

Rheological Behavior of Polymer Melts with Natural Fibers

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ABSTRACT: Flow behavior of polymer liquids filled with short fibers (particulate fillers) was theoretically analyzed from the point of view of the free volume theory. Assuming that the filler addition changes the occupied volume, while the temperature variations cause mainly the free volume changes, a general expression describing the viscosity of the system as a function of the filler content, temperature variations, and rheological properties of the pure polymer liquid was derived. If the viscosity curve of the unfilled polymer is described by the Carreau equation, the corresponding viscosity curve of the filled polymer is also represented by an equation of Carreau type. However, this equation has other values of Newtonian viscosity and the power exponent in

comparison with the initial equation. Both parameters depend on the filler content and temperature. The derived equation predicts a viscosity rise and a stronger non-Newtonian behavior of the system with increasing filler content. The temperature rise exerts an opposite effect on the rheological behavior. The theoretical predictions are in good accordance with viscosity measurements for low-density polyethylene and polystyrene melts filled with short cotton, flax, and hemp fibers. © 2005 Wiley Periodicals, Inc. *J Appl Polym Sci* 97: 1401–1409, 2005

Key words: thermoplastics; fibers; viscosity; free volume theory

INTRODUCTION

Modification of thermoplastic and thermoset polymers by the addition of different organic and inorganic fillers is a very abundant source of new polymeric materials with unique application properties given the tremendous possibilities in choice of filler and its content in the composition. The used fillers differ in chemical and physical properties, size, shape, and surface character, which in the first range influence the application and processing properties of the composition. Organic and inorganic fiber fillers of natural and artificial origin constitute a significant group of fillers applied for reinforcing and toughening of both thermoplastic and thermoset polymers. Especially for thermoplastics, the application of short fibers can significantly change the rheological and processing properties of the system in comparison with the virgin polymer. In the scientific literature many papers devoted to studies on rheological properties of thermoplastic polymers filled with fibers were published. They contain, for instance, polyethylene and polypropylene (polyolefins),^{1–4} polystyrene,⁵ poly-

amide,⁶ polycarbonate,⁷ and elastomers (rubbers and thermoplastic elastomers)^{8–10} filled mainly with glass,^{1–7} artificial,^{5,6,9} and natural^{4,5,8,10} fibers. The rheological behavior of polymer–fiber systems was the subject of several review works.^{11–13} The viscosity measurements performed for many polymer–fiber systems lead to the conclusion that the fiber addition increases, as a rule, the viscosity of the system that becomes additionally more non-Newtonian, i.e., its viscosity is more dependent on the shear rate in comparison with the virgin polymer. The fiber addition also changes significantly the elastic properties of the melt. One of the most interesting phenomena is a rise of the first normal stress difference accompanied by a lowering of the die swell.¹⁴ The behavior of fiber suspensions was also analyzed theoretically by means of the continuum mechanics methods.¹⁵

The aim of this paper is the formulation and experimental verification of the free volume theory based analytical description of the effects of filler addition and temperature changes on the viscosity of fiber suspensions in non-Newtonian liquids. The generalization of the description for the systems with yield stress is also discussed.

THEORETICAL CONSIDERATIONS

The effect of fiber filler on the viscosity of the polymer–filler compositions can be determined on the ba-

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sis of the free volume theory. According to the theory, the viscosity of any system depends on the relative content of the occupied volume V_o (total volume of all molecules in the system) and of the free volume V_f (volume of all empty spaces between molecules). The viscosity of the system, η (for any volumetric filler content ϕ , temperature T , and shear rate γ), describes the Doolittle equation:

$$\ln \eta = A + B \frac{V_o}{V_f} = A + \theta \quad (1a)$$

where A and B are material constants (independent of ϕ , T , γ).

If the free and occupied volumes are related to the mass unit of material, their sum is the specific volume V .

$$V_o + V_f = V \quad (1b)$$

The general assumption with respect to the filled systems is that the Doolittle equation (1a) applies both to the pure and the filled polymer and the constants A and B are determined by the continuous phase (polymer) only. Based on this assumption the viscosity changes of the composition, which are due to the filler content, temperature, and shear rate variations, can be corelated to a composition without filler ($\phi = 0$) at some known temperature ($T = T_o$) and in the Newtonian flow region ($\gamma = N$) in the following way:

$$\begin{aligned} \ln \eta(\gamma, T, \phi) - \ln \eta(\gamma, T, 0) &= \theta(\gamma, T, \phi) - \theta(\gamma, T, 0) \\ &= \theta(\gamma, T_o, 0) \cdot \frac{\theta(\gamma, T, 0)}{\theta(\gamma, T_o, 0)} \cdot \left[\frac{\theta(\gamma, T, \phi)}{\theta(\gamma, T, 0)} - 1 \right] \end{aligned} \quad (2a)$$

$$\begin{aligned} \ln \eta(\gamma, T, 0) - \ln \eta(\gamma, T_o, 0) &= \theta(\gamma, T, 0) - \theta(\gamma, T_o, 0) \\ &= \theta(\gamma, T_o, 0) \cdot \left[\frac{\theta(\gamma, T, 0)}{\theta(\gamma, T_o, 0)} - 1 \right] \end{aligned} \quad (2b)$$

$$\ln \eta(\gamma, T_o, 0) - \ln \eta(N, T_o, 0) = \theta(\gamma, T_o, 0) - \theta(N, T_o, 0). \quad (2c)$$

Eliminating the quantities $\eta(\gamma, T, 0)$, $\theta(\gamma, T, \phi)$ and $\theta(\gamma, T_o, 0)$ from Eq. (2a), (2b), and (2c) and omitting logarithms one obtains the relationship

$$\frac{\eta(\gamma, T, \phi)}{\eta_o} = \left[\frac{\eta(\gamma, T_o, 0)}{\eta_o} \right]^{\alpha\beta} \exp[\theta_o(\alpha\beta - 1)], \quad (3)$$

where for convenience the following abbreviations are introduced:

$$\alpha = \frac{\theta(\gamma, T, 0)}{\theta(\gamma, T_o, 0)} \quad (4a)$$

$$\beta = \frac{\theta(\gamma, T, \phi)}{\theta(\gamma, T, 0)} \quad (4b)$$

$$\eta_o = \eta(N, T_o, 0) \quad (4c)$$

$$\theta_o = \theta(N, T_o, 0). \quad (4d)$$

The quantities η_o and θ_o in Eqs. (4c) and (4d) relate to the flow of the pure polymer at the temperature T_o in the Newtonian flow region N .

Assuming the linear temperature changes of occupied and free volumes it can be shown that the Doolittle equation is equivalent to the Vogel–Tamman equation, i.e., the parameter θ for any value of the shear rate can be expressed as¹⁶

$$\theta = \frac{D}{T - T_r}, \quad (5)$$

where D and T_r are material parameters.

From the point of view of the free volume theory the parameter T_r in Eq. (5) determines the hypothetical temperature at which the free volume of the system disappears, i.e., the viscosity becomes infinite. It is known that the Vogel–Tamman equation describes quantitatively the viscosity of many systems in relatively wide temperature intervals. The specific case of the Vogel equation corresponding to $T_r = 0$ and $D = E/R$, where E is the flow activation energy and R the gas constant, is the Arrhenius equation. The assumption $T_r = 0$ means that the free volume of any system vanishes only at the absolute zero. This somewhat unrealistic assumption (especially for very large polymer molecules) means that the Arrhenius equation is able to represent the temperature dependence of the viscosity for the majority of polymeric systems only in relatively narrow temperature intervals. However, it is much more frequently applied than the Vogel equation, because it requires the knowledge of only one material parameter with strictly defined physical meaning, i.e., the flow activation energy E .

The effect of the shear rate on the changes of the parameter θ manifests itself mainly by the dependence of the parameter D (or the activation energy E) on shear rate. In such a case Eq. (5) makes possible a simple definition of the constants α and θ_o in Eq. (3):

$$\alpha = \frac{T_o - T_r}{T - T_r} \quad (6)$$

$$\theta_o = \frac{D_o}{T_o - T_r}, \quad (7)$$

where D_o is the value of D in the Newtonian flow region.

Parameter β in Eq. (3) defined by Eq. (4b) can be determined taking into account some additional assumptions:

- The addition to the polymer of rigid filler (powders or short fibers) causes an increase in the total occupied volume of the system without any change in the total free volume;
- The occupied volume of a multicomponent system is an additive quantity;
- The shear rate variations do not significantly affect the occupied volume;
- The volume content of the filler is small enough to evoke no significant hydrodynamic and steric effects during the flow.

Based on the above assumptions and using Definition (1a) of parameter θ and Formula (4b) one obtains

$$\begin{aligned}\beta &= \frac{x_p V_{op} + x_w V_w}{x_p V_{fp}} \times \frac{V_{fp}}{V_{op}} = 1 + \frac{x_w V_w}{x_p V_{op}} \\ &= 1 + \delta \frac{x_w V_w}{x_p V_p^o} = 1 + \frac{\delta \phi}{1 - \phi}, \quad (8)\end{aligned}$$

where x_p, x_w = weight fractions of polymer and filler; V_w = specific volume of filler; V_{op}, V_{fp} = occupied and free volumes of polymer; V_p^o = specific volume of polymer at (quasi)static conditions, i.e., without shearing or in the Newtonian flow region.

