Estimated blend viscosities by a simple and workable model

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The Lecyar model, derived by remodelling the McAllister model, is able to describe satisfactorily the viscosity–composition dependence for several blend systems exhibiting positive, negative and mixed deviations. In the present work, the model is applied to polycarbonate/acrylonitrile–butadiene–styrene blends and polyacetal (polyoxymethylene)/thermoplastic polyurethane blends, with the latter having an elastomer as one of the constituents. The model provides a good fit in both cases.

(Keywords: blends; viscosity; model)

Introduction

Interest in polymer blends stems from the desire to develop new polymeric materials with novel and balanced properties at low cost. Measurements and/or theoretical predictions of the rheological properties of polymer blends are essential from the processing point of view. Several simple interpolative models, such as those proposed by Heitmiller *et al.* and Hayashida *et al.*, are applicable only to the binary blend systems where the viscosity and its first derivative with respect to composition are monotonic over the composition range. However, these models are handicapped when required to predict the viscosities of blend systems having positive, negative and mixed deviations from the linear behaviour. To account for these variations, further models were developed, of which the McAllister three-body model was found to describe the viscosity–composition dependence accurately, provided the viscosities of one or more intermediate compositions were known. The model is:

$$\begin{aligned}\ln v_B = {} & x_1^3 \ln v_1 + x_2^3 \ln v_2 + 3x_1^2 x_2 \ln v_{12} + 3x_1 x_2^2 \ln v_{21} \\ & + 3x_1^2 x_2 \ln[(2M_1+M_2)/3] \\ & + 3x_1 x_2^2 \ln[(M_1+2M_2)/3] \\ & + x_1^3 \ln M_1 + x_2^3 \ln M_2 - \ln(x_1 M_1 + x_2 M_2)\end{aligned} \tag{1}$$

where v is the kinematic viscosity, M the molecular weight and x the mole fraction. Subscripts 12 and 21 represent interaction viscosities obtained from measurements of pure component viscosities and at least two intermediate blends. But the McAllister model is very cumbersome to use, for it requires many data such as melt densities, molecular weights and kinematic viscosities which are difficult to determine. Hence Carley[1] has used a simple and workable model – the Lecyar model. The model is:

$$\begin{aligned}\ln \eta_B &= A'm_1^3 + B'm_2^3 + C'm_1^2 m_2 + D'm_1 m_2^2 \\ &= Am_1^3 + Bm_1^2 + Cm_1 + D\end{aligned} \tag{2}$$

(since m_2 can be replaced by $(1-m_1)$), where m_i are mass fractions, A' and B' the natural logarithms of pure-resin viscosities, while C' and D' may be taken as three times the logarithms of interaction viscosities. This simplified model is obtained by dropping the terms involving only x and M, by switching from mole fraction to mass fraction, and by making the model explicit in dynamic rather than kinematic viscosity. In a comparative study involving five binary systems, Carley and Crossan[2] found that both models accounted for over 90% of the viscosity variation and that the Lecyar model performed on a par with the McAllister model in most of the binary systems investigated, except in cases where the molecular-weight ratio was large. Their studies were primarily concerned with plastic/plastic systems; for this work we have selected a plastic/rubber system, namely polyoxymethylene (POM)/thermoplastic polyurethane (TPU) in addition to a plastic/plastic system (polycarbonate (PC)/acrylonitrile–butadiene–styrene (ABS)).

Experimental

Both PC (Makrolon, Bayer AG)/ABS (natural-200 SP, ABS Plastics Ltd, India) and POM (Celcon M 140, Hoechst Celanese)/TPU (Estane 58311, Goodrich) blends were prepared by using a single screw extruder provided with a special mixing head at the screw end. An advanced autostart and autocalculate melt flow-rate system (Rosand Precision Ltd, UK) was used to measure the volumetric flow-rate (VFR, ml/10 min) of the blends with the aid of a piston-following lever (tracer). The apparatus can be regarded as a simple rheometer operating in the constant-shear stress mode and at low shear rate. The experimental data on the VFR *versus* load were converted to viscosity *versus* shear rate using known relations reported in the literature[3,4]. Rabinowitsch corrections were applied to the viscosity values. However, Bagley end corrections could not be applied as we do not have dies with different L/D ratios.

