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Fuzzy viscometric analysis of polymer–polymer miscibility based on fuzzy regression

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ABSTRACT

This study investigates the application of fuzzy regression to the viscometric analysis of polymer–polymer miscibility by using experimental viscosity data for polystyrene (PS), poly(styrene-co-acrylonitrile) (PSAN) and PS/PSAN blends in $CHCl_3$ and DMF at different temperatures. The first stage includes the calculations of the fuzzy thermodynamic interaction parameter based on the results from the fuzzy regression models. In the second stage, the possibility and necessity measure-dependent results of the immiscibility (or miscibility) are presented and compared with the traditional miscibility estimations. This study shows that the fuzzification of traditional regression as well as the decision making on miscibility may have a good potential to be used for viscometric studies.

1. Introduction

Viscometry is a widely used method for investigating the polymer–polymer interaction and miscibility in dilute polymer solutions [1–6]. There are many criteria to estimate polymer–polymer miscibility by using the viscometry method such as Garcia et al.'s [7] viscosity interaction parameter ($[\Delta\eta]_m$) and Sun et al.'s [8] thermodynamic interaction parameter (α). The common starting point for their calculations is the prediction of the viscometric parameters for pure polymers and their blend compositions on the basis of the classical Huggins equation [9] by conventional (linear) regression analysis. However, this type of regression method can be problematic due to the fact that **i)** the regression model (i.e., Huggins model) may not be well-defined and sharp [10] and **ii)** the aptness of the model as well as its parameters is difficult to justify since the viscosity data set available for the regression analysis is often too small. These are also the reasons why the fuzzy linear regression (hereafter called fuzzy regression) can be used as a viable alternative to classical (statistical) linear regression [11] in estimating the viscometric parameters. Fuzzy regression first introduced by Tanaka et al. [12] is a non-statistical method and, unlike statistical regression, the deviations between observed and predicted values in fuzzy regression are assumed to depend on the vagueness of the system structure expressed by the parameters of regression model, not on measurement errors. There are three main approaches for fuzzy regression analysis: The possibilistic approach employs linear programming where minimizing the sum of spreads of the estimated outputs is generally considered as the objective function [13], while least squares approach aims at minimizing the distance between the predicted and observed fuzzy outputs [14]. Quadratic programming approach integrates the central tendency of least squares and possibilistic properties of fuzzy regression [15]. A literature survey shows that different versions of fuzzy regression analysis have been successfully applied to various engineering and technological forecasting problems [16–21].

This study is the first to investigate the potential usefulness for using fuzzy regression in the viscometric analysis of polymer–polymer miscibility and its novelty lies in the following fuzzy aspects of the viscometric analysis: Firstly, Khan and Baloch's [22] experimental viscosity data for PS/PSAN blend systems in $CHCl_3$ and DMF that are fitted by fuzzy regression analyses based on quadratic programming [15] to the Huggins equation [9] are investigated at different temperatures. This allows fuzzy calculations of Sun et al.'s [8] thermodynamic interaction parameter (α) using the fitted fuzzy viscometric parameters for each studied system. Secondly, two measures (possibility and necessity) of possibility theory [23,24] are implemented to evaluate these fuzzy results for making decision about immiscibility or miscibility. Results are presented and assessed in order to examine the applicability of fuzzy regression analysis as well as possibility theory in viscometric studies.

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2. Theory and calculation

A fuzzy regression model is generally given as follows [12]:

$$\tilde{Y}(\boldsymbol{X}) = \tilde{A}_0 + \tilde{A}_1 X_1 + \cdots + \tilde{A}_n X_n = \tilde{\boldsymbol{A}}\boldsymbol{X} \quad (1)$$

where $\boldsymbol{X} = (1, X_1, \cdots, X_n)^T$ is an input vector, $\tilde{\boldsymbol{A}} = (\tilde{A}_0, \cdots, \tilde{A}_n)$ is the vector of fuzzy coefficients $\tilde{A}_i$ $(i = 0, \cdots n)$ in the forms of symmetric triangular fuzzy numbers consisting of a center a_i and a spread c_i, denoted as $\tilde{A}_i = (a_i, c_i)_L$ with its membership function $\mu_{\tilde{A}_i}(X) = L\left(\frac{X - a_i}{c_i}\right)$, $c_i > 0$, $\tilde{Y}(\boldsymbol{X})$ is the estimated fuzzy output represented as $\tilde{Y}(\boldsymbol{X}) = (\boldsymbol{a}^T\boldsymbol{X}, \boldsymbol{c}^T|\boldsymbol{X}|)_L$ with its symmetric triangular membership function [15] $\mu_{\tilde{Y}(\boldsymbol{X})}(Y)$:

$$\mu_{\tilde{Y}(\boldsymbol{X})}(Y) = \left\{ \begin{array}{c} L\left((Y - \boldsymbol{a}^T\boldsymbol{X})/\boldsymbol{c}^T|\boldsymbol{X}|\right), \ \boldsymbol{X} \neq 0 \\ 1, \boldsymbol{X} = 0, Y = 0 \\ 0, \boldsymbol{X} = 0, Y \neq 0 \end{array} \right\} \quad (2)$$

where Y is crisp output, L is the shape function of the fuzzy numbers, $\boldsymbol{a} = (a_0, \cdots, a_n)$, $\boldsymbol{c} = (c_0, \cdots, c_n)$, $\boldsymbol{a}^T\boldsymbol{X}$ and $\boldsymbol{c}^T\boldsymbol{X}$ are a center and a spread of the fuzzy output $\tilde{Y}(\boldsymbol{X})$, respectively. When a h-level set of $\tilde{Y}(\boldsymbol{X})$ is defined as $[\tilde{Y}(\boldsymbol{X})]_h = \{Y | \mu_{\tilde{Y}(\boldsymbol{X})}(Y) \geq h\} = [Y_h^L, Y_h^U]$, its lower (Y_h^L) and upper (Y_h^U) bounds are as follows:

$$Y_h^L = \boldsymbol{a}^T\boldsymbol{X} - \left|L^{-1}(h)\right|\boldsymbol{c}^T|\boldsymbol{X}| \quad (3)$$

$$Y_h^U = \boldsymbol{a}^T\boldsymbol{X} + \left|L^{-1}(h)\right|\boldsymbol{c}^T|\boldsymbol{X}|. \quad (4)$$

Based on the above definitions, fuzzy regression by quadratic programming (QP) approach is an optimization problem with a quadratic objective function and linear constraints, as shown below [15]:

$$\begin{aligned} &\min_{\boldsymbol{a},\boldsymbol{c}} J = k_1 \sum_{j=1}^{p} \left(Y_j - \boldsymbol{a}^T\boldsymbol{X}_j\right)^2 + k_2 \sum_{j=1}^{p} \boldsymbol{c}^T|\boldsymbol{X}_j||\boldsymbol{X}_j|^T\boldsymbol{c} \\ &\text{subject to } \ \boldsymbol{a}^T\boldsymbol{X}_j - \left|L^{-1}(h)\right|\boldsymbol{c}^T|\boldsymbol{X}_j| \leq Y_j, \ \ j = 1, \cdots, p \\ &\qquad\qquad\quad \boldsymbol{a}^T\boldsymbol{X}_j + \left|L^{-1}(h)\right|\boldsymbol{c}^T|\boldsymbol{X}_j| \geq Y_j, \ \ j = 1, \cdots, p \\ &\qquad\qquad\quad c_i \geq 0, \ \ i = 0, \cdots, n \end{aligned} \quad (5)$$

where p is a data size, k_1 and k_2 are weight coefficients varying between 0 and 1, and the h value, which is between 0 and 1, can be referred to as a degree of fit of the fuzzy regression model to the given data set [11].

In this study, the implementations were performed using computer programs that were written in MATLAB run on an Intel Core i7 based PC.

