.
- Chung, T. S.; Lin, W.-H.; Vora, R. H. *J Membr Sci* 2000, 167, 55.
- He, T.; Jiang, C. Z. *Membr Sci Technol* 1998, 18, 43.
- Li, Z. S.; Jiang, C. Z. *J Membr Sci* 2000, 174, 87.
- Li, S.-G. Ph.D. Thesis, University of Twente, The Netherlands, 1994.
- Isono, Y.; Nagasawa, M. *Macromolecules* 1980, 13, 862.
- Milas, M.; Rinaudo, M.; Knipper, M.; Schuppiser, J. L. *Macromolecules* 1990, 23, 2506.
- Brown, W.; Nicolai, T. *Colloid Polym Sci* 1990, 268, 977.
- Graessley, W. W. *Adv Polym Sci* 1974, 16, 1.
- Candau, F.; Regalado, E. J.; Selb, J. *Macromolecules* 1998, 31, 5550.
- Raspaud, E.; Lairez, D.; Adam, M. *Macromolecules* 1995, 28, 927.
- Martin, A. F. Presented at the American Chemical Society Meeting, Memphis, TN, April 1942.
- Geerisse, H.; Schmidt, J. R.; Wolf, B. A. *J Appl Polym Sci* 1982, 27, 1277.
- Geerisse, H.; Roos, J.; Wolf, B. A. *Makromol Chem* 1985, 186, 787.