The volume fraction of fibers at static conditions ϕ ($\phi_p = 1 - \phi$) is defined by

$$\phi = \frac{x_w V_w}{x_w V_w + x_p V_p^o}. \quad (9)$$

Parameter δ in Eq. (8) results from the assumption that no significant effect of the shear rate on the occupied volume exists. This follows from the fact that the occupied volume is determined by very strong atomic forces, while the free volume is mainly affected by considerably weaker intermolecular forces. This makes it possible to express the occupied volume by means of the quantities, which are valid for static conditions using Eq. (1a) and (1b):

$$V_{op} = V_p^o \frac{\theta_o}{B + \theta_o} = V_p^o \frac{1}{\delta}. \quad (10)$$

Equations (8) and (10) are principally valid only for "ideal fillers," which have very small dimensions and do not interact with polymer molecules, i.e., which cause neither steric nor hydrodynamic effects. Allowing for steric and hydrodynamic effects that may change the free and occupied volumes, a more general definition of β can be obtained,¹⁷

$$\beta = 1 + \frac{\theta_o^{-1} [\eta] \phi}{1 - \frac{\phi}{\phi_o}}, \quad (11)$$

where $[\eta]$ can be treated as the limiting viscosity for the system and ϕ_o is a material constant.

Equation (11) is probably more appropriate for very short fibers and powder fillers. Theoretical studies of the viscosity of systems with (infinitely) long parallel oriented fibers suggest the value $\phi_o = 1$ in Eq. (11).¹³ Such a form of Eq. (11) corresponds in turn with Eq. (8) with the parameter δ that is a material constant accounting for the steric and hydrodynamic effects mentioned above and hence is not necessarily defined by Expression (10).

The dependence of the apparent viscosity of unfilled polymer on the shear rate can be determined based on one of the known equations, e.g., power law, the Cross equation, or the Carreau equation.¹⁸ The most interesting result within the whole shear rate interval is reached with the use of the Carreau equation,

$$\eta(\gamma, T_o, 0) = \frac{\eta_o}{[1 + (\lambda\gamma)^2]^{\frac{1-n}{2}}}, \quad (12)$$

where λ and n are material constants.

Substituting Eq. (12) into Eq. (3) and taking Expressions (6–11) into account it is easy to show that the viscosity of a filled polymer melt as a function of the filler volume fraction and of the shear rate can be written as

$$\eta(\gamma, T, \phi) = \frac{\eta_o^*}{[1 + (\lambda\gamma)^2]^{\frac{1-n^*}{2}}}, \quad (13)$$

where

$$\eta_o^* = \eta_o \cdot \exp\left\{\frac{D_o}{T_o - T_r} \left(1 + \frac{\delta\phi}{1 - \phi}\right) \frac{T_o - T_r}{T - T_r} - 1\right\} \quad (13a)$$

$$n^* = 1 - (1 - n) \left(1 + \frac{\delta\phi}{1 - \phi}\right) \frac{T_o - T_r}{T - T_r}. \quad (13b)$$

Equation (13) is also the Carreau equation but the values of the Newtonian viscosity and of the exponent are changed in comparison with the unfilled polymer. It follows from Eqs. (13a) and (13b) that the filler addition to polymer increases the Newtonian viscosity and decreases the exponent of the system. Consequently, the viscosity of composition (at a constant shear rate) rises with growing filler content. Simultaneously, the behavior of the filled system becomes more non-Newtonian in compari-

TABLE 1
Power Law Constants for Compositions of Polyethylene with Cotton and Flax

Composition	Fiber content (%)	423 K		438 K		453 K	
		K [Pas · s ^{<i>n</i>}]	<i>n</i>	K [Pas · s ^{<i>n</i>}]	<i>n</i>	K [Pas · s ^{<i>n</i>}]	<i>n</i>
Polyethylene–cotton	0	17,656	0.507	11,445	0.544	8,297	0.584
	10	29,563	0.460	17,718	0.495	14,952	0.525
	20	39,939	0.417	28,315	0.442	18,715	0.485
	30	68,809	0.356	54,102	0.378	31,792	0.427
Polyethylene–flax	0	17,656	0.507	11,445	0.544	8,297	0.584
	10	26,774	0.469	18,704	0.486	12,267	0.556
	20	41,200	0.400	31,563	0.419	19,769	0.478
	30	68,738	0.326	50,177	0.366	41,869	0.387

son with the unfilled polymer because the exponent diminishes with increasing filler concentration. On other hand the temperature increase (at a constant filler content) evokes the exactly opposite effect, i.e., it lowers the viscosity and arises the exponent. For sufficiently high shear rates the summand “+1” in the denominator of Eq. (12) or (13) can be neglected. It leads to the equation of the power law type having the same exponent (*n* or *n*^{*}) as the corresponding Carreau equation.