Results and discussion

The viscosity of the PC/ABS and POM/TPU blends as a function of composition at various shear rates is shown in *Figures 1* and *2*, respectively. The solid lines denote the fit given by the Lecyar model. In both systems, the model fits the data with standard error of estimates (S_e) comparable with those obtained by other investigators. Although this model is not able to predict the values exactly, it predicts qualitatively the general trend of blend viscosities. Also, comparisons are made with the interpolative Hayashida model, which is given

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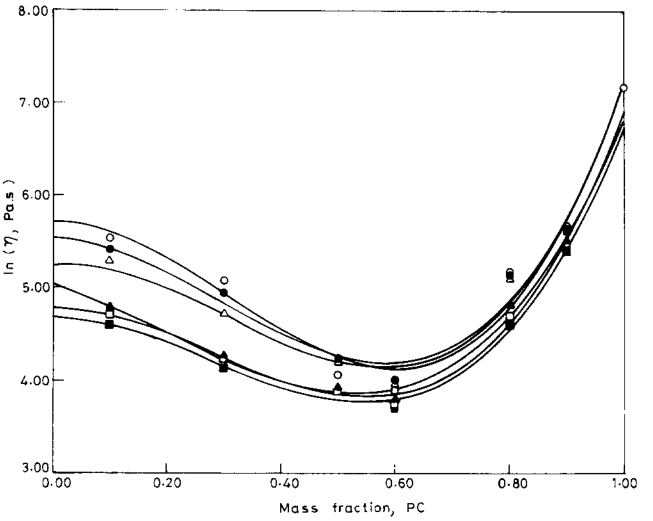

Figure 1 Viscosity–composition plots for PC/ABS blends at various shear rates at 270°C as predicted by the Lecyar model. Shear rate (s^{-1}): ○, 100; ●, 150; △, 200; ▲, 500; □, 600; ■, 800

by:

$$1/\eta_B = f_2/\eta_1 + f_1/\eta_2 \qquad (3)$$

where f_1 and f_2 represent any type of fractions. It is obvious from *Figure 3* that the interpolative Hayashida model cannot predict the compositional change of viscosity in both systems. The values of the Lecyar coefficients along with the S_e values are presented in *Table 1*.

The existence of maximum viscous and elastic properties of two-phase systems at certain composition ratios has been explained by Han and Yu[5]. As the compatibility (miscibility) or incompatibility of the system has a bearing on the form of the viscosity–composition curves, a detailed analysis on these blends is of significance. The negative deviation of PC/ABS blends from linear behaviour indicates their incompatible nature. This is corroborated by Burns and Kim[6] who have noted a lowering of viscosity with the addition of

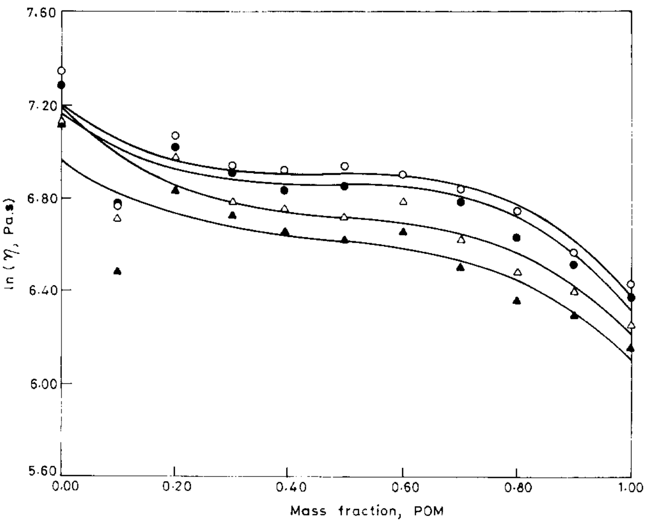

Figure 2 Viscosity–composition plots for POM/TPU blends at various shear rates at 190°C as predicted by the Lecyar model. Shear rate (s^{-1}): ○, 100; ●, 150; △, 200; ▲, 300

