Free Volume Theory for Rheological Properties of Polymer Blends

RYSZARD STELLER and DANUTA ŻUCHOWSKA, *Institute of Organic and Polymer Technology, Technical University of Wrocław, Wybrzeże Wyspiańskiego 27, 50-370 Wrocław, Poland*

Synopsis

Theoretical model representing rheological properties of multicomponent blends as functions of their composition and properties of individual components was proposed. Applicability of this model was experimentally verified for two binary blends. In both cases a good agreement of theoretical predictions with experimental data was stated.

INTRODUCTION

One of the most important problems in studying polymer blends is to find general relationships between different properties of blends and their composition as well as appropriate properties of pure components.

The behavior of blends of defined morphological structure and composition essentially depends on their physical states determined by temperature and pressure. Hence, for characterization of blends in different physical states, different properties, phenomena, and mechanisms should be taken into account.

The behavior of blends in molten state principally depends on rheological properties of individual components and additional interactions between these components at phase boundaries. The interaction mechanisms are usually very complicated functions of chemical and physical structures and components, flow conditions, and blend composition. These factors should be taken into account in any mathematical model, which adequately describes the rheological properties of blends.

Many empirical, semiempirical, and theoretical relationships describing rheological properties of blends as functions of their composition and appropriate properties of components exist.[1-8] These expressions, however, have as a rule a limited applicability, since they quantitatively describe the properties of systems of limited number of components and defined phase structure in narrow range of deformation conditions.

The aim of this article is the theoretical description of rheological properties of multicomponent polymer blends based on the free volume theory[2] and its experimental verification for some binary blends. This approach eliminates many faults connected with the studies cited.

THEORETICAL

Experimental studies of many polymer systems[2] have shown that their viscosity η can be adequately described using Doolittle's equation[9]:

$$\ln \eta = \frac{V_0}{V_f} B + C \tag{1}$$

where V_0 is the occupied volume resulting from the volume of separate atoms and their thermal motions, V_f is the free volume considered as an additional empty space resulting from steric effects and thermal motions of whole molecules, B is the empirical constant practically independent of nature of system and temperature and approximately equal to unity,[10] and C is the empirical constant dependent on the system but independent of temperature.

Simple relationship exists between volume V and the quantities V_0 and V_f:

$$V = V_0 + V_f \tag{2}$$

The effect of temperature on quantities in eq. (2) is different in various intervals fixed by characteristic temperatures of phase transitions T_g (glass temperature) and T_m (melting temperature). For $T < T_g$ V_f is practically constant, and the thermal expansion of polymer is entirely determined by changes of V_0^2.

Within the range $T_g < T < T_m$ it can be assumed that the changes of V and V_f are characterized by different thermal expansion coefficients,[2] which testifies to some thermal expansion of V_0 due to the relative small content of V_f in the system. According to other suggestions,[2] however, the change of V is determined only by the change of V_f, i.e., for $T_g < T < T_m$, V_0 remains practically constant.

In the case of molten polymers, i.e., for $T > T_m$, it should be assumed that the increase of V_0 with increasing temperature, which essentially results from the thermal motions of atoms, is negligibly small as compared with the suitable change of V_f principally resulting from the thermal motions of whole molecules. This statement can be expressed by

$$\frac{\partial V_f}{\partial T} \gg \frac{\partial V_0}{\partial T} \tag{3}$$

This behavior can be explained by considering that the forces of atomic bonds are much larger than those of intermolecular interactions. Hence, the thermal motions of atoms should be significantly smaller than those of whole molecules. Moreover, for $T > T_m$ the free volume content in the system is considerably higher than that at lower temperatures.

