BERENIKA HAUSNEROVA[1)*)], NATALIE ZDRAZILOVA[1)], TAKESHI KITANO[2)], PETR SAHA[1)]

Rheological properties of carbon fibre filled low-density polyethylene under the parallel steady and oscillatory shear flows

Summary — Investigations of the flow properties of low-density polyethylene compounded with carbon fibre under the parallel superposed steady and oscillatory shear flows were performed. The effect of the steady shear on the viscoelastic properties as well as the effect of fibre content on the superposed flow properties were discussed. Overall, superposed flow conditions enhanced viscoelastic response (dynamic viscosity, storage modulus) of the filled systems. The critical angular frequency, where phase angle becomes 90^{o} and storage modulus decreases sharply to zero, was found to be largely dependent on the volume fraction of fibre, regardless of the superposed shear rate. Whereas superposed flow properties of the pure PE melt changed monotonously, those of the composites showed peaks in corresponding dependencies, even if under simple shear flows they behaved in the similar manner as PE matrix.

Key words: low-density polyethylene, carbon fibre, fibre filled system, superposed flow, parallel superposition, steady shear flow, oscillatory flow.

WŁAŚCIWOŚCI REOLOGICZNE POLIETYLENU MAŁEJ GĘSTOŚCI NAPEŁNIANEGO WŁÓKNAMI WĘGLOWYMI OKREŚLANE W WARUNKACH RÓWNOLEGŁEJ SUPERPOZYCJI USTALONYCH I OSCYLACYJNYCH PRZEPŁYWÓW ŚCINAJĄCYCH

Streszczenie — Badano właściwości reologiczne polietylenu małej gęstości napełnianego różnymi ilościami włókien węglowych (tabela 1) z zastosowaniem różnych szybkości ścinania. Stwierdzono, że zarówno składowa rzeczywista modułu zespolonego (G') jak i lepkość dynamiczna (η') napełnianych próbek osiągają większe wartości w warunkach superpozycji ustalonego i oscylacyjnego przepływu niż z zastosowaniem tylko oscylacyjnego przepływu, a stopień wzrostu zależy od złożonej szybkości ścinania ($\dot{\gamma}_0$), prędkości kątowej (ω) i zawartości włókien (V_r) (rys. 2, 3, 5—9). Maksymalne wartości składowej rzeczywistej modułu zespolonego (G'_{max}) i lepkości dynamicznej (η'_{max}) znormalizowane względem prostego przepływu oscylacyjnego generalnie rosną ze zwiększaniem wartości V_r i maleją ze wzrostem ω (rys. 10). Wartość krytyczna prędkości kątowej (ω_c), w której kąt przesunięcia fazowego (δ) osiąga 90^{o} powodując gwałtowny spadek G', silnie zależy od V_f, a praktycznie nie zależy od $\dot{\gamma}_0$ (rys. 12).

Słowa kluczowe: polietylen małej gęstości, włókno węglowe, układy napełniane włóknem, przepływ złożony, superpozycja równoległa, ustalony przepływ ścinający, przepływ oscylacyjny.

It is well known that dynamic viscoelastic behavior of polymer melts and solutions is linear at small strains corresponding to the equilibrium spectrum of relaxation time, while flow behavior in the steady shear flow is essentially non-linear, especially under larger strains.

It is assumed that in the concentrated polymer solutions and melts there exists continuous appearing and disappearing of entanglements of the molecular chains, composing a looser three-dimensional structure. Under simple shear flow field molecules' chains disentanglement occur, their positions change, and the new entanglements originate. In very slow flow field (low strain rate), the rate of appearance and/or disappearance of the entanglements of the molecular chains is balanced. However, as strain rate increases, the rate of this disappearance becomes larger than that of the appearance, and thus the system will have less number of entanglements, and will loose its structure. Consequently, the system will show decrease in both viscous (non-Newtonian) and elastic properties at high strain rates.

If an entangled liquid flows under constant shear rate, the composed structure will correspond to the given shear rate. If the relaxation time spectra of the system can be determined from the viscoelastic properties measured under these conditions, it will provide new information concerning the structure changes in the material. This is the purpose of superposition experiments of steady shear flow on dynamic oscillatory flow.

[1)] Tomas Bata University in Zlín, Faculty of Technology, Polymer Centre, TGM 275, 762 72 Zlín, Czech Republic.

[2)] National Institute of Advanced Industrial Science and Technology, Research Centre of Macromolecular Technology, 1-1-1 Higashi, Tsukuba, Ibaraki 305-8565, Japan.

[*)] Corresponding author; e-mail: hausnerova@ft.utb.cz, tel: +420 57 603 1422; fax: +420 57 603 1444

Constitutive equations have to be applicable to analyze the various flow fields, and the superposed behavior is thought to be one of the useful flow patterns to prove the validity of these relations. Analytical results of the application of various constitutive equations for different types of superposed flows were reviewed and summarized [1—3].

Generally, there are two types of superposed flow: a parallel superposition of steady shear and oscillatory flows, and an orthogonal superposition of the two flows. The experimental studies of the former, carried out by many researchers [4—12], and of the latter, reported by Mewis *et al.* [10], have shown that the analyses of the orthogonal superposed flow are rather easier than those of the parallel superposed flow.

Polymer melts, including filled systems, are molded under a variety of complex deformations (flows), which are often far from the simple steady or oscillatory shears. It is very important to investigate the viscoelastic behavior under the deformation outside the range of linear viscoelasticity, such as oscillatory flow under large strain amplitude, or superposition of oscillatory and steady shear flows. While the flow properties of thermoplastics in an annular die under both parallel and orthogonal superpositions of oscillatory flow on steady shear flow are studied [13—15], the experimental studies devoted to filled systems were carried scarcely [16—20]. Rheological properties of filled polymer melts depend strongly on the flocculation degree of fillers, which is governed by their shape, size and size distribution, surface structure of dispersed fillers, and also interactions between disperse medium and fillers.

Fibrous particles, whose flow properties under simple steady shear or oscillatory flow were investigated extensively [21—26], are especially prone to conform the three-dimensional network structures. The purpose of this paper is to investigate the rheological behavior of fibre filled polymer melts undergoing the parallel superposed steady and oscillatory shear flows. The effect of steady shear on viscoelastic properties such as dynamic viscosity and storage modulus, as well as the effect of fibre content on the superposed flow properties are discussed.

Linear superposition of steady shear and oscillatory flows — theoretical considerations

Rheological testing, in which steady shear and oscillatory flows are superposed parallel or orthogonal in a viscometric flow field, is called superposed shear flow measurement. In this method, rotational viscometers (cone-plate or parallel plate) operating at constant rotation speed or oscillating with constant strain amplitude (oscillatory angle) are generally used. Steady shear rate and angular frequency are the variables in this experiment, and influences of these parameters on viscoelastic properties, such as dynamic viscosity and storage modulus, are investigated. Determination of rheological properties from the superposed flow measurements provides new information about the structure of polymer fluids, which cannot be obtained under simple steady or oscillatory shear flow measurements.

The previous research [16] on the superposed flows was limited to the materials showing linear viscoelastic response. Overall, shear rate (strain rate) applied on the material, ($\dot\gamma$) is given by:

$$\dot\gamma = \dot\gamma_0 + Re\left(\dot\gamma_0^0 e^{i\omega t}\right) \qquad (1)$$

where: $\dot\gamma_0$ — *steady shear rate superposed on oscillatory flow,* ω — *angular frequency of oscillatory flow,* $Re(\dot\gamma_0^0 e^{i\omega t})$ — *real part of the shear rate dependent on angular frequency,* $\dot\gamma_0^0$ — *amplitude of shear wave.*

From Eq. (1), shear stress (τ) acting on the material is given as:

$$\tau = \tau_0 + Re\left(\tau_0^0 e^{i\omega t}\right) = \eta\dot\gamma_0 + Re\left(\eta_{\|}^{*}\dot\gamma_0^0 e^{i\omega t}\right) \qquad (2)$$

where: η — *steady shear viscosity,* τ_0^0 — *shear stress obtained from the oscillatory flow,* $\eta_{\|}^{*}$ — *complex viscosity determined under the parallel superposed flow.*

The following relation is given, similar to simple oscillatory flow:

$$\eta_{\|}^{*}(\omega,\dot\gamma_0) = \eta_{\|}'(\omega,\dot\gamma_0) - i\eta_{\|}''(\omega,\dot\gamma_0) \qquad (3)$$

From Eq. (3), Eq. (2) can be rewritten as:

$$\tau = \eta\dot\gamma_0 + \left(\eta' / \dot\gamma_0^0 \sin\delta\right)\sin(\omega t + \delta) \qquad (4)$$

Overall shear rate of the material, changes between $(\dot\gamma + \dot\gamma_0^0)$ and $(\dot\gamma - \dot\gamma_0^0)$ periodically, and η' corresponds to the dynamic viscosity obtained from the simple oscillatory flow measurement. From Eq. (4), it is found that the oscillatory part of shear stress becomes zero, when $\omega t = n\pi - \delta$.

The total shear stress and shear rate under the superposed shear flow shown in the above equations are given by simple superposition of steady and oscillatory shear flows. However, these relations are successfully used only for simple fluids. For the materials, which show remarkable non-linear flow properties (filled polymers), the validity of the above equations has not been confirmed yet, and therefore, it is an important subject for discussion.

Generally, there are two methods of the superposed flow measurement:

— method A: oscillatory shear flow is superposed on steady shear flow, which is kept at constant shear rate; angular frequency is changed stepwise;

— method B: shear flow is superposed on oscillatory flow, which is kept at constant angular frequency; shear rate is changed gradually.

Although generally the results obtained by both methods coincide well within the experimental errors, the measurements in this study were carried out by the method A, because of a long time needed to approach the steady shear flow condition according to method B.

EXPERIMENTAL

Materials

— low density polyethylene powder (PE-LD), trade name Flowthene G701, characterised by *MFR* = 7.8 g/10 min (190 °C, 2.16 kg) (Seitetsu Kagaku Ind. Co. Ltd.)

— carbon fibre (CF), trade name Beshight 12 000, diameter of 7 μm, 3 mm chopped strand (Toho Rayon Co. Ltd.).

To prepare the polymer-filler system this two components in different proportion were used.

Sample preparation

Weighted amounts of chopped CF and powdered PE-LD were dry mixed, then supplied into the elastic extruder (designed and constructed at the National Institute of Advanced Industrial Science and Technology in Japan) and processed at temperature of 200 °C. After cooling in a water bath, the extrudate was cut into pellets of around 5 mm length by a pelletizer, and then, after drying in an air oven, the pellets were extruded again in order to obtain the well-dispersed fibre filled samples. Finally, the pellets were compression molded into sheets of 3 mm thick under 5 MPa at 200 °C.

Method of testing

The fibre content (weight fraction) was determined gravimetrically after incinerating the matrix polymer. The volume fraction (V_f) of the fibre at the testing temperature was calculated from the densities of both components. The method for determination of the fibre length and its distribution was described in our previous paper [25]. The mean length of the fibres ranged from 0.2 to 0.46 mm, and decreased with the increase in the fibre content. Sample codes and volume fraction of fibres in the samples are shown in Table 1.

Table 1. Sample codes and volume fractions of carbon fibre (V_f) in CF/PE-LD systems

Code of sample	V_f, vol. %
PE	0
CF5/PE	4.70
CF10/PE	9.81
CF15/PE	14.94
CF20/PE	19.95

Method of superposed flow measurement

Superposed rheological properties of pure and fibre filled polyethylene melts were determined in a cone-plate type rheometer (Weissenberg Rheogoniometer, Carri-Med R21). The cone had radius of 1.25 cm and angle of 2°. All the measurements were performed at 200 °C. The angular frequency of the dynamic measurements varied from 0.02 to 60 rad/s, and strain amplitude in a shear unit was 1.75 %. The superposed shear rate was selected between 0.05 and 5 s^{-1}.

The procedure is as follows: the unidirectional shear flow with a fixed shear rate is started, torque gradually increases, and then approaches to a stable state at low shear rate (at high shear rates it has to overcome a stress overshoot first). When the stable shear flow is reached, an oscillatory shear flow is superposed on it. After the superposition, time-dependent torque varies sinusoidal with a phase lag (difference) to the oscillatory displacement.