3. Results and discussion

In the first stage, evidence for miscibility or immiscibility was searched for PS/PSAN blend systems in $CHCl_3$ and DMF by the use of Khan and Baloch's [22] experimental viscosity data (Table 1) through the application of thermodynamic interaction parameter [8] α under fuzziness. Starting with the fuzzification of the Huggins model [9] which express the specific viscosity (η_{sp}) for a single-solute solution as a function of the concentration (C), as follows: $\widetilde{\left(\frac{\eta_{sp}}{C}\right)} = \widetilde{[\eta]} + \tilde{b}C$, the values of $\tilde{b}$ (fuzzy viscosity interaction parameter) and $\widetilde{[\eta]}$ (fuzzy intrinsic viscosity) were determined for the polymers ($\tilde{b}_{11}$, $\tilde{b}_{22}$, $\widetilde{[\eta]}_1$, $\widetilde{[\eta]}_2$) and their blend compositions ($\tilde{b}_m$, $\widetilde{[\eta]}_m$) by solving the QP problem (Eq. 5) with $h = 0, k_1 = 1$ and $k_2 = 0.01$. A real-valued genetic algorithm (GA) [25,26] was employed to obtain the optimal fuzzy coefficients of the fuzzy regression models. The various parameters involved in the GA algorithm were selected as follows: The size of the randomly generated initial population was set to 100. The selection operator was implemented by using the tournament selection method [27,28] to reproduce chromosomes in proportional to the fitness values. The function to calculate the fitness (F) was expressed by the following equation:

$$F = \frac{1}{J_m} \quad (6)$$

where J_m is the modified objective function based on Deb's [29] penalization method:

$$J_m = \left\{ \begin{array}{l} J \text{ if } \left(\boldsymbol{a}^T\boldsymbol{X}_j - \left|L^{-1}(h)\right|\boldsymbol{c}^T|\boldsymbol{X}_j| - Y_j\right) \leq 0 \text{ and } \left(-\boldsymbol{a}^T\boldsymbol{X}_j - \left|L^{-1}(h)\right|\boldsymbol{c}^T|\boldsymbol{X}_j| + \boldsymbol{Y}_j\right) \leq 0 \\ J_{max} + \left(\boldsymbol{a}^T\boldsymbol{X}_j - \left|L^{-1}(h)\right|\boldsymbol{c}^T|\boldsymbol{X}_j| - Y_j\right) + \left(-\boldsymbol{a}^T\boldsymbol{X}_j - \left|L^{-1}(h)\right|\boldsymbol{c}^T|\boldsymbol{X}_j| + Y_j\right) \text{ otherwise} \end{array} \right\} \quad (7)$$

Table 1
Reduced viscosity data for PS, PSAN, and their blends in DMF and $CHCl_3$ measured at various temperatures [22].

			Composition (PS/PSAN)				
			0/100	30/70	50/50	70/30	100/0
Solvent	C (g/dL)	T (°C)	$\frac{\eta_{sp}}{C}$ (dL/g)	$\frac{\eta_{sp}}{C}$ (dL/g)	$\frac{\eta_{sp}}{C}$ (dL/g)	$\frac{\eta_{sp}}{C}$ (dL/g)	$\frac{\eta_{sp}}{C}$ (dL/g)
DMF	0.25	20	0.742	0.655	0.585	0.512	0.438
	0.5		0.761	0.672	0.616	0.558	0.471
	0.75		0.784	0.698	0.647	0.603	0.517
	1		0.809	0.724	0.674	0.652	0.552
	0.25	30	0.728	0.639	0.567	0.485	0.421
	0.5		0.749	0.669	0.598	0.509	0.457
	0.75		0.772	0.688	0.627	0.532	0.483
	1		0.798	0.713	0.663	0.569	0.514
	0.25	40	0.698	0.605	0.527	0.453	0.402
	0.5		0.726	0.629	0.559	0.474	0.423
	0.75		0.757	0.654	0.594	0.507	0.448
	1		0.779	0.687	0.626	0.532	0.479
$CHCl_3$	0.25	20	1.792	1.734	1.647	1.685	1.484
	0.5		1.825	1.758	1.671	1.704	1.517
	0.75		1.862	1.793	1.695	1.728	1.567
	1		1.906	1.833	1.735	1.756	1.619
	0.25	30	1.744	1.675	1.617	1.646	1.552
	0.5		1.771	1.707	1.639	1.675	1.577
	0.75		1.814	1.743	1.675	1.696	1.614
	1		1.852	1.785	1.707	1.734	1.653
	0.25	40	1.685	1.624	1.588	1.609	1.507
	0.5		1.713	1.657	1.615	1.638	1.528
	0.75		1.747	1.696	1.644	1.675	1.569
	1		1.794	1.743	1.681	1.702	1.606