Existing experimental data suggest that this description can be applied probably for the majority of polymer melts containing short fibers and powder fillers. However, it should be noted that such systems (especially with powders) frequently possess a distinct yield stress value, τ_p , resulting from interactions between filler particles, which is also a function of filler content and temperature.¹³ In this case the viscosity equation can be written as

$$\eta_p(\gamma, T, \phi) = \frac{\tau_p(T, \phi)}{\gamma} + \eta(\gamma, T, \phi), \quad (14)$$

where the function $\eta(\gamma, T, \phi)$ is defined by Eq. (13).

Unfortunately, the yield stress as a function of the temperature and filler content cannot be probably determined using the assumptions of the classical free volume theory, i.e., neglecting the particle–particle in-

teractions, which at suitably low stress level preclude the deformation of the system. However, using other flow models, e.g., the cell theory,¹³ the definition of $\tau_p(T, \phi)$ is generally possible.

EXPERIMENTAL

Four kinds of compositions based on commercial low-density polyethylene (Malen E) and compacted expandable polystyrene waste filled with cotton, flax, and hemp short fibers were prepared. All compositions (LDPE–cotton, LDPE–flax, PS–flax, PS–hemp) containing fibers in the amount of 0–30 wt % were gained by melt mixing with the use of two-roll-mill at temperatures of 433 K for LDPE and 453 K for PS during 7 min. To improve the homogeneity of the blends a small amount of a compatibilizer was added into the melt during blending. Both polymers without fiber addition were prepared in the same manner. The obtained systems were ground and in this form used for viscosity measurements by means of a conventional capillary viscometer. The measurements were carried out at three temperatures for every system. All compositions and measurement temperatures are presented in Tables 1 and 2, which are discussed in the next section.

TABLE 2
Power Law Constants for Compositions of Polystyrene with Hemp and Flax

Composition	Fiber content (%)	443 K		463 K		483 K	
		K [Pa · s ^{<i>n</i>}]	<i>n</i>	K [Pa · s ^{<i>n</i>}]	<i>n</i>	K [Pa · s ^{<i>n</i>}]	<i>n</i>
Polystyrene–hemp	0	28,680	0.487	11,220	0.549	2,314	0.609
	10	49,240	0.402	15,010	0.466	5,823	0.523
	20	91,180	0.307	33,550	0.395	9,405	0.501
	30	174,900	0.248	48,230	0.344	22,610	0.463
Polystyrene–flax	0	28,680	0.487	11,220	0.549	2,212	0.609
	10	45,630	0.408	15,750	0.479	3,866	0.550
	20	77,440	0.343	20,790	0.440	6,535	0.526
	30	100,050	0.308	25,320	0.408	9,615	0.502

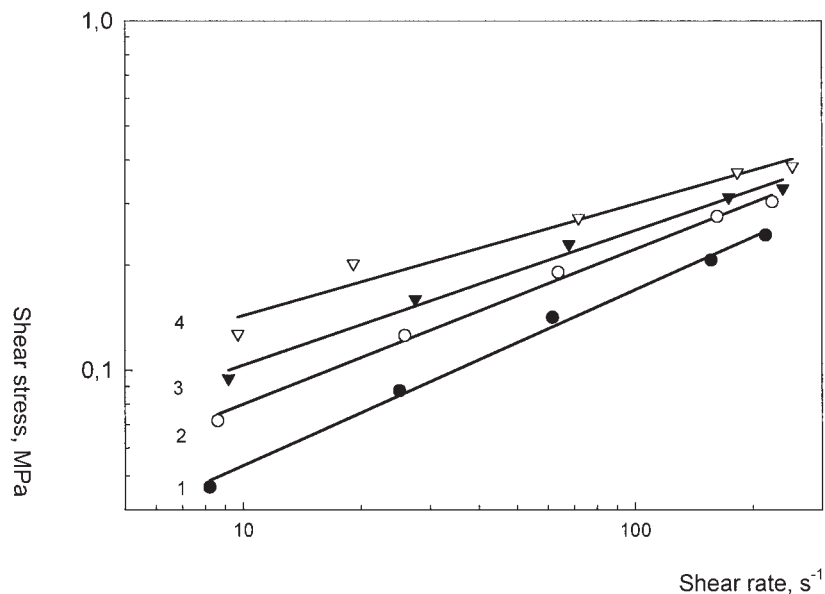


Figure 1 Flow curves of polyethylene–flax compositions at 423 K. Fiber content [wt %]: 1, 0; 2, 10; 3, 20; 4, 30.

RESULTS AND DISCUSSION

Figures 1–4 present typical examples of the flow curves obtained in the measurements. Independently of the system and temperature, the flow curves in double logarithmic coordinates are represented by straight lines, i.e., the flow behavior can be adequately described by the power law

$$\ln \tau = \ln K + n^* \ln \dot{\gamma}, \quad (15)$$

where τ and K are the shear stress and material constant, respectively.

The straight lines in all figures have generally a “fan-shape” course resulting from a shear stress level increase and a slope decrease with growing fiber content.

The power law constants K and n^* evaluated by the least-square method according to Eq. (15) for all compositions and temperatures are summarized in Table 1 and 2.

It was mentioned above that the power law behavior results from the Carreau equation for high shear rate values. Therefore, the power law constant K can be expressed in terms of constants of the Carreau equation, (13), in the following manner:

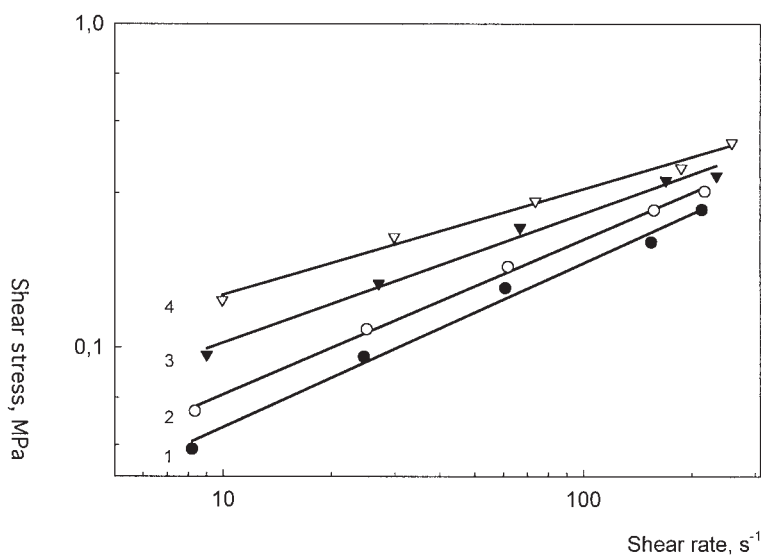


Figure 2 Flow curves of polyethylene–cotton compositions at 423 K. Fiber content [wt %]: 1, 0; 2, 10; 3, 20; 4, 30.

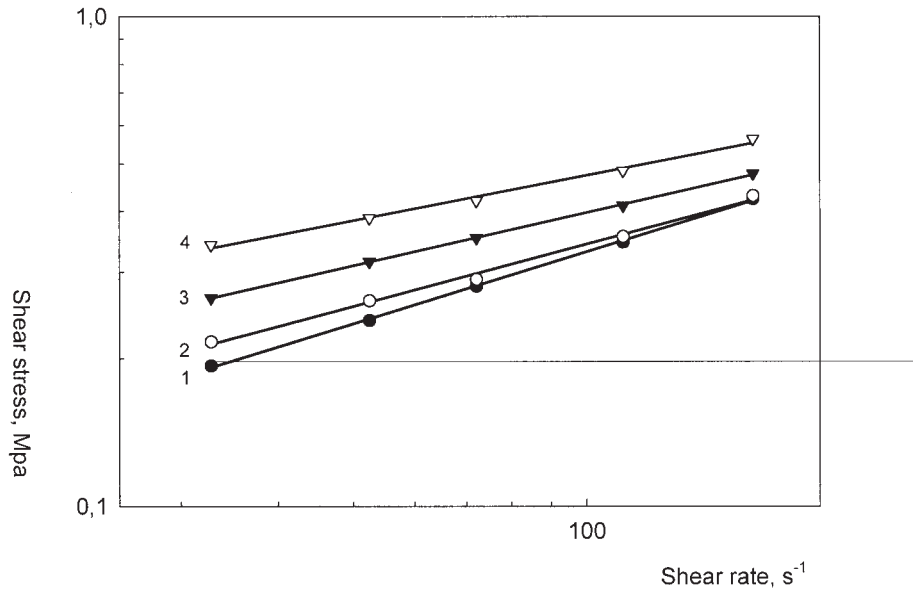


Figure 3 Flow curves of polystyrene–flax compositions at 443 K. Fiber content [wt %]: 1, 0; 2, 10; 3, 20; 4, 30.

$$K = \eta_o^* \cdot \lambda^{n^*-1}. \quad (16)$$

Substituting Expressions (13a) and (13b) into Eq. (16) and rearranging, one obtains

$$\ln K = \left[\ln \eta_o - \frac{D_o}{T_o - T_r} \right] - \left[\ln \lambda^{1-n} - \frac{D_o}{T_o - T_r} \right] \cdot \left(1 + \frac{\delta\phi}{1-\phi} \right) \frac{T_o - T_r}{T - T_r}. \quad (17)$$

It is evident from the data presented in Tables 1 and 2 that an increase in fiber content in a composition

lowers the power law exponent n^* and arises the proportionality constant K independently of the polymer–fiber system. The temperature effect on the constants K and n^* is exactly inverse. Quite similar qualitative behavior was also observed for polypropylene filled with glass and jute fibers.⁴ These observations are in an excellent qualitative agreement with theoretical predictions based on the free volume theory, which are expressed by Eqs. (13b) and (17).

The volume fractions of fibers corresponding to known measurement temperatures in Eqs. (13b) and (17) should be determined according to Expression (9).

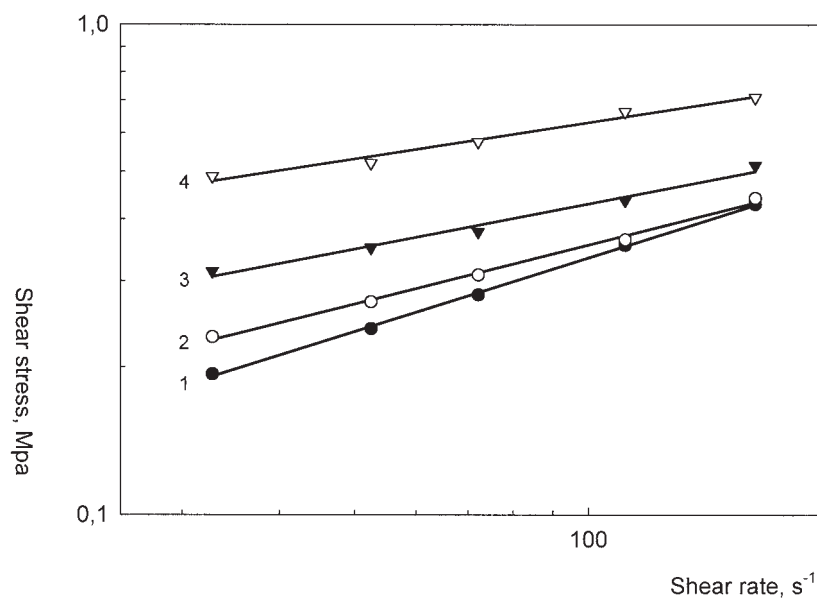


Figure 4 Flow curves of polystyrene–hemp compositions at 443 K. Fiber content [wt %]: 1, 0; 2, 10; 3, 20; 4, 30.

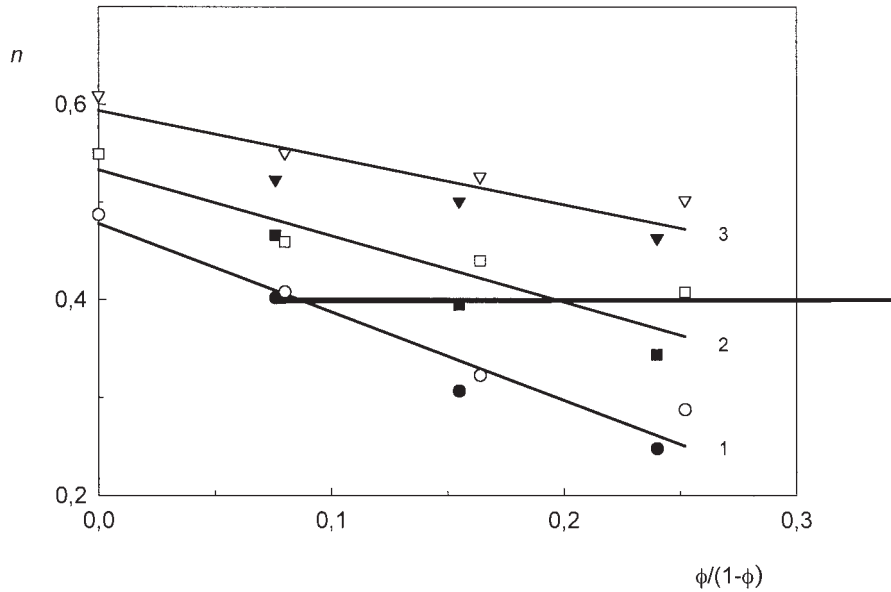


Figure 5 Dependence of power law exponent n on fiber content for compositions of polystyrene with flax (empty symbols) and hemp (filled symbols). Measurement temperatures [K]: 1, 443; 2, 463; 3, 483.

The temperature dependence of the specific volumes of LDPE and PS are given in the literature.¹⁹ It was found that the maximum specific volume changes resulting from these data for extreme temperatures within the measurement intervals (423–453 K for LDPE and 443–483 K for PS) are only about 2%. Therefore, the mean values of the specific volumes for both polymers were assumed: $V_{PE}^o = 1.29 \text{ cm}^3/\text{g}$ and $V_{PS}^o = 1.02 \text{ cm}^3/\text{g}$.

The specific volumes of natural fibers used in experiments, which were found in the literature, are restricted only to room temperature.²⁰ Taking into account some small thermal expansion of all fibers, the following mean values of the specific volumes for the measurement conditions were assumed: $V_{\text{cotton}} = 0.85 \text{ cm}^3/\text{g}$, $V_{\text{flax}} = 0.80 \text{ cm}^3/\text{g}$, $V_{\text{hemp}} = 0.75 \text{ cm}^3/\text{g}$.

It follows from Eqs. (13b) and (17) that both n^* and $\ln K$ at constant temperature should be linearly depen-

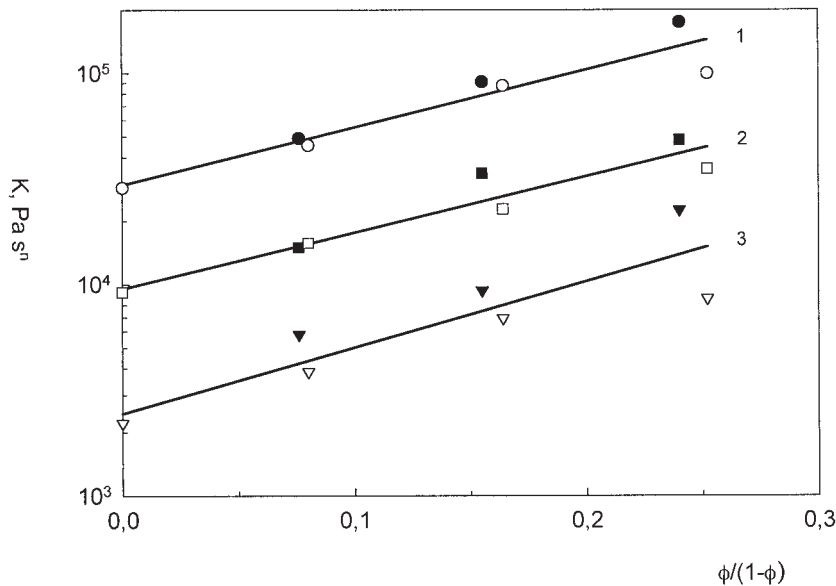


Figure 6 Dependence of power law constant K on fiber content for compositions of polystyrene with flax (empty symbols) and hemp (filled symbols). Measurement temperatures [K]: 1, 443; 2, 463; 3, 483.

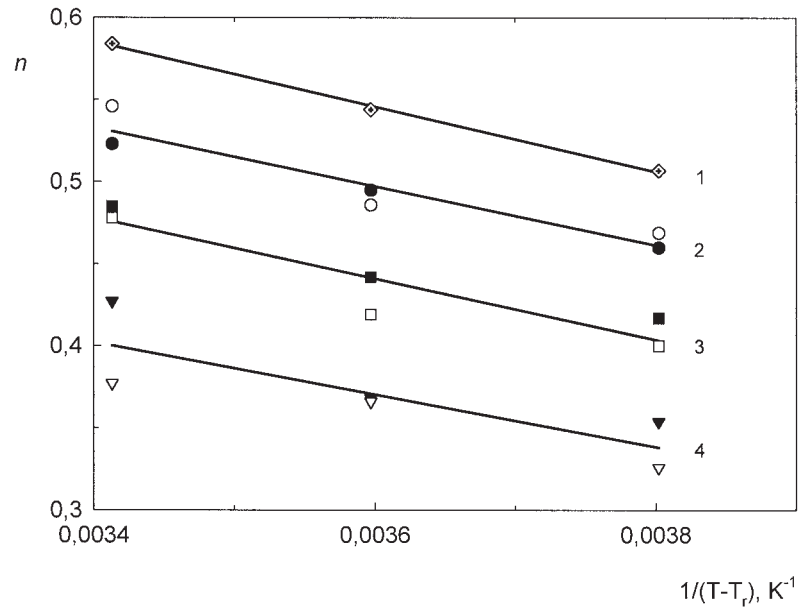


Figure 7 Dependence of power law exponent n on temperature for compositions of polyethylene with flax (empty symbols) and cotton (filled symbols). Fiber content [wt %]: 1, 0 (PE); 2, 10; 3, 20; 4, 30.

dent on the quantity $\phi/(1 - \phi)$. These theoretical predictions are compared, for example, with experimental data for the compositions of LDPE with cotton and flax in Figs. 5 and 6. The straight lines obtained by the least-square method correspond to compositions containing both cotton and flax fibers at similar temperatures. Despite a visible scattering of experimental points, especially at a higher fiber content, the theoretically predicted linear relationship is quite well fulfilled and practically independent of the fiber type for

all temperatures. The observed scattering of experimental points is partially due to the relatively low reproducibility of flow curve measurements, especially for systems containing a higher amount of fibers. Very similar plots result also for the PS compositions with vegetable fibers.

Equations (13b) and (17) predict that both n^* and $\ln K$ should be linear functions of $1/(T - T_r)$ at a constant fiber content. These relationships are shown as examples for PS compositions with flax and hemp

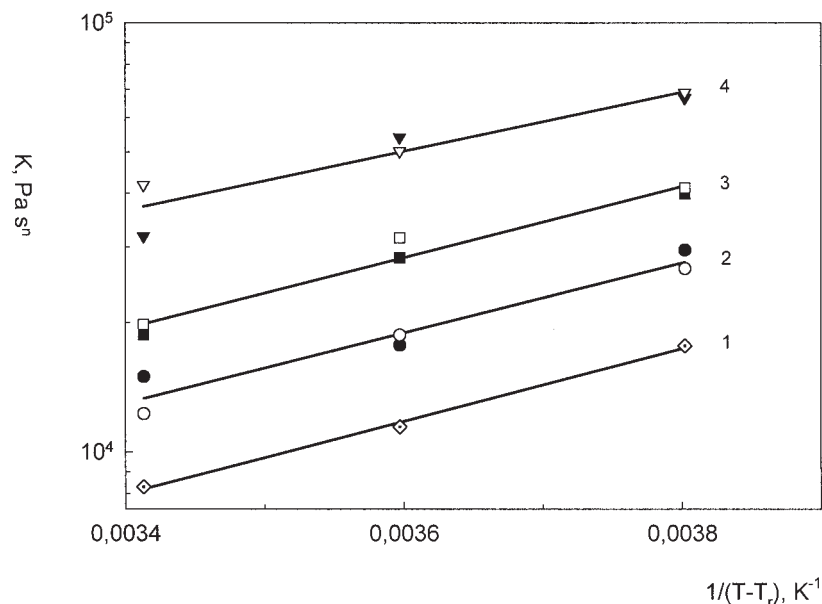


Figure 8 Dependence of power law constant K on temperature for compositions of polyethylene with flax (empty symbols) and cotton (filled symbols). Fiber content [wt %]: 1, 0 (PE); 2, 10; 3, 20; 4, 30.

fibers in Figs. 7 and 8. The plots were drawn using the value of $T_r = 325$ K for PS ($T_r = 160$ K for LDPE) according to the literature data.¹⁹

The linear relationship predicted by Eqs. (13b) and (17) is also in this case quite well confirmed by measurements. Despite some scattering of experimental data, especially at a higher fiber content, it seems that the fiber type does not effect significantly the rheological behavior of the investigated systems. A very similar picture arises also for the compositions of LDPE with cotton and flax fibers.

CONCLUDING REMARKS

The free volume theory based description of rheological behavior of polymer melts filled with short vegetable fibers can explain (at least qualitatively) many flow phenomena observed in such systems. Assuming $\phi = 0$ in Eqs. (13a), (13b), and (17) the temperature dependence of the viscosity of pure polymer melts can be described. It was also demonstrated¹⁷ that similar calculations performed for melts containing a gas addition lead to expressions, which correctly reflects the flow properties of such systems. The gas addition, which principally changes only the free volume of the system (in contrast to a filler addition), results in a viscosity decrease and a rise in the exponent, i.e., the polymer melts containing gases become less viscous and more Newtonian. It is also possible to take the effects of other factors, e.g., pressure, into account. In conclusion, the method presented above is a useful tool that enables the theoretical prediction of viscous

properties of different multicomponent polymer systems during shear flow.

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