RESULTS AND DISCUSSION

Steady and oscillatory shear flow properties

Complex viscosity ($|\eta^*|$) versus angular frequency (ω) curves for pure PE-LD and CF filled PE-LD systems, which were determined by oscillatory shear flow measurements, are depicted in Figure 1 together with steady shear viscosity (η) versus shear rate ($\dot{\gamma}$) plots represented by the broken lines. As can be seen, the complex viscosity of all tested materials decreases monotonously with angular frequency, and the discrepancy between complex and steady shear viscosities increases with increase in the fibre content. In the region of low ω values, the η slopes differ much from that of PE sample, which is Newtonian; the curves become steeper as the fibre con-

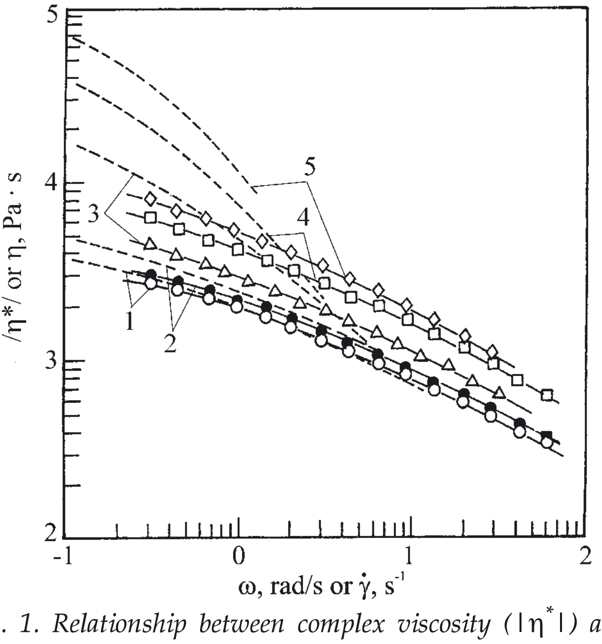


Fig. 1. Relationship between complex viscosity ($|\eta^*|$) and angular frequency (ω) of unfilled PE-LD and CF/PE-LD melts. Particular samples are denoted as follows: 1 — PE, 2 — CF5/PE, 3 — CF10/PE, 4 — CF15/PE, 5 — CF20/PE; broken lines represent shear viscosity (η) versus shear rate ($\dot{\gamma}$)

tent is increased. However, at high shear rates they approach the curve of the unfilled PE-LD, indicating that the composed fibre structure changes drastically under rather high shear, where fibres tend to orient to the flow direction.

These rheological phenomena are generally observed for various heterogeneous systems, and it seems that the change of the structure composed by fibres under simple steady shear deformation differs from that under oscillatory flow field.

Superposed flow properties of unfilled PE-LD melt

The effect of the superposition of oscillatory flow on steady shear one for the unfilled PE sample melt is demonstrated in Fig. 2 to 4. Fig. 2 shows the relationship between storage (G') and loss (G''), moduli and ω, as a parameter of superposed shear rate, $\dot{\gamma}_0$, at 200 °C. Both G' and G'' decrease with the increase in $\dot{\gamma}_0$, and the degree of their decrease is relatively larger in the low angular frequency region. Also, it can be seen that the degree of the decrease in G' is higher than that in G''. Dynamic viscosity (η′) and G', for PE samples melts as a function of superposed shear rate ($\dot{\gamma}_0$) are shown as parameters of ω in Fig. 3. The broken lines represent the corresponding values at the particular ω obtained by simple (non-superposed) oscillatory flow measurement. From these figures it becomes clear that both values tend to decrease monotonously with the increase in $\dot{\gamma}_0$, and also the degree of this change diminishes as ω is increased. This behavior is in a good agreement with the results obtained for polymer melts and solutions in the previous works [4—7].

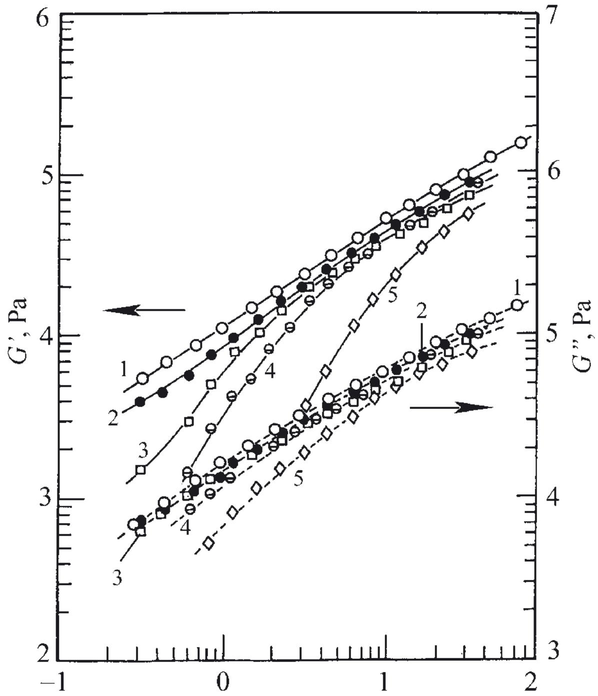


Fig. 2. Influence of angular frequency (ω) on: a) storage modulus (G') and b) loss modulus (G'') of unfilled PE sample; parameter, the superposed shear rate ($\dot{\gamma}_0$), changes as: 1 — 0 s^{-1} (0 Pa), 2 — 0.05 s^{-1} (2 · 10^2 Pa), 3 — 0.5 s^{-1} (14 · 10^2 Pa), 4 — 1 s^{-1} (20 · 10^2 Pa), 5 — 5 s^{-1} (46 · 10^2 Pa); the data given in brackets represent values of corresponding shear stress