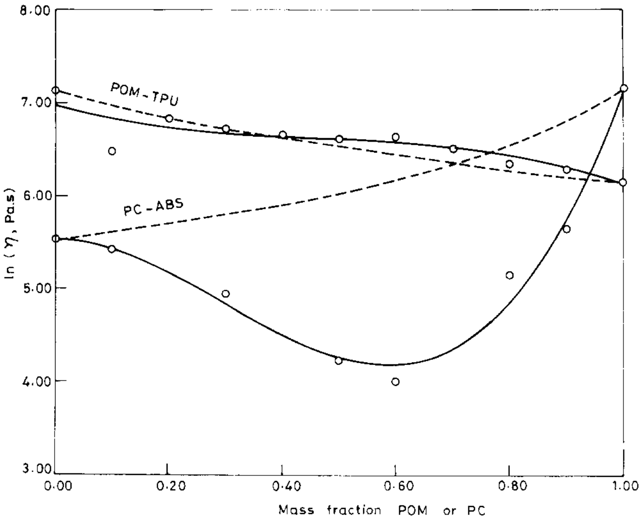

Figure 3 Viscosity–composition plots for PC/ABS and POM/TPU blend systems at a shear rate of 150 s^{-1} as predicted by the Hayashida and Lecyar models. ○, Experimental; – – –, Hayashida model; ——, Lecyar model

Table 1 Lecyar coefficients

Blend system	Shear rate (s^{-1})	*A*	*B*	*C*	*D*	S_e
PC/ABS	50	14.814	−13.705	0.080	5.876	0.1699
	100	13.930	−11.873	−0.572	5.721	0.2335
	150	13.333	−11.622	−0.070	5.537	0.1694
	200	13.679	−12.501	0.768	5.233	0.1681
	300	12.169	−10.264	0.123	5.022	0.1651
	400	6.692	−1.620	−3.713	5.342	0.1199
	500	9.045	−5.346	−1.932	5.036	0.0901
	600	11.955	−10.004	0.152	4.777	0.0708
	800	11.177	−9.147	0.004	4.680	0.0835
POM/TPU	25	−3.211	4.373	−1.992	7.221	0.1303
	50	−3.205	4.336	−1.991	7.175	0.1231
	100	−3.107	4.603	−2.488	7.198	0.1334
	150	−2.409	3.305	−1.756	6.966	0.1561
	200	2.314	−5.252	2.810	6.208	0.1012
	250	1.412	−3.406	1.702	6.306	0.0924
	300	10.154	−24.288	17.917	2.175	0.0453

ABS. Also, the occurrence of the maximum level of extrudate swell at 50% PC[6] and the minimum level of viscosity at around 50% PC (as envisaged in our study) is behaviour typical of incompatible blends.

With regard to POM/TPU blends, we notice a mixed deviation, i.e. a positive–negative deviation. The small extent of deviation, in contrast to the large extent expected from completely incompatible systems, appears to indicate the partial miscibility arising due to hydrogen bonding[7]. This type of mixed deviation from the additivity rule may be related to phase inversions[8].

While making these interpretations, we have taken note of the statement of Utracki and Kamal[9] who recognize that it is very difficult to say whether a polymer blend is compatible or not, solely from viscosity measurements. Hence it is imperative that the rheological data are coupled with d.s.c., d.m.a. and other information to throw more light on the compatibility of the blends. A detailed study on the rheological behaviour of POM/TPU blends using Rheograph-2001 is being carried out and the data will be fitted to the Lecyar model to assess the performance of the model.

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