Differentiating both sides of eq. (2) with respect to temperature and taking into account expression (3) one obtains

$$\frac{\partial V}{\partial T} = \frac{\partial V_f}{\partial T} \tag{4}$$

Equation (1) can be differentiated with respect to temperature and then the quantities V_0 and $\partial V_f / \partial T$ eliminated by means of expressions (2) and (4), which leads to algebraic equation of second order:

$$\left(\frac{\partial \ln \eta}{\partial T} \middle/ \frac{\partial \ln V}{\partial T} \middle/ B \right) V_f^2 - V V_f + V^2 = 0 \tag{5}$$

Denoting

$$\delta = \left(1 - 4\,\frac{\partial \ln \eta}{\partial T}\bigg/\frac{\partial \ln V}{\partial T}\bigg/B\right)^{1/2} \tag{6}$$

one obtains

$$V_f = \frac{2}{\delta + 1}\,V \tag{7}$$

Further important expressions result from (2) and (7):

$$V_0 = \frac{\delta - 1}{\delta + 1}\,V \tag{8}$$

$$\frac{V_0}{V_f} = \frac{1}{2}\,(\delta - 1) \tag{9}$$

Equations (7)–(9) can be applied for any polymer system (e.g., for pure polymers and polymer blends) that fulfills conditions (1) and (3). They make possible the calculation of the free volume V_f and occupied volume V_0 at any temperature $T > T_m$ from the known thermal characteristic of the system, i.e., from the relationships

$$\eta = \eta(T) \tag{10a}$$

$$V = V(T) \tag{10b}$$

To find the relation between rheological properties of molten blend and analogous properties of pure components, two basic assumptions should be introduced:

1. Occupied volume of blend V_{ob} is an additive quantity, i.e.,

$$V_{ob} = \sum_{i=1}^{n} w_i V_{oi} \tag{11}$$

where w_i is the weight fraction of the ith component and V_{oi} is the occupied volume of ith component (per mass unit).

2. Free volume of blend V_{fb} is a nonadditive quantity, i.e.,

$$V_{fb} = \sum_{i=1}^{n} w_i V_{fi} + F(w_1, \ldots, w_j, \ldots, w_n) \tag{12}$$

where V_{fi} is the free volume of the ith component (per mass unit).

The function F describing the nonadditivity of V_{fb} fulfills the condition

$$F(1, \ldots, 0, \ldots 0) = \cdots = F(0, \ldots, 1, \ldots, 0)$$
$$= \cdots = F(0, \ldots, 0, \ldots 1) = 0 \tag{13}$$

The value of F can be calculated from the expression

$$F = V_b - \sum_{i=1}^{n} w_i l_i \tag{14}$$

where V_b is the specific volume of blend and V_i is the specific volume of ith component, which directly comes from eqs. (2), (11), and (12).

Taking into account expressions (8) and (11), one obtains the following relationship:

$$\frac{\delta_b - 1}{\delta_b + 1} V_b = \sum_{i=1}^{n} w_i \frac{\delta_i - 1}{\delta_i + 1} V_i \tag{15}$$

On the one hand eq. (15) can be treated as a special form of eq. (11), which makes possible the assumption of occupied volume for blends to be experimentally verified. On the other hand eq. (15) can be used to calculate one of the blend properties such as activation energy of flow or thermal expansion coefficient if the properties of pure components and other properties of blends are known and the additivity of occupied volume for blends can be assumed.

A direct calculation of the blend viscosity based on the free volume theory is not possible since for blends the physical meaning of constant $C(C_b)$ in eq. (1) is not exact. To obtain an expression for direct calculation of viscosity, the analytical form of constant C_b as a function of composition and properties of components should be defined. It can be done in many different ways. For this reason only two hypothetical cases will be considered:

$$C_b = \sum_{i=1}^{n} \phi_i C_i \tag{16a}$$

$$C_b = \sum_{i=1}^{n} w_i C_i \tag{16b}$$

where ϕ_i is the volume fraction of the ith component and C_i is the value of constant C for the ith component.

The relation between volume and weight fractions is given by

$$\phi_j = \frac{w_j V_j}{\sum\limits_{i=1}^{n} w_i V_i} \tag{17}$$

Applying eq. (1) separately for blend and pure components and using condition (16a) as well as expressions (7)–(14), after some transformations one obtains

$$\ln \eta_b = \sum_{i=1}^{n} \phi_i \ln \eta_i + \frac{\sum_{i=1}^{n} w_i \left[(\delta_i - 1)/(\delta_i + 1) \right] V_i}{V_b - \sum_{i=1}^{n} w_i [(\delta_i - 1)/(\delta_i + 1)] V_i} - \frac{1}{2} \sum_{i=1}^{n} \phi_i (\delta_i - 1) \quad (18)$$

Generally eq. (18) allows the blend viscosity to be calculated if the properties of components and the specific volume of blend are known.

Similar expression for η_b can be obtained using condition (16b). For this purpose the values of ϕ_i appearing in eq. (18) whould be replaced by w_i. From expression (18) it can be seen that for ideal blends satisfying the conditions $V_{fi} = \text{const}$, $V_{oi} = \text{const}$, and $F = 0$, the rule of logarithmic additivity is fulfilled, i.e., the values of second and third terms are zero. For the expression modified according to condition (16b) the requirement $V_{oi} = \text{const}$ is not necessary to fulfill the rule of logarithmic additivity.

Considerations presented here lead to the conclusion that by suitable choice of C_b as a function of blend composition and properties of components, one can obtain many different equations describing the blend viscosity.

For immiscible systems, which additionally demonstrate very weak interactions at the phase boundary, the nonadditive change of the free volume described by function F should not exist, i.e., $F = 0$. Hence, eq. (18) can be simplified to

$$\ln \eta_b = \sum_{i=1}^{n} \phi_i \ln \eta_i + \frac{1}{2} \frac{\sum_{i=1}^{n} w_i [(\delta_i - 1)/(\delta_i + 1)] V_i}{\sum_{i=1}^{n} w_i [1/(\delta_i + 1)] V_i} - \frac{1}{2} \sum_{i=1}^{n} \phi_i (\delta_i - 1) \quad (19)$$

In such case the blend viscosity is a unique function of composition and suitable properties of pure components.

EXPERIMENTAL

Materials

Isotactic polypropylene (iPP) (Malen P), radial block copolymer butadiene–styrene (B/S) (Solprene 475), and hydrogenated block copolymer isoprene–styrene (EP/S) (Shellvis 50) were used for investigations. More exact characteristics of these materials as well as preparation and some properties of iPP–B/B and iPP–EP/S blends were presented in previous articles.[11,12]

Viscosity Measurements

Viscosity measurements of iPP–B/S and iPP–EP/S blends were carried out within the whole composition range at temperatures 448, 463, 478, and 493 K using a capillary viscometer. Details of measurements and some results have also been reported.[11,12]

Measurements of Specific Volume

Specific volumes of blends and pure polymers were measured by means of a piston capillary viscometer equipped with capillary of diameter $d = 2.18$ mm and length $l = 4d$. Piston diameter D (ca. 10 mm) was determined in each temperature with accuracy ∓ 0.01 mm to eliminate errors caused by thermal expansion of metal.

Polymeric material placed in viscometer reservoir was carefully compressed to remove air bubbles and then left at desired temperature for about 10 min. The piston speed v was set up to obtain an average shear rate in the capillary of 1–2 s^{-1}. The measurement of specific volume V at given temperature consists in determination of the melt mass m, which was extruded from the capillary within the time t at known piston speed v and piston diameter D:

$$V = \frac{\prod D^2 \, vt}{4m} \tag{20}$$

To provide sufficient accuracy of measurements, extrudate sample (extrusion time about 15 min) was carefully controlled for the presence of air bubbles. All samples with visible gas inclusions were rejected. The mean value of specific volume from 3–5 measurements was taken as an end result.

It should be noted that this method provides sufficiently accurate results (∓ 0.003 cm^3/g) only if the system shows no considerable tendencies to bubble formation due to the low thermal stability or to the presence of low molecular additives.