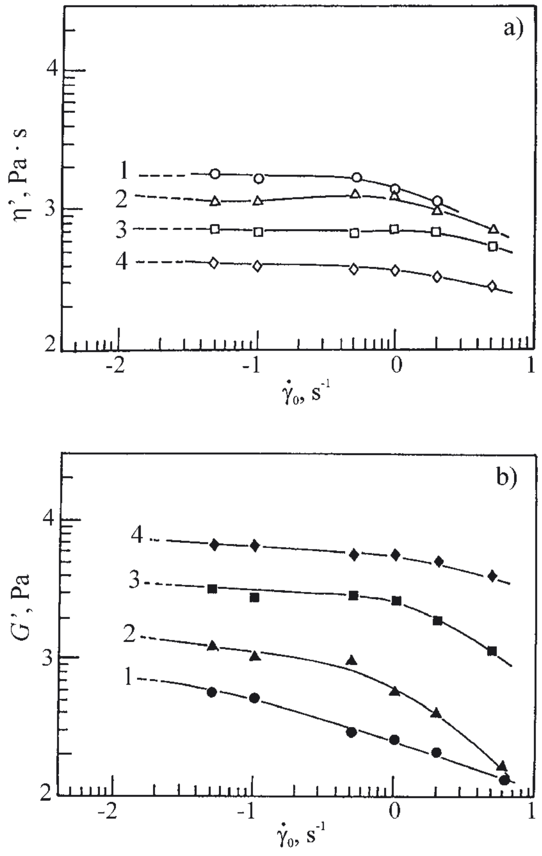


Fig. 3. Influence of superposed shear rate ($\dot{\gamma}_0$) on: a) dynamic viscosity (η′) and b) storage modulus (G') for unfilled PE sample at various angular frequencies (ω): 1 — 0.6 rad/s, 2 — 1.6 rad/s, 3 — 6 rad/s, 4 — 20 rad/s

It is well known that when measuring sinusoidal oscillatory flow properties of a viscoelastic material, the phase lag or phase difference occurs between oscillatory displacement and corresponding torque (shear stress); the phase angle is 90° for a Newtonian fluid and 0° for an elastic material. On the other hand, the phase angle of the viscoelastic material is a function of ω, and gradually increases toward 90° with declining ω. It is very interesting to investigate whether the phase angle of the viscoelastic materials will change under the superposition of the oscillatory flow on the steady shear, and if the degree of the phase angle change depends on the superposed steady shear rate.

Phase angle (δ) defined as the difference between the oscillatory part of shear stress and that of shear strain, and calculated from the ratio of loss to storage moduli, is shown in Fig. 4 as a function of angular frequency for PE sample at various $\dot{\gamma}_0$. The value of δ at each ω increases

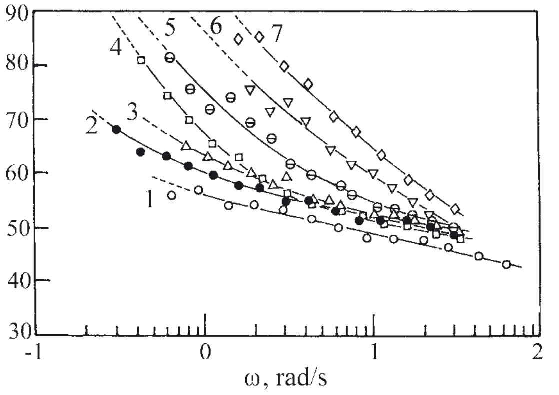


Fig. 4. Phase angle (δ) versus angular frequency (ω) curves of unfilled PE sample; parameter, the superposed shear rate ($\dot{\gamma}$), changes as: 1 — 0 s^{-1}, 2 — 0.05 s^{-1}, 3 — 0.1 s^{-1}, 4 — 0.5 s^{-1}, 5 — 1 s^{-1}, 6 — 2 s^{-1}, 7 — 5 s^{-1}

with the increase in $\dot{\gamma}_0$, and it may be possible, from the extrapolation of the curves, to determine the critical angular frequency (ω_c) in which the phase angle becomes 90°.

Superposed flow properties of CF filled PE melts

The values of *G'* and *G"* of the CF10/PE composite do not change monotonously with varying $\dot{\gamma}_0$ as those of the unfilled PE sample (Fig. 2), but increase once and then decrease with rising $\dot{\gamma}_0$. This trend is even stronger for higher content of CF in PE-LD matrix, as observed in Fig. 5. Steady shear flow properties of highly filled polymer melts are generally difficult to measure, and therefore it is supposed that obtaining the reasonable results from superposed flow measurements at high shear rates will be rather complicated. This case is represented by sample CF20/PE in this study.

Relationship between η' and $\dot{\gamma}_0$ as well as *G'* dependence on $\dot{\gamma}_0$ at various ω for CF10/PE is illustrated in Fig. 6. The broken lines stand for the values from the simple oscillatory flow measurements at each corresponding ω. It is found that η' at low ω increases with $\dot{\gamma}_0$, and then decreases after overcoming a maximum. However, at high angular frequency this value decreases monotonously with $\dot{\gamma}_0$. Similar shear rate dependent behavior is observed for storage modulus, *G'*, Fig. 6b. Shear rate dependent viscoelastic properties of CF20/PE system are close to those of CF10/PE system; both η' and *G'* show maxima at even higher angular frequency.

In order to demonstrate the dependence of $\dot{\gamma}_0$ on η' and *G'* at various ω frequencies more clearly, the norma-

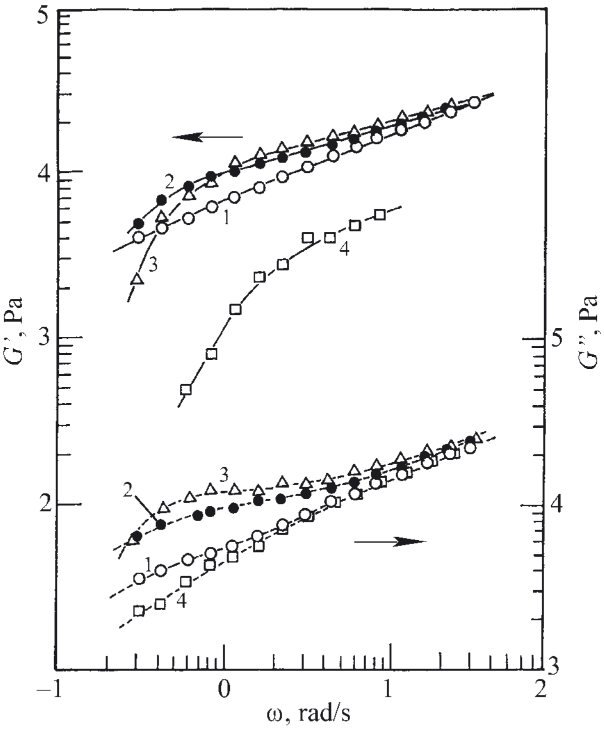
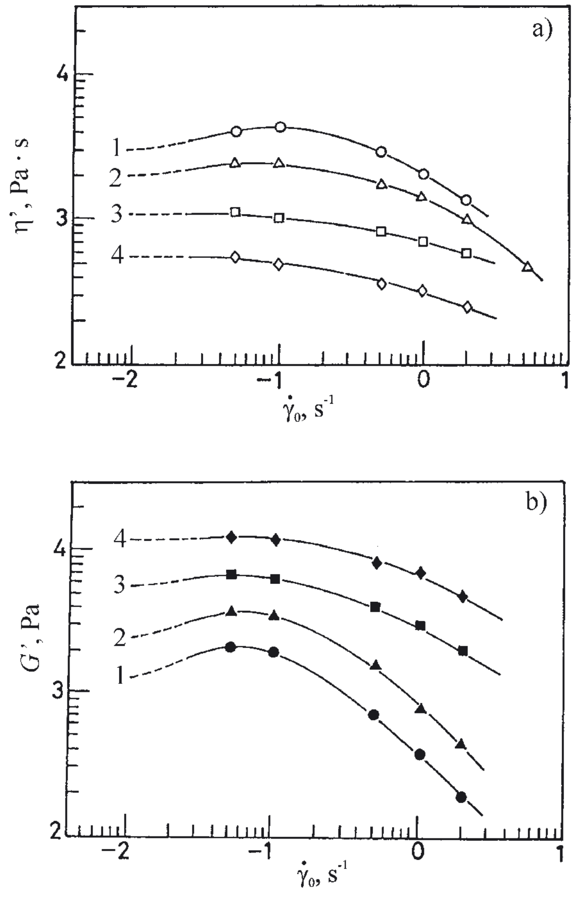


Fig. 5. Storage and loss moduli (G', G") versus angular frequency (ω) curves of CF20/PE system; parameter, the superposed shear rate ($\dot{\gamma}$), changes as: 1 — 0 s^{-1} (0 Pa), 2 — 0.05 s^{-1} (54 · 10^{2} Pa), 3 — 0.1 s^{-1} (80 · 10^{2} Pa), 4 — 0.5 s^{-1} (120 · 10^{2} Pa); the data given in brackets represent values of corresponding shear stress



→

Fig. 6. Influence of superposed shear rate ($\dot{\gamma}_0$) on: a) dynamic viscosity (η') and b) storage modulus (G') for CF10/PE system at various angular frequencies (ω): 1 — 0.6 rad/s, 2 — 1.6 rad/s, 3 — 6 rad/s, 4 — 20 rad/s

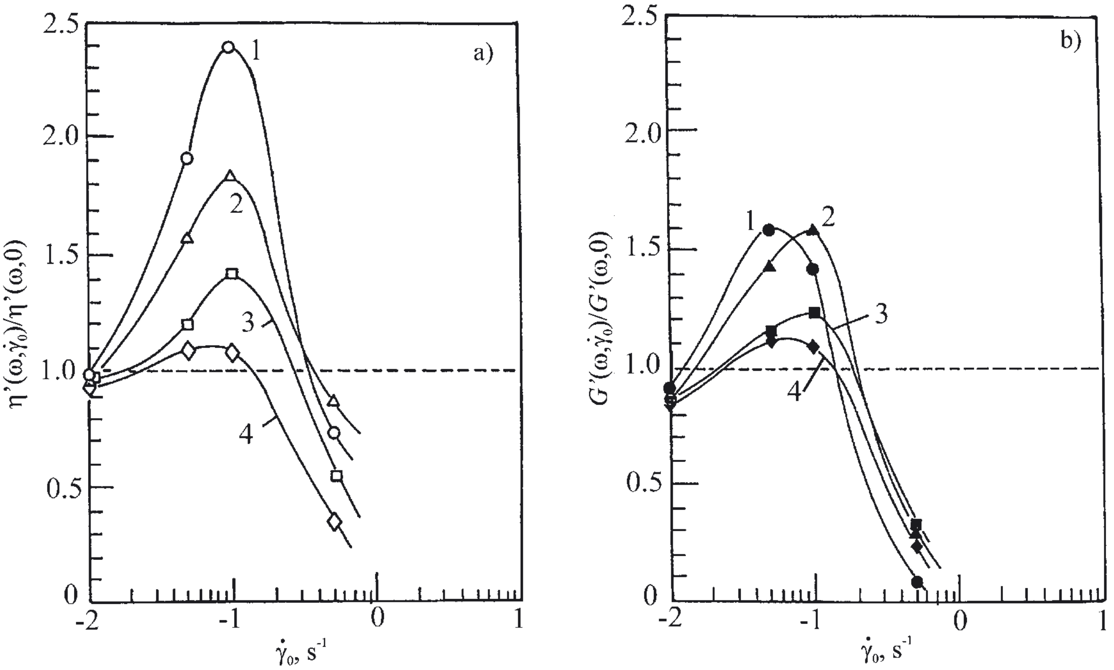


Fig. 7. Influence of the superposed shear rate ($\dot{\gamma}_0$) on: a) dynamic viscosity (η') and b) storage modulus (G') normalized by their values from simple oscillatory flow for CF20/PE system at various angular frequencies (ω): 1 — 0.6 rad/s, 2 — 1.6 rad/s, 3 — 6 rad/s, 4 — 20 rad/s

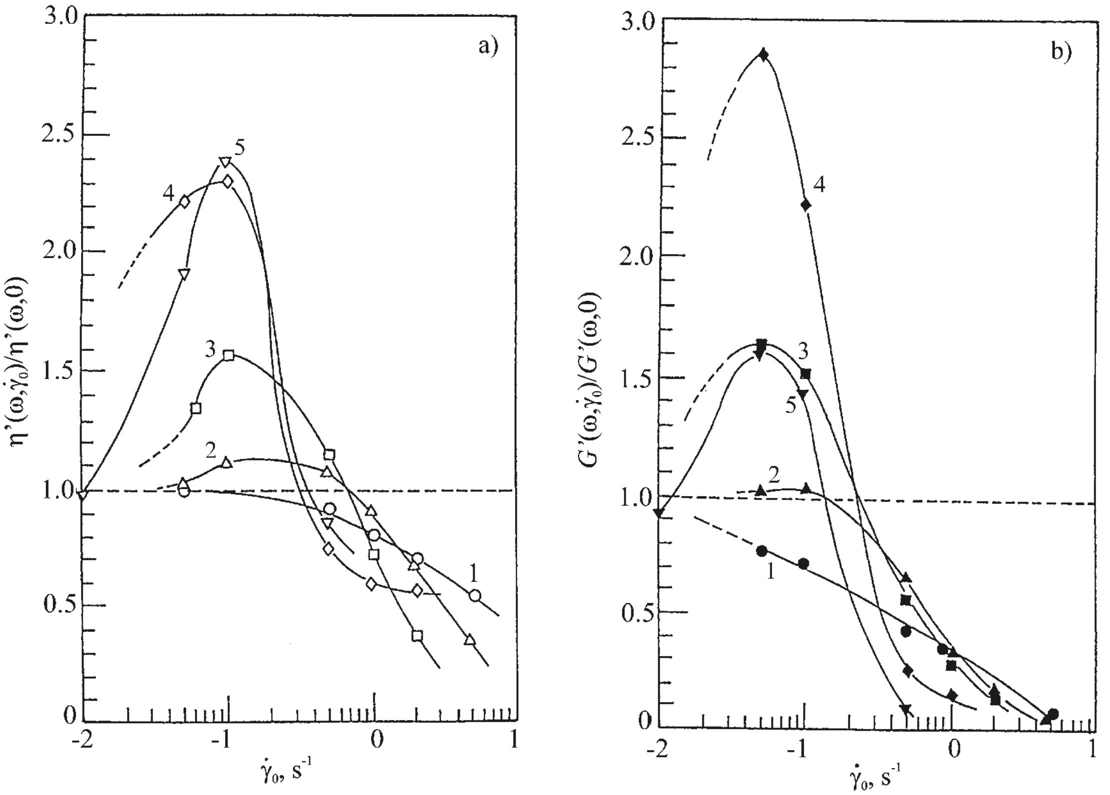


Fig. 8. Influence of the superposed shear rate ($\dot{\gamma}_0$) on: a) dynamic viscosity (η') and b) storage modulus (G') normalized by their values from simple oscillatory flow for unfilled PE sample and CF/PE melts at the angular frequency of 0.6 rad/s; particular samples are denoted as follows: 1 — PE, 2 — CF5/PE, 3 — CF10/PE, 4 — CF15/PE, 5 — CF20/PE

lized plots of η' and G' versus the superposed shear rate as a parameter of angular frequency were shown in Fig. 7 for CF20/PE system. The normalized functions have maxima at high ω, and $\dot{\gamma}_0$, in which dynamic viscosity shows the maximum, is higher than that of the maximum G' for both filled systems.

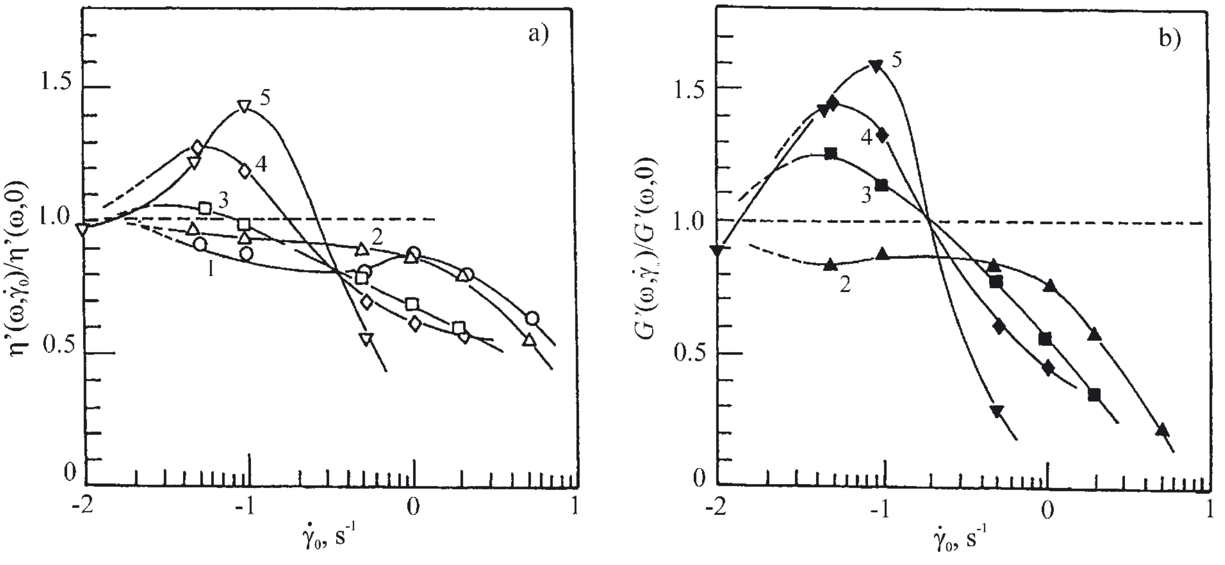


Fig. 9. Influence of the superposed shear rate ($\dot{\gamma}_0$) on: a) dynamic viscosity (η') and b) storage modulus (G') normalized by their values from simple oscillatory flow for unfilled PE sample and CF/PE melts at the angular frequency of 6 rad/s; particular samples are denoted as follows: 1 — PE, 2 — CF5/PE, 3 — CF10/PE, 4 — CF15/PE, 5 — CF20/PE

