Supplementary Materials

Development of Porous Polyacrylonitrile Composite Fibers: New Precursor Fibers with High Thermal Stability

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Note S1:

1. Phase Diagram of PAN/H$_2$O/DMF Ternary System

1.1. Binodal Curve

According to the expanded Flory–Huggins theory, the Gibbs free energy of mixing for a ternary system is represented as follows [1]:

$$\frac{\Delta G_m}{RT} = n_1 \ln\phi_1 + n_2 \ln\phi_2 + n_3 \ln\phi_3 + g_{12} n_1 \phi_2 + g_{13} n_1 \phi_3 + g_{23} n_2 \phi_3 \tag{1}$$

where n_i and ϕ_i are the number of moles and volume fraction of component i, respectively, R is the gas constant, T is the absolute temperature, g_{ij} is concentration-dependent binary interaction parameters between component i and j. The subscripts refer to non-solvent (1), solvent (2), and polymer (3). Only binary interaction parameters are considered; meanwhile g_{13} and g_{23} are considered as concentration-independent.

According to the description of chemical potential, the following three equations are deduced:

$$\frac{\Delta\mu^1}{RT} = \ln\phi^1 + 1 - \phi^1 - \frac{\vartheta^1}{\vartheta^2}\cdot\phi^2 - \frac{\vartheta^1}{\vartheta^3}\cdot\phi^3 + (g^{12}\phi^2 + g^{13}\phi^3).(\phi^2 + \phi^3) - \frac{\vartheta^1}{\vartheta^2}g^{23}\phi^2\phi^3$$
$$- u_1 u_2 \phi_2\left(\frac{dg_{12}}{du_2}\right) - \phi_1 \phi_3{}^2\left(\frac{dg_{13}}{d\phi_3}\right) - \frac{\vartheta_1}{\vartheta_2}\phi_2 \phi_3{}^2\left(\frac{dg_{23}}{d\phi_3}\right) \tag{2}$$

$$\frac{\Delta\mu^2}{RT} = \ln\Phi^2 + 1 - \Phi^2 - \frac{\vartheta^2}{\vartheta^1}\cdot\Phi^1 - \frac{\vartheta^2}{\vartheta^3}\cdot\Phi^3 + \left(\frac{\vartheta^2}{\vartheta^1}g^{12}\Phi^1 + g^{23}\Phi^3\right)(\Phi^1 + \Phi^3) - \frac{\vartheta^2}{\vartheta^1}g^{13}\Phi^1\Phi^3$$
$$+ \frac{\vartheta^2}{\vartheta^1}u^1 u^2 \Phi^1\left(\frac{dg^{12}}{du^2}\right) - \frac{\vartheta^2}{\vartheta^1}\Phi^1\Phi^{32}\left(\frac{dg^{13}}{d\Phi^3}\right) - \Phi^2\Phi^{32}\left(\frac{dg^{23}}{d\Phi^3}\right) \tag{3}$$

$$\frac{\Delta\mu_3}{RT} = ln\Phi_3 + 1 - \Phi_3 - \frac{\vartheta_3}{\vartheta_1}\Phi_1 - \frac{\vartheta_3}{\vartheta_2}\Phi_2 + (\frac{\vartheta_3}{\vartheta_1}g_{13}\Phi_1 + \frac{\vartheta_3}{\vartheta_2}g_{23}\Phi_2)(\Phi_1 + \Phi_2) - \frac{\vartheta_3}{\vartheta_1}g_{12}\Phi_1\Phi_2$$
$$+ \Phi_3[\frac{\vartheta_3}{\vartheta_1}\Phi_1(\frac{dg_{13}}{d\Phi_3}) + \frac{\vartheta_3}{\vartheta_2}\Phi_2(\frac{dg_{23}}{d\Phi_3})](\Phi_1 + \Phi_2)$$

(4)

Based on the definition of the binodal curve, the following equation is employed:

$$\Delta\mu_{i,\,A} = \Delta\mu_{i,\,B}(I = 1, 2, 3)$$

(5)

where the subscripts A and B refer to the polymer-rich and polymer-poor phases, respectively. According to mass conservation law:

$$\sum_{i=1}^{3}\Phi i = 1(I = 1, 2, 3)$$

(6)

Equations (5) and (6) include five coupled nonlinear equations with six unknowns: $\phi_{1,\,A}, \phi_{2,\,A}, \phi_{3,\,A}, \phi_{1,\,B}, \phi_{2,\,B}$, and $\phi_{3,\,B}$.

1.2. Spinodal Curve

The spinodal curve of a ternary system provides the following equation [1]:

$$G_{22}\,G_{33} = (G_{23})^2$$

(7)

The free energies G_{22}, G_{23}, and G_{33} can be declared as follows:

$$G_{22} = \frac{1}{\Phi_1} + \frac{\vartheta_1}{\vartheta_2\Phi_2} - 2g_{12} + 2(u_1 - u_2)(\frac{dg_{12}}{du_2}) + u_1u_2(\frac{d^2g_{12}}{du_2{}^2})$$

(8)

$$G_{23} = \frac{1}{\Phi_1} - (g_{12} + g_{13}) + \frac{\vartheta_1}{\vartheta_2}g_{23} + u_2(u_1 - 2u_2)(\frac{dg_{12}}{du_2}) + u_1u_2{}^2(\frac{d^2g_{12}}{du_2{}^2}) - \Phi_3(\frac{dg_{13}}{d\Phi_3})$$
$$+ \frac{\vartheta_1}{\vartheta_2}\Phi_3(\frac{dg_{23}}{d\Phi_3})$$

(9)

$$G_{33} = \frac{1}{\Phi_1} + \frac{\vartheta_1}{\vartheta_3\Phi_3} - 2g_{13} + 2u_2{}^2(1 - u_1)(\frac{dg_{12}}{du_2}) + u_1u_3{}^2(\frac{d^2g_{12}}{du_2{}^2}) + 2(\Phi_1 - \Phi_3)(\frac{dg_{13}}{d\Phi_3})$$
$$+ \Phi_1\Phi_3(\frac{d^2g_{13}}{d\Phi_3{}^2}) + \frac{2\vartheta_1}{\vartheta_2}\Phi_2(\frac{dg_{23}}{d\Phi_3}) + \frac{\vartheta_1}{\vartheta_2}\Phi_2\Phi_3(\frac{d^2g_{23}}{d\Phi_3{}^2})$$

(10)

In addition, the components of ternary system obey the mass conservation law:

$$\sum_{i=1}^{3}\Phi i = 1 \qquad i = 1, 2, 3$$

(11)

Equations (7) and (11) include two coupled nonlinear equations with three unknowns: ϕ_1, ϕ_2, and ϕ_3.

2. Critical Point

The critical point composition meets the following equation [1]:

$$G_{222}G_{33}{}^2 - 3G_{223}G_{23}G_{33} + 3G_{233}G^2{}_{23} - G_{22}G_{23}G_{333} = 0$$

(12)

Equations (11) and (12) also include two coupled nonlinear equations with three unknowns: ϕ_1, ϕ_2, and ϕ_3. Thus, assuming one of the unknowns as an independent variable, the binodal curve, spinodal curve, and critical point can be calculated using least square method with the help of the nonlinear function of Lsqnonlin in MATLAB.

3. H₂O–DMF Binary System

According to the literature [2], the Flory–Huggins interaction parameters for various solvent–non-solvent binary systems can be expressed by the following equation:

$$g_{12} = \alpha + \beta/(1-\gamma\phi_2) \tag{13}$$

Where g_{12} is a concentration-dependent interaction parameter of the H_2O–DMF system. α, β, and γ are three parameters which differ for different binary systems and ϕ_2 is the volume fraction of DMF. For H_2O–DMF binary system at 25°C, the values of α, β, and γ are 0.218, 0.276, and -0.622, respectively [3].

4. DMF–PAN Binary System

There are many approaches to determine the solvent–polymer (DMF–PAN) interaction parameter (g_{23}), namely intrinsic viscosity according to Rudin model or solubility parameter (δ).

$$\delta = (\rho\Sigma G/M) \tag{14}$$

G is the molar absorption constant, ρ (gr/cm³) is density, M (gr/mol) is molecular weight of mer.

Using the following formula, the two-component interaction parameter can be calculated.

$$g_{ij} = \frac{v_i}{RT}(\delta_i - \delta_j)^2 \tag{15}$$

Where V_i is the molar volume of DMF, δ_i and δ_j are the solubility parameters of component i and component j, respectively, T is the absolute temperature, and R is the gas constant. At the first step, the solubility parameter (δ) of the PAN copolymer should be determined to evaluate g_{23}.

According to Equations (14) and (15) as well as Table S1 and S2, g_{23} turned out to 0.05. The accuracy of g_{23} was secondary as its influence on the phase diagram was insignificant.

Table S1. Molar absorption constant at 16°C [4].

Group	G(cal-cm³)$^{0.5}$mol^{-1}	Group	G(cal-cm³)$^{0.5}$mol^{-1}
-CH3	214	>C<	-93
-CH2-	133	COO	310
-CH<	28	H	100
CN	410	-	-

Table S2. Chemical structure and calculated solubility parameter.

Chemical Structure	δ(MPa)$^{1/2}$
$\left(CH_2-\overset{\overset{H}{\mid}}{\underset{\underset{C\equiv N}{\mid}}{C}}\right)_n$	26.5
$\left(CHCH_2\right)_n$ $\mid$ $COOCH_3$	16.13
DMF	24.82

5. H$_2$O –PAN Binary System

In this study, the values of non-solvent–polymer interaction parameter (g_{13}) was determined by obtaining the best fit of the theoretical binodal point curve to the experimental point curve and the value of 1.95 was reached [5].

6. Algorithm Description

Altena et al. [6] have computed the ternary phase diagram by calculating the minimum of the objective function with the least squares method. Here, we define the objective function of the binodal curve (F) as follows:

$$F = \sum f_i^2 \tag{16}$$

where $f_1 = \Delta\mu_{1,A} - \Delta\mu_{1,B}$, $f_2 = \frac{\vartheta_1}{\vartheta_2}(\Delta\mu_{2,A} - \Delta\mu_{2,B})$, and $f_3 = \frac{\vartheta_1}{\vartheta_3}(\Delta\mu_{3,A} - \Delta\mu_{3,B})$. We defined the objective functions of the spinodal curve as follows:

$$f_1 = (G_{23})^2 - G_{22}.G_{33} \tag{17}$$

$$f_2 = 1 - \phi_1 - \phi_2 - \phi_3 \tag{18}$$

MATLAB 7.0 (MathWorks, Natick, MA) software has been employed to compute the phase diagram of the H_2O–DMF–PAN ternary system. We assumed that $\phi_{3,B}$ was negligible as the amount of PAN in the polymer-lean phase was very low. The initial composition of the polymer-rich phase is supposed to be a point on the ternary phase diagram which is close to the PAN side on the PAN–H_2O axis, and the initial composition of the polymer-lean phase is close to the H_2O side.

7. Investigation of Properties of the PAN Fibers in Various Researches

Table S3. An overview on the properties of the PAN fibers prepared in our work and previous studies. .

Ref.	Spinning Material/Filler	Preparation Method	Crystallinity (%)	Weight Loss (%)	T_d (°C)	ΔH (Wg^{-1})
[4]	PAN/GO	Wet spinning	20.4	42.4	N.R.	N.R.
[7]	PAN/FGNS-1.0	Wet spinning	N.R.	48.61	N.R.	5.20
[8]	PANb-CCG0.5	Wet spinning	N.R.	N.R.	~295	N.R.
[9]	PAN-GNP	Pressurized gyration	N.R.	N.R.	~250	N.R.
[10]	2% P-MWNT/PAN	Electrospinning	N.R.	~10	N.R.	N.R.
Present Work	**PAN/GO/H$_2$O**	**Wet spinning**	**26**	**48.2**	**307.1**	**3.41**

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