RESULTS AND DISCUSSION

Results of measurements of specific volume V for iPP–B/S and iPP–EP/S blends within the whole composition range can be adequately represented in the form of linear dependence of specific volume on temperature:

$$V = V_{448}[1 + \alpha_f(T - 448)] \tag{21}$$

where $T_0 = 448$ K was arbitrarily chosen as a reference temperature. The values of V_{448} and α_f obtained from experimental data by means of the least squares method are presented in Table I. Previous studies[11,12] have shown that the viscosity of iPP–B/S and iPP–EP/S systems as functions of temperature can be adequately described by the Arrhenius equations:

$$\ln \eta = \frac{E}{RT} + K \tag{22}$$

where K is the material constant, R the gas constant, and E the activation energy of flow. Because of non-Newtonian behavior of molten blends and pure polymers, their rheological properties should be compared at the same shear rate. The values of E/R and $\ln \eta$ for both systems at two extreme values of shear rates 20 and 500 s^{-1} (chosen as the reference quantities) are presented in Table II.

TABLE I
Thermal Expansion of iPP–B/S and iPP–EP/S Blends

System	Copolymer content (wt %)	Parameters of eq. (21)	
		V_{448} (cm^3/g)	$\alpha_f \times 10^4$ (deg^{-1})
iPP–B/S	0	1.306	10.14
	15	1.276	8.72
	25	1.248	8.14
	50	1.194	9.53
	75	1.138	8.10
	100	1.086	6.22
iPP–EP/S	0	1.305	10.01
	5	1.299	9.33
	10	1.294	9.01
	15	1.288	8.76
	20	1.283	9.74
	25	1.279	10.10
	50	1.249	9.33
	75	1.219	8.76
	100	1.191	8.24

Following expressions (6), (21), and (22) and assuming $B = 1$ according to[10] "experimental" value of δ takes the form

$$\delta = \left(1 + \frac{4EV}{RT^2\alpha_f} \right)^{1/2} \tag{23}$$

The suitable experimental values of occupied volume for blends and pure components were determined from expressions (8) and (23). "Theoretical" values of occupied volume for blends were calculated from eq. (15) ($n = 2$) using known experimental values of occupied volume for pure components.

Figures 1–4 present the comparison of theoretical and experimental values of occupied volume at two extreme temperatures for iPP–B/S and iPP–EP/S systems at shear rates 20 and 500 s^{-1}, respectively. Correlations of theoretical and experimental data obtained for other temperatures and shear rates were very similar. From Figures 1–4 it can be seen that the maximum deviations of experimental and theoretical values of occupied volume do not exceed 2%. Taking into account that these values were determined from many independent measurements of various parameters at different temperatures with limited accuracy, the obtained agreement should be acknowledged as satisfactory.

Some increase of occupied volume with increasing temperature (ca. 1%, i.e., 0.01 cm^3/g at the mean value of occupied volume 1 cm^3/g) is probably due to a small thermal expansion of occupied volume. The thermal expansion of occupied volume, however, is much smaller than that of free volume (ca. 15%), which confirms the validity of assumption (3).

From Figures 1–4 it can be seen that with increasing shear rate some decrease of occupied volume takes place. There are probably two factors responsible for this behavior. On the one hand an increase of shear rate leads to diminution of thermal mobility of polymer matrix due to some stiffening of the melt struc-

System	Shear rate (s^{-1})	Copolymer content (wt %)	E/R (deg)	$\ln \eta, \eta$ (MPa)			
				448 K	463 K	478 K	483 K
iPP–B/S	20	0	3047	11.982	11.768	11.525	11.373
		15	2758	12.067	11.904	11.622	11.501
		25	2763	12.104	11.908	11.732	11.584
		50	3438	12.283	12.050	11.808	11.584
		75	3750	12.506	12.288	12.002	11.750
		100	4628	12.849	12.518	12.308	11.967
	500	0	2541	10.166	9.999	9.798	9.668
		15	2482	10.287	10.096	9.922	9.783
		25	2569	10.331	10.117	9.970	9.798
		50	2518	10.387	10.171	10.013	9.870
		75	2333	10.494	10.291	10.131	10.020
		100	2131	10.644	10.534	10.365	10.216
iPP–EP/S	20	0	2682	12.205	11.993	11.801	11.662
		5	2705	12.225	12.051	11.832	11.685
		10	2765	12.284	12.090	11.865	11.733
		15	2800	12.307	12.134	11.915	11.745
		20	2886	12.397	12.159	11.964	11.809
		25	2871	12.369	12.166	12.909	11.779
		50	2706	12.704	12.424	12.303	12.061
		75	2846	13.048	12.855	12.581	12.387
		100	3537	13.424	13.206	12.910	12.721
	500	0	2288	10.258	10.022	9.886	9.787
		5	2481	10.304	10.098	9.921	9.802
		10	2438	10.353	10.115	9.947	9.859
		15	2478	10.389	10.151	9.963	9.872
		20	2470	10.398	10.127	10.011	9.879
		25	2469	10.409	10.226	10.076	9.899
		50	2482	10.546	10.282	10.155	10.028
		75	2516	10.727	10.521	10.349	10.215
		100	2523	11.036	10.859	10.671	10.527

ture. On the other hand the observed phenomenon may be the apparent one resulting from the fact that the specific volume of blends was measured only at small shear rates. It is expected that the shear stress growth increases the free volume. Hence the specific volume should also increase. Simultaneously the thermal expansion of polymer should be smaller due to a stiffening of polymer chains by the shear stress. Taking into account eqs. (8), (15), and (23), it follows that that values both of parameter δ and of occupied volume V_0 for blends and pure components at higher shear rates should be greater as those calculated from values of specific volume measured at small shear rates, i.e., probably practically independent of shear rate. Because of technical reasons, however, an exact measurement of specific volume at high shear rates in our experiments was impossible.

It has been confirmed that numerical values of occupied volume [calculated via eq. (23)] strongly depend on parameters V_{448} and α_f. Hence, the specific volumes of blends and pure polymers should probably be measured with higher accuracy (ca. ∓ 0.001 cm^3/g) as that obtained in our studies (ca. ± 0.003 cm^3/g) to improve the agreement of experimental and theoretical data.
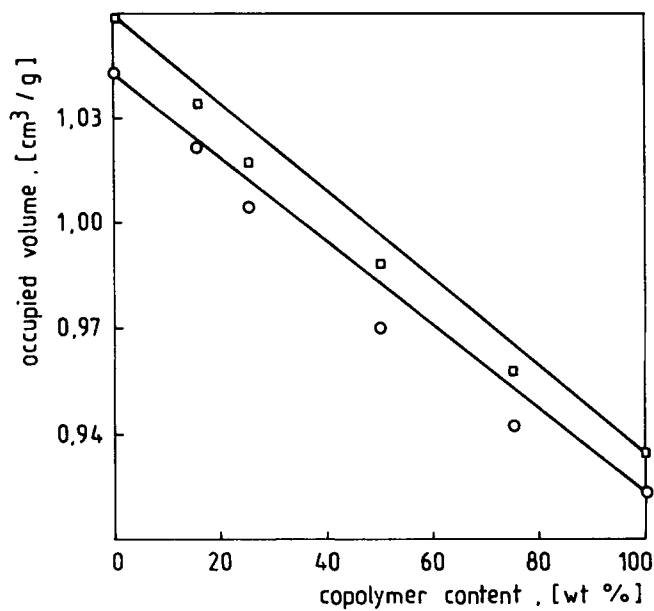
Fig. 1. The effect of blend composition on occupied volume of iPP–B/S system at different temperatures and the shear rate 20 s^{-1}: — theoretical calculations; experimental data: (○) 448 K, (□) 493 K.
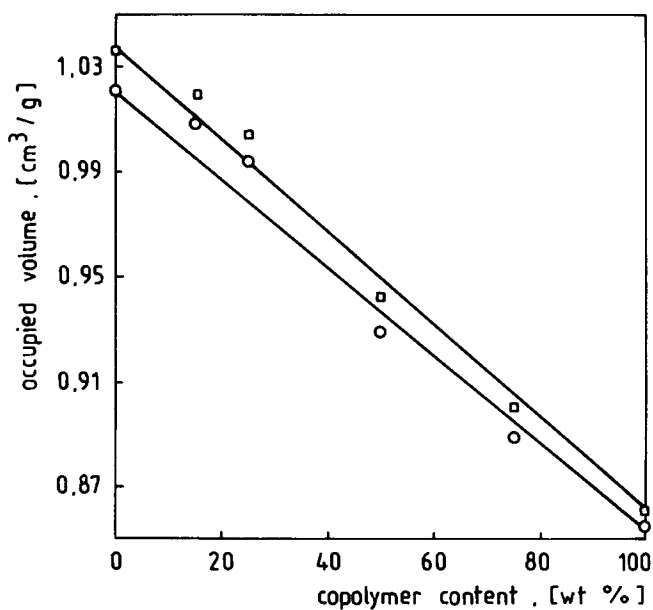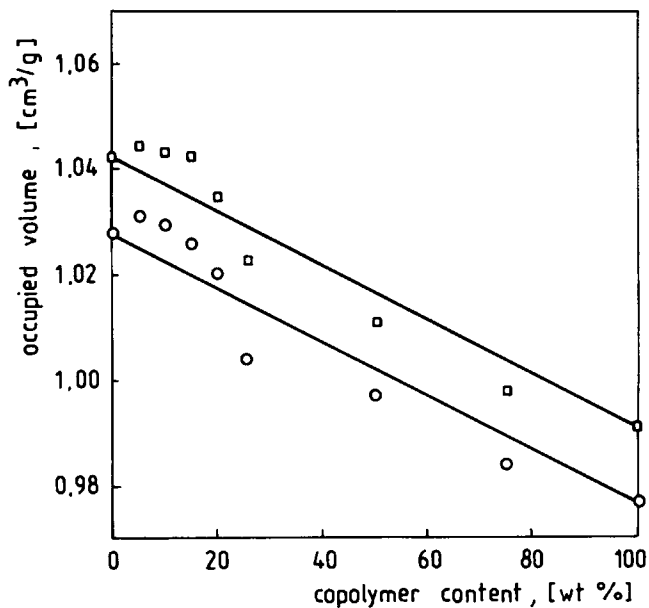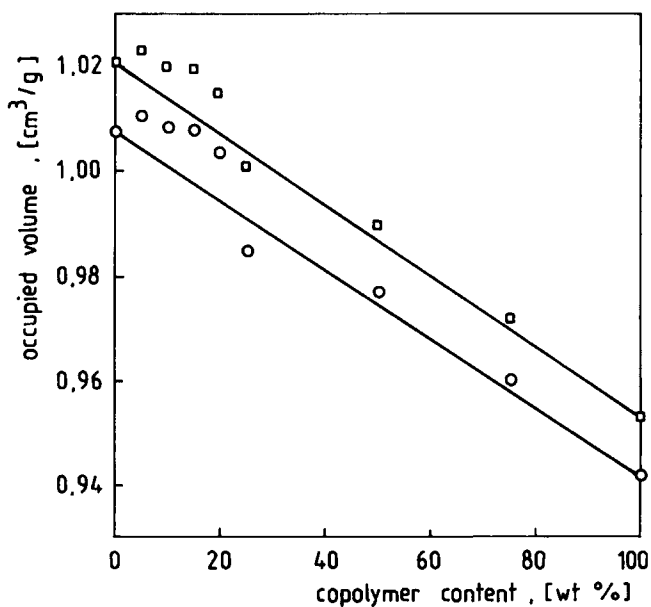

Fig. 2. The effect of blend composition on occupied volume of iPP–B/S system at different temperatures and the shear rate 500 s^{-1}: — theoretical calculations; experimental data: (○) 448 K, (□) 493 K.
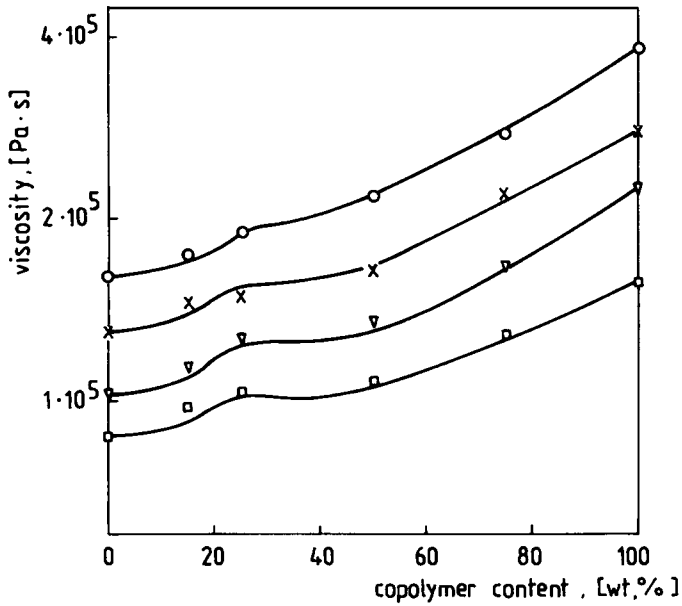
Fig. 3. The effect of blend composition on occupied volume of iPP–EP/S system at different temperatures and the shear rate 20 s^{-1}: — theoretical calculations; experimental data: (O) 448 K, (□) 493 K.

Fig. 4. The effect of blend composition on occupied volume of iPP–EP/S system at different temperatures and the shear rate 500 s^{-1}: — theoretical calculations; experimental data: (O) 448 K, (□) 493 K.

Fig. 5.   The effect of blend composition on viscosity of iPP–B/S system at different temperatures and the shear rate 20 s^{-1}: — theoretical calculations; experimental data: (O) 448 K, (×) 463 K, (∇) 478 K, (□) 493 K.
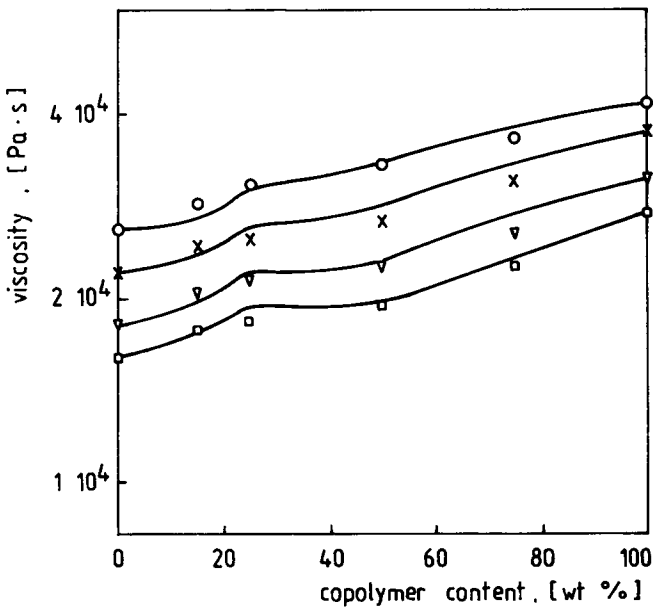

Fig. 6.   The effect of blend composition on viscosity of iPP–B/S system at different temperatures and the shear rate 500 s^{-1}: — theoretical calculations; experimental data: (O) 448 K, (×) 463 K, (∇) 478 K, (□) 493 K.

The same requirements also relate to the accuracy of viscosity calculations, which base on eq. (18) as well as on its modified version obtained by replacing ϕ_i by w_i. Figures 5–8 show the comparison of theoretical values of viscosity calculated from eq. (18) and experimental values measured at different temperatures for iPP–B/S and iPP–EP/S systems at the shear rates of 20 and 500 s^{-1}, respectively. The comparison of theoretical and experimental data for other shear rates from the interval 20–500 s^{-1} are very similar. It can be seen that relatively good agreement of experimental and theoretical data was also obtained, since the maximum deviations do not exceed 5%. Theoretical curves for iPP–B/S and iPP–EP/S systems resulting from the modified form of eq. (18) differ from those in Figures 5–8 by no more than 1–2%. For this reason they were not plotted.

CONCLUSIONS

Theoretical and experimental studies on rheological properties of iPP–S and iPP–EP/S blends lead to the following conclusions:

1. Application of the free volume theory for description of rheological properties of bindary polymer blends makes it possible to express the blend properties as suitable functions of composition and characteristics of individual components.

2. The theoretical model proposed here can be easily applied for description of rheological behavior of multicomponent blends. This model can also be modified to describe the rheological properties of other polymer systems
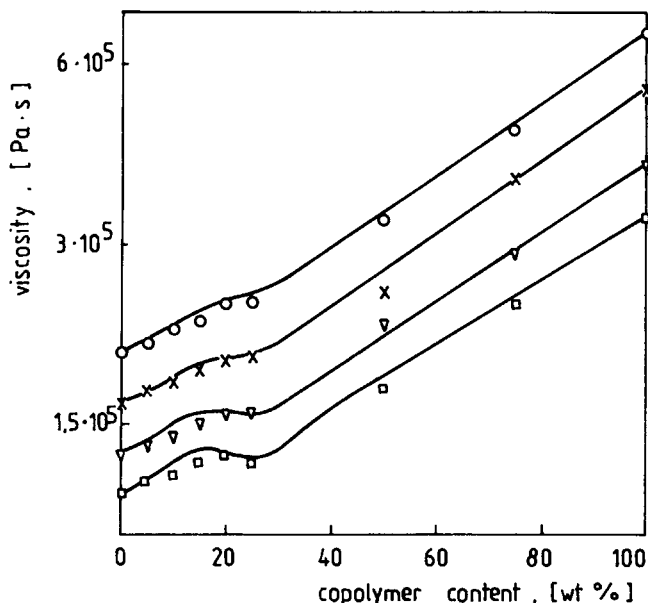

Fig. 7. The effect of blend composition on viscosity of iPP–EP/S system at different temperatures and the shear rate 20 s^{-1}: — theoretical calculations; experimental data: (O) 448 K, (×) 463 K, (∇) 478 K, (□) 493 K.
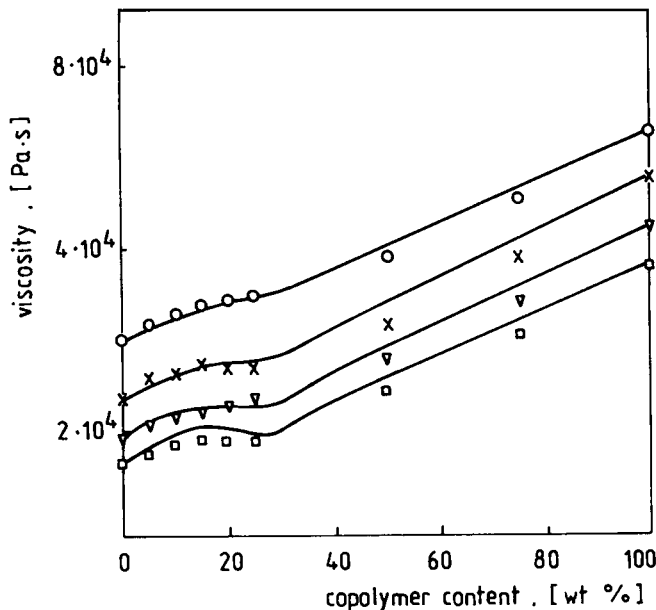
Fig. 8.   The effect of blend composition on viscosity of iPP–EP/S system at different temperatures and the shear rate 500 s^{-1}: — theoretical calculations; experimental data: (O) 448 K, (×) 463 K, (∇) 478 K, (□) 493 K.

such as filled and plasticized polymers. Further theoretical and experimental studies, however, are necessary for this purpose.

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