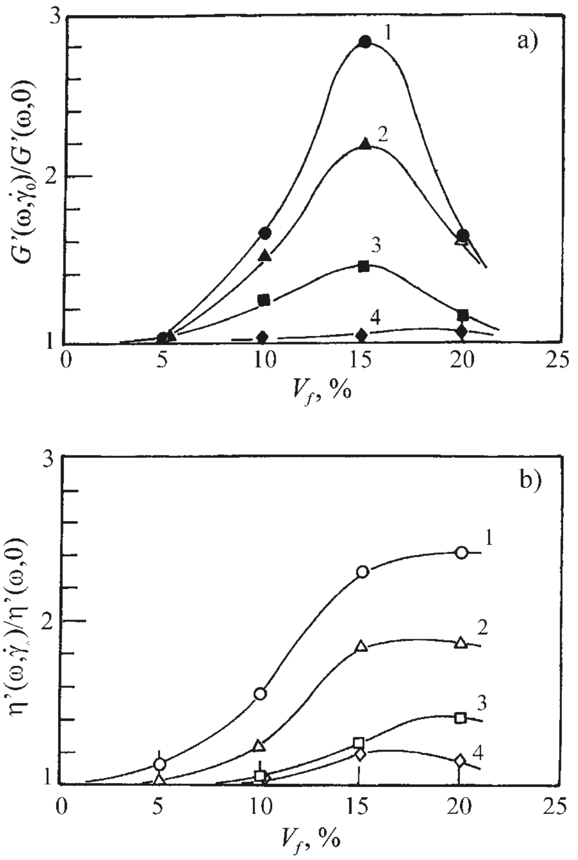


Fig. 10. Influence of volume fraction of fibre (V_f) on: a) maximum storage modulus (G'_{max}) and b) maximum dynamic viscosity (η'_{max}) normalized by their values from simple oscillatory flow at various angular frequencies (ω): 1 — 0.6 rad/s, 2 — 1.6 rad/s, 3 — 6 rad/s, 4 — 20 rad/s

Normalized η' and G' for unfilled PE sample and CF/PE systems with various fibre contents as functions of $\dot{\gamma}_0$ are shown at two different ω values: 0.6 and 6 rad/s in Fig. 8 and 9, respectively. At ω of 0.6 rad/s, the maximum value of η' increases with the fibre content, however, the increase in the maximum values of G' is not monotonous as in Fig. 8a. This behavior is strongly dependent on ω as confirmed in Fig. 9, representing the results at ω = 6 rad/s.

Fig. 10 demonstrates the relationship between the maximum storage modulus [$G'(\omega,\dot{\gamma}_0)_{\max}$] normalized by G' from simple oscillatory flow, and V_f, as a parameter of ω. All dependencies exhibit the peak point at approximately 15 vol. % of CF, while falling monotonously with increasing ω. Similar plots for normalized maximum dynamic viscosity [$\eta'(\omega,\dot{\gamma}_0)_{\max}/\eta'(\omega,0)$] dependence have different pattern. As one of the reasons for this discrepancy, it may be thought that G' of CF20/PE system under the superposition of steady shear flow does not increase monotonously with rising angular frequency even if G' under simple oscillatory flow does. On the opposite, dynamic viscosity of the sample under the superposed flow increases in the same manner as that under simple oscillatory flow.

From the comparison of δ curves of unfilled PE sample (Fig. 4) with those of CF/PE systems (Fig. 11), it is found that δ values at zero or low $\dot{\gamma}_0$ for fibre filled systems are generally lower than those of unfilled PE sample over a wide range of angular frequency. This is reasonable since the elastic properties are highly affected by the addition of fibres. Further, δ becomes lower than that under simple oscillatory flow for CF10/PE system (not shown in figure). From the rheological point of view it is very interesting that the fibre filled systems show higher dynamic elastic properties under the superposition of the shear flows at some critical conditions.

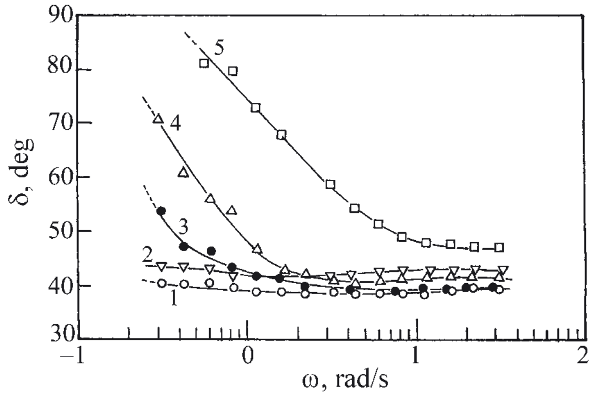


Fig. 11. Influence of angular frequency (ω) on phase angle (δ) for CF20/PE system; parameter, the superposed shear rate ($\dot{\gamma}_0$), changes as: 1 — 0 s^{-1}, 2 — 0.01 s^{-1}, 3 — 0.05 s^{-1}, 4 — 0.1 s^{-1}, 5 — 0.5 s^{-1}

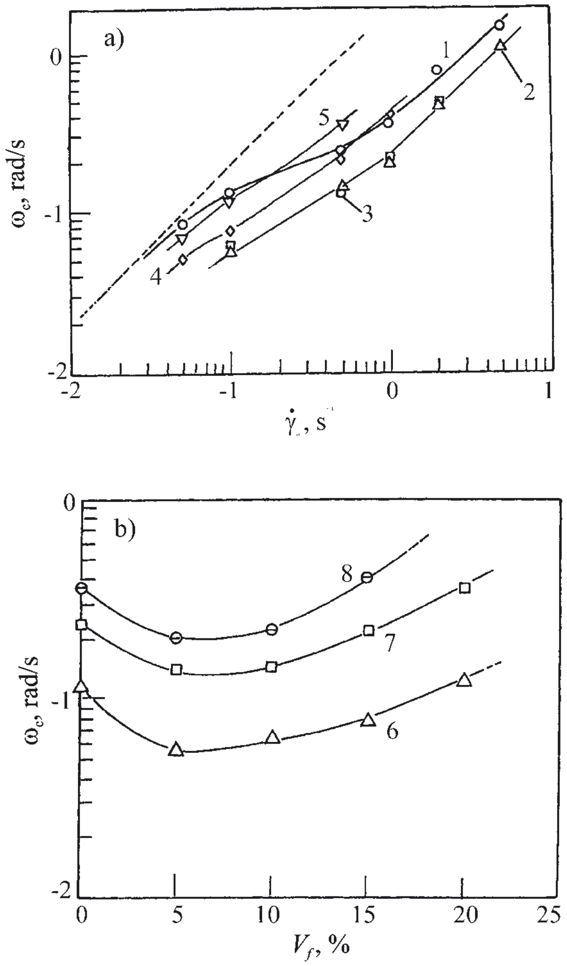


Fig. 12. Critical angular frequency (ω_c) for unfilled PE sample and CF/PE melts as a function of: a) superposed shear rate ($\dot{\gamma}_0$) for: 1 — PE, 2 — CF5/PE, 3 — CF10/PE, 4 — CF15/PE, 5 — CF20/PE systems (broken line represents $\varpi_c = {}^1/_2\dot{\gamma}_0$ relationship); b) volume fraction of fibre (V_f) for shear rate ($\dot{\gamma}$) varied as 6 — 0.1 s^{-1}, 7 — 0.5 s^{-1}, 8 — 1 s^{-1}

The critical angular frequency (ω_c) can be estimated from the extrapolation of δ= f(ω) curve as a parameter of superposed shear rate. The obtained values of ω_c are depicted in Fig. 12. Fig. 12a shows the relationship between ω_c and $\dot{\gamma}_0$ for all measured materials. In the figure, the broken line shows the relation:

$$\omega_c = \frac{1}{2}\dot{\gamma}_0 \qquad (5)$$

which was obtained for various polymer solutions and melts in the previous studies [4—7]. Concerning our data, it is found that ω_c of both pure PE sample and CF/PE melts are lower than ${}^1/_2\dot{\gamma}_0$, especially at high $\dot{\gamma}_0$ values. Furthermore, CF/PE data at each $\dot{\gamma}_0$ decrease once with increasing fibre content, and after passing a minimum they increase with rising fibre content, as clearly shown in Fig. 12b, representing ω_c versus V_f at several superposed shear rates. The character of the dependence is the same regardless of $\dot{\gamma}_0$ level. The value of ω_c normalized by that of unfilled PE sample as a function of V_f plots may be superimposed into a single curve, supporting the idea that ω_c change of CF filled systems is dependent largely on V_f.

CONCLUSION

Short carbon fibre filled low density polyethylene composites were prepared by melt mixing, and their rheological properties in molten state were characterized with a specific regard to the effect of fibre content on the parallel superposed shear. The following results were obtained:

— Both storage modulus and dynamic viscosity of the composites under the superposed steady shear flow show higher values than those obtained under simple oscillatory flow, especially at the low superposed shear rate region. The degree of the increase in these viscoelastic functions is dependent on the superposed shear rate, angular frequency and fibre content.

— The maximum values of dynamic viscosity and storage modulus normalized by those under simple oscillatory flow are generally increased by addition of carbon fibres, and decreased by rising angular frequency. However, as functions of volume fraction of fibre, both values show distinct pattern due to the different effects of the superposed shear flow on dynamic viscosity and storage modulus, especially for high fibre content systems. Fibre filled systems show, in comparison to simple shear, higher dynamic elastic properties under the superposition of the shear flows at some critical conditions.

— The critical angular frequency, in which phase angle becomes 90° and storage modulus decreases sharply and approaches gradually to zero, was estimated by the extrapolation of the phase angle versus the angular frequency curves at each superposed shear rate for the both unfilled PE sample and CF/PE systems. Its course is dependent largely on the volume fraction of fibre, but independent on the superposed shear rate.

REFERENCES

1. Booij H. C.: *Rheol. Acta* 1966, **5**, 215.
2. Booij H. C., Palmen J. H. M.: *Rheol. Acta* 1982, **21**, 376.
3. Vermant J., Walker L., Moldenaers P., Mewis J.: *J. Non-Newton Fluid* 1998, **79**, 173.
4. Osaki K., Tamura M., Kurata M., Kotaka T.: *J. Soc. Mat. Sci.* 1963, **12**, 339.
5. Osaki K., Tamura M., Kurata M., Kotaka T.: *J. Phys. Chem.* 1965, **69**, 4185.
6. Kurata S., Nakamura M.: *Kobunshi Kagaku* 1967, **24**, 807.
7. Kataoka T., Ueda S.: *J. Polym. Sci. Part A-2* 1969, **7**, 475.
8. Gregory B., Hiltner A., Bear E.: *Polym. Eng. Sci.* 1987, **27**, 568.
9. Khomami B., Wilson G. M.: *J. Non-Newtonian Fluid* 1995, **58**, 47.
10. Vermant J., Moldenaers P., Mewis J.: *Rev. Sci. Instrum.* 1997, **68**, 4090.
11. Tirtaamadja V., Tam K., Jenkins R. D.: *Macromolecules* 1997, **30**, 1426.
12. Mewis J., Kaffashi B., Vermant J.: *Macromolecules* 2001, **34**, 1376.
13. Isayev A. I., Wong C. M.: *J. Polym. Sci. Pol. Phys.* 1988, **26**, 2303.
14. Wong C. M., Isayev A. I.: *Rheol. Acta* 1989, **28**, 176.
15. Wong C. M., Chen C. H., Isayev A. I.: *Polym. Eng. Sci.* 1992, **30**, 1574.
16. Masi P., Nicodemo L., Nicolais L., Taglialatela G.: *Rheol. Acta* 1982, **21**, 598.
17. Vlastos G., Letche D., Koch B.: *Biorheology* 1997, **34**, 19.
18. Mewis J., Biebaut G.: *J. Rheol.* 2001, **45**, 799.
19. Kitano T., Kimijima K., Oyanagiand Y., Saha P.: *Proceedings of the International Pacific Conference on Rheology*, Kyoto 2001, 136.
20. Russo L., Maffettone P. L.: *J. Rheol.* 2003, **47**, 129.
21. Czarnecki L., White J. L.: *J. Appl. Polym. Sci.* 1980, **25**, 1217.
22. Steller R., Meissner W.: *Polimery* 2002, **47**, 332.
23. Zieliński J.: *Polimery* 2002, **47**, 305.
24. Stabik J.: *Polimery* 2004, **49**, 712.
25. Kitano T., Funabashi M., Klason C., Kubat J.: *Int. Polym. Proc.* 1988, **3**, 67.
26. Ausias G., Aggassant J. F., Vincent N., Laufleur P. G., Lavoie P. A., Carreau P. J.: *J. Rheol.* 1992, **36**, 525.

Received 17 XII 2004.