

P O L I M E R Y

MIESIĘCZNIK POŚWIĘCONY CHEMII, TECHNOLOGII I PRZETWÓRSTWU POLIMERÓW

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Rheological behavior of fiber-filled polymer melts at low shear rate

Part. I. MODELING OF RHEOLOGICAL PROPERTIES

Summary — In this review the models applied for the description of non-Newtonian liquids were presented. Highly filled polymer melts showing distinct yield stress are such liquids. The effects of forces of geometrical and physical interactions among the filler particles on the properties were discussed. These interactions forces depend on the type, size and shape of filler particles and in case of fibers also on their orientation. The deformations and flow of fibers assemblies in the melt under shear stress were discussed. The equations used for description of three- or two-dimensionally oriented fibers sets are presented.

Key words: polymer melt, filler, modeling of rheological properties, viscosity, yield stress, shear rate.

CHARAKTERYSTYKA REOLOGICZNA W ZAKRESIE MAŁYCH SZYBKOŚCI ŚCINANIA STOPÓW POLIMERÓW NAPEŁNIONYCH WŁÓKNAMI. Cz. I. MODELOWANIE WŁAŚCIWOŚCI REOLOGICZNYCH

Streszczenie — W pracy przeglądowej przedstawiono modele stosowane do opisu właściwości reologicznych cieczy nienewtonowskich, którymi są stopy polimerów o wysokim stopniu napełnienia wykazujące wyraźną granicę plastyczności. Omówiono wpływ na omawiane właściwości sił oddziaływań geometrycznych i fizycznych między cząstkami napełniacza. Siły tych oddziaływań zależą od rodzaju, wielkości i kształtu cząstek napełniacza, a w przypadku włókien, także od ich orientacji. Przedyskutowano także deformacje i przepływ zespołów włókien w stopie pod wpływem naprężeń ścinających. Przedstawiono równanie stosowane w przypadku zespołów włókien o orientacji trójwymiarowej oraz dwuwymiarowej.

Słowa kluczowe: stop polimeru, napełniacz, modelowanie właściwości reologicznych, lepkość, granica plastyczności, szybkość ścinania.

Filled thermoplastics with short fibres belong to a new class of engineering materials with high commer-

cial importance [1—5]. Compared to pure polymers, these materials possess improved physical properties, such as stiffness and strength. During manufacturing they flow through channels or cavities in the molten

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state, thus it is very important to know their rheological behavior, as it influences the physical properties of the final product strongly. It is expected that the flow conditions and flow properties of fibre-filled polymer melts affect the structures developed by fibres or fibre orientation in the polymer matrix as it was described for example in [6].

Up to now, considerable research has been directed towards the melt flow properties of these materials. However, most of the investigations have been limited to high shear rate (extrusion-based shear viscosity measurements). It is well known that polymer melts highly loaded with fibre show complex and different flow behavior at low shear rate region compared to that at high shear rate [7]. In previous papers an extensive set of rheological data, including steady shear viscosity, first normal stress difference and dynamic viscoelastic properties of various kinds of short fibre-filled polymers in a relatively low strain rate region was presented [8—18].

The present work consists of two parts. In the first part the state-of-the-art in the rheology based on the papers dealing with flow of highly concentrated particle- and fibre-filled polymer solutions, suspensions and melts at low shear rate will be presented. In the second part experimental results concerning rheological behavior of short fibre-filled polymer melts, mainly at low shear rate region will be described.

RHEOLOGICAL PROPERTIES OF HIGHLY FILLED SYSTEMS SHOWING THE YIELD STRESS

An interpretation of viscosity and yield stress in dense slurries was presented by Wildemuth and Williams [19]. Shear viscosity of highly concentrated particle-filled solutions was measured in the shear rate range of 10^{-3} to 10^2 s^{-1} using a cone-plate rheometer. The relative viscosity (η_r) is given here as

$$\eta_r = \left(1 - \frac{\Phi}{\Phi_M}\right)^{-[\eta]\Phi_M} \quad (1)$$

where: Φ — volume fraction of the particles, Φ_M — maximum packing fraction for the high-shear microstructure, which should reveal the roles of particle size distribution and the character of suspending fluid, $[\eta]$ — intrinsic viscosity.

A new model that invokes the stress dependence of Φ_M correlates η_r well under non-Newtonian conditions with simultaneous prediction of yield stress at sufficiently high value Φ . A critical result is that the shear stress (τ) [instead of shear rate ($\dot{\gamma}$)] governs the microstructure and rheology. $\Phi_M(\tau)$ dependence was found to change from its low-shear value — Φ_{M0} (in the range of 0.6—0.7) typical of disordered and aggregated systems, towards its high-shear limits — $\Phi_{M\infty}$ (close to 0.74) which is characteristic for close-packed fully-dispersed spheres. Yield stresses (τ_y) would arise ($\eta \rightarrow \infty$ at $\tau \rightarrow \tau_y$) when $\Phi_{M0} \leq \Phi \leq \Phi_{M\infty}$ and can be presented as:

$$\tau_y = \left[A \left(\frac{\Phi}{\Phi_{M0}} - 1 \right) \left(1 - \frac{\Phi}{\Phi_{M\infty}} \right) \right]^{\frac{1}{m}} \quad (2)$$

where: A , m — constants which were derived on the basis of stress-induced microstructure change and relation $\Phi_M(\tau)$.

White [20], on the other hand, proposed a theory of rheological behavior of polymer melts highly loaded with small particles (less than $1 \mu m$), which exhibited yield values in steady shear flow. This behavior is generally attributed to particle interactions, which lead to the formation of gel. Flow may only be initiated when sufficient stress or strain energy is applied to break the gel structure. The author discussed three-dimensional theory on the base of von Mises yield-criterion [21].

Another equation was obtained by phenomenological modification of Tanaka-White model, which provided flexibility to the description of suspension viscosity of the system exhibiting an apparent yield stress [22]. One way to describe the effect of an apparent yield stress is to express the viscosity as a function of shear rate. The equation incorporates the shear-thinning behavior of the matrix polymer:

$$\eta = \tau_y (\dot{\gamma})^{-1} + K_c (\dot{\gamma})^{n-1} \quad (3)$$

where: n — power law index of matrix polymer, K_c — consistency index of the filled system.

The above equation is volume-fraction independent and needs to incorporate the concentration. In the case of Newtonian medium, the modified Bingham model is expressed as:

$$\eta = \tau_y (\dot{\gamma})^{-1} + \mu_M \left(1 - \frac{\Phi}{\Phi_M} \right)^{-2} \quad (4)$$

where: μ_M — Newtonian viscosity of polymer matrix.

However, polymers have commonly non-Newtonian behavior, so the viscosity of filled systems can be presented on the base of Bird-Carreau equation for the medium:

$$\eta = \tau_y (\dot{\gamma})^{-1} + \eta_0 \left(1 - \frac{\Phi}{\Phi_M} \right)^{-2} \left[1 + (\lambda \dot{\gamma})^{\frac{n-1}{2}} \right] \quad (5)$$

where: η_0 — zero-shear viscosity of the filled system, λ — constant depending on the volume fraction of the filler.

Constant λ is specified as:

$$\lambda = \lambda_M \left(1 - \frac{\Phi}{\Phi_M} \right)^{-2} \quad (6)$$

where: λ_M — constant representing the shear viscosity of matrix polymer.

Another paper deals with rubber-modified polymer [23]. The conclusion of the study is that the viscosity increase at small shear rates is more pronounced for higher concentrations and smaller particles. It can be interpreted as the effect of the filler on yield stress. Yield stress here is independent on temperature within the accuracy of the measurements and is significantly higher for elongation than for shear.

In the rheology of suspensions the yield stress is usually determined according to the plot proposed by Casson [24] ($\sqrt{\dot{\gamma}}$ vs. $\sqrt{\tau}$), and the extrapolation of the linear part of the curve to $\sqrt{\dot{\gamma}} = 0$ gives the square root of the yield stress. However, in some cases a straight line can only be drawn if the values at very small shear rates are neglected.

Lobe and White [25] studied the influence of carbon black (CB) on the rheological properties of polystyrene. They found that at the loading between 10 and 20 vol. % the system took on the characteristics of gel and the response was similar to that of a Schwedoff body [25]. They proposed a stress-deformation history constitutive equation. Another result of the study was finding a yield value not only for shear flow, but also for elongational deformation. In case of these systems one should think in terms of yield surfaces rather than yield values. The mechanical model representing gel behavior (high modulus and memory at low stresses, and deformation with a yield value corresponding with viscoelastic fluid at higher deformation rates) was the Schwedoff model modified to the following form:

$$\tau = \tau_y + \int_0^{\infty} G e^{-\frac{z}{\lambda}} d\gamma/dz \quad (7)$$

where: λ — relaxation time, G — shear modulus of the fluid.

The interaction forces between the filler particles, resulting in the formation of a three-dimensional particle network, play an important role in rheological and processing behaviors of filled thermoplastics. For closely packed systems, the inertia of the particles as well as geometrical and physical interactions of the particles caused by packing prevent the particles from relative motions below the yield stress level.

When tensile or stretching forces are applied to the network during deformation, they increase the distance between particles and the particles move with respect to each other. For the material to flow, these forces must exceed a critical value, which is also affected by the filler. The influence of the interfacial interactions on the yield stress was investigated experimentally for CB- and mica-filled PE-HD [26]. The relation between yield stress and interfacial interactions was explained on the base of stress-strain curves of the systems. For pure polymer no yield stress was observed, but as the concentration increased, the ability to form a network and strength of the network increased. Yield behavior of filler suspensions in gel medium was also investigated [27]. The presence or absence of a yield stress in concentrated dispersion is of great importance for the flow and physical stability of many industrial products. Barnes and co-worker followed the yield stress through measurements with use of a stress controlled rheometer [28, 29]. The actual value, however, was much smaller than that obtained by previous methods of linear extrapolation from high shear rates/shear stresses. The relation between the viscosity and the volume fraction of a suspension was

given in the following equation, which is similar to eq. (1):

$$\eta = \eta_s \left(1 - \frac{\Phi}{\Phi_m} \right)^{-[\eta]\Phi_m} \quad (8)$$

where: η_s — viscosity of the suspension medium.

The exponent $[\eta]\Phi_m$ is approximately 2, Φ_m is a measure of ordering (hence controlling the viscosity) and varies with τ according to equation:

$$\left(\frac{1}{\Phi_{m0}} - \frac{1}{\Phi_{m\infty}} \right) / \left(\frac{1}{\Phi_m} - \frac{1}{\Phi_{m\infty}} \right) = 1 + B\tau \quad (9)$$

where: Φ_{m0} , $\Phi_{m\infty}$ — asymptotic values of the maximum volume fraction at zero and infinite shear stress, respectively; B — constant with the dimension of inverse stress.

When Φ_m in eq. (8) is replaced with that in eq. (9), the following equation is obtained for viscosity:

$$\eta = \eta_s \left\{ 1 - \Phi \left[\left(\frac{1}{\Phi_{m0}} - \frac{1}{\Phi_{m\infty}} \right) \left(\frac{1}{1 + B\tau} \right) + \frac{1}{\Phi_{m\infty}} \right] \right\}^{-2} \quad (10)$$

The parting line between a finite viscosity at low shear stress and an infinite viscosity at finite shear stress is at $\Phi = \Phi_{m0}$. Above this volume fraction τ_y increases continuously and becomes infinite at $\Phi = \Phi_{m\infty}$. It can be derived from the equations:

$$\tau_y = \frac{\Phi_{m\infty}}{B\Phi_{m0}} \left(\frac{\Phi - \Phi_{m0}}{\Phi_{m\infty} - \Phi} \right) \quad (11)$$

The yield stresses for various types of fillers in polymer melts can be determined from the Casson plots [24]. In experimental research [9, 30] it was found for particle-filled polyethylene that the yield stress estimated from the Casson plots increased exponentially with increase in Φ . While there are some doubts about the presence of a true yield stress for suspensions in which the particles are not small enough for colloidal interactions, an apparent yield stress is, in most cases, obtained from Casson plots for highly filled materials.

Rheological properties of fibre-filled polymer melts were studied by Mutel and Kamal [31] using a rotational rheometer. An important factor of the flow behavior was the initial state of fibre orientation in the system. Oscillatory shear tests yielded highly strain dependent loss and storage moduli even at very small strain amplitudes. However, stress response was found to be sinusoidal in most cases, although the properties were strain dependent. Unlike for particle fillers, for fibre-filled systems yield behavior was not observed, except at high concentrations (above 30 vol. %) or for long non-rigid fibres. The Casson plots revealed yield stresses of about 100 Pa, what was only 4 % of the minimum stress obtained at the lowest shear rate. Furthermore, large stress overshoots were observed followed by thixotropic behavior, which is attributed to the slow change in fibre orientation. The fluid was highly anisotropic, and fibre-wall interactions contributed significantly to the stress during transient flows.

Kataoka *et al.* [15] on the other hand, followed the suitability of parallel-plate viscometer for rheological studies of fibre-filled polymer melts. They found that the flow curves obtained under different loads were almost parallel to the $\dot{\gamma}$ -axis, and the yield stress was only apparent and not determined uniquely for materials with high fibre content. From the comparison with the data obtained from the Casson plots it is clear that the existence of yield stress induces the unstable flow for squeezing between parallel plates.

Onogi *et al.* [32] discussed the correlation between rheological behavior and re-formation of a structure formed by dispersed fibres in polymer solutions, and its destruction at higher shear rates. They observed the yield stress, although only apparent one, for low fibre content, in contrast to the suspensions with spherical particles, and showed that yield stress for titanate fibres (aspect ratio $a_r > 40$) in polystyrene solution is proportional to Φ [3] at the whole range of the fibre content.

Similar dependence of the yield stress on the fibre concentration was discussed for flexible fibre-filled suspensions [8, 10]. Here, yield stress of short and flexible fibre systems is again nearly proportional to Φ [22], but for other more flexible-fibre filled systems the slopes of the curves τ_y versus Φ become lower. It was concluded that the reasons for these results are interactions between fibres and the wall, and also the aspect ratio, size and flexibility of the fibres played their roles in apparent yield stress appearance. Rheological properties of the medium, on the other hand, were less significant.

Dynamic viscoelastic properties of long glass fibre reinforced polypropylene in molten state were measured, and the yield behavior of the materials was discussed in another paper [12]. The yield value of complex modulus (G^*) is a critical value at which the material starts to flow. It was supposed that for the oscillatory flow of filled systems a similar to Casson's equation dependence of G^* on angular frequency (ω), could be constructed. If the relation between the complex modulus yield value (G_y^*) and Φ are plotted in semi-logarithmic coordinates, G_y^* of the composite increases abruptly for $0.1 \leq \Phi \leq 0.15$, and then the increase is only moderate. The influence of fibre length and content on the dynamic viscoelastic properties of glass fibre reinforced polypropylene in molten state was also investigated experimentally [16], and an abrupt increase in G_y^* with rising fibre length was observed. Furthermore, G_y^* increased linearly with the fibre content up to 15 vol. % loading.

The Casson plots also served for the assessment of metal fibre (Al, Cu) and carbon fibre (CF) filled polymers [11]. When the $\log \tau_y$ is plotted versus Φ , we can obtain a straight line. These results revealed that the yield stress increased exponentially with fibre content; the yield stresses of the systems depended strongly upon the fibre aspect ratio and fibre rigidity.

DEFORMATION AND FLOW OF FIBRE ASSEMBLY UNDER SHEAR

Three-dimensionally oriented fibre assembly

The constitutive equations for deformation of three-dimensionally oriented fibre assembly were discussed by Yamada and Horikawa [33, 34]. They can be useful for discussion of the deformation and flow of fibre-filled polymer systems under low shear/strain rate. The notion expects an assembly where fibres consist of parts "b" (effective fibre elements — have no ends and affect the stress on the assembly under deformation), and parts "a" (non-effective fibre elements — have two free ends and do not influence the deformation behavior). The stress tensor (τ_{ij}) can be expressed as:

$$\tau_{ij} = \frac{N_f l^2 E \Gamma}{V} \int_0^{2\pi} \int_0^\pi \int_0^\pi \epsilon_{k\ell} s_i s_j s_k s_\ell \Omega(\theta, \psi) \sin \theta d\theta d\psi \quad (12)$$

where: N_f — total number of fibres per unit volume, l — fibre length, V — volume of the fibre assembly, E — tensile modulus of the fibre, $\epsilon_{k\ell}$ — strain tensor, s_i, s_j, s_k, s_ℓ — orthogonal coordinates presented by polar coordinates (r, θ, ψ), $i, j, k, \ell = 1, 2, 3$, $\Omega(\theta, \psi)$ — fibre orientation distribution function, Γ — effective element fraction which gives the part of effective fibre elements in the total number of elements.

When m is the number of points where a fibre is in contact with other fibres, Γ is a function of m :

$$\Gamma = \left(\frac{m-1}{m+1} \right)^3 \left(\frac{m+5}{m+1} \right) \quad (13)$$

As the number of elements of a fibre is $(m + 1)$, the probability that an element which has two free ends will be in the non-effective part is a , and the probability to be in the effective part is $b = 1 - a$. They are given by the following equations:

$$a = \frac{2}{m+1} \quad (14)$$

$$b = \frac{m-1}{m+1} \quad (15)$$

Equation (13) shows that Γ is smaller than the value of b in the small region of m , and both Γ and b approach to 1 when m is higher than 100. From the investigation of the fibre assembly geometry, the number m is given as:

$$m = \frac{2d(N_f - 1)\ell^2 I}{V} \quad (16)$$

where: d — fibre diameter, I — fibre orientation function.

Function I is given by the following equations:

$$I = \int_0^{2\pi} \int_0^{2\pi} \int_0^\pi \int_0^\pi \Omega(\theta, \psi) \Omega(\theta', \psi') |\sin x| \sin \theta \sin \theta' d\theta d\psi d\theta' d\psi' \quad (17)$$

$$\sin x = \left\{ 1 - [\cos \theta \cos \theta' + \sin \theta \sin \theta' \cos(\psi - \psi')]^2 \right\}^{1/2} \quad (18)$$

From eq. (16), when $N_f \gg 1$ m is given as:

$$m = \frac{8 \pi d^2 N_f \ell}{\pi 4 V d} I \quad (19)$$

The relations of Φ and aspect ratio of fibres (a_r) are:

$$\Phi = \frac{\pi d^2 N_f \ell}{4 V} \tag{20a}$$

$$a_r = \frac{\ell}{d} \tag{20b}$$

Then

$$m = \frac{8}{\pi} \Phi a_r I \tag{21}$$

and τ_{ij} is given as

$$\tau_{ij} = \frac{4}{\pi} \frac{\Phi a_r \Gamma E}{d} \int_0^{2\pi} \int_0^\pi \varepsilon_{k\ell} s_i s_j s_k s_\ell \Omega(\theta, \psi) \sin\theta d\theta d\psi \tag{22}$$

The values of m and τ_{ij} are proportional to Φ and a_r of the product. When ε_{kl} and function $\Omega(\theta, \psi)$ are given, the shear stress τ_{ij} ($i \neq j$) or shear modulus can be calculated from eq. (22). Considering that the yield stress shows the critical value of the shear deformation of fibre assembly, we can obtain some information concerning the relation among yield stress and characteristics of the fibre assembly, such as volume fraction, fibre length or aspect ratio, fibre orientation and so on. Fibre orientation distribution function and shear modulus will be now taken into deeper consideration.

When γ is given as simple displacement of a plane against other parallel plane of rectangular parallelepiped in the fibre assembly in which the fibres are oriented randomly, the change of fibre orientation distribution function under simple shear is given as a function of elongation ratios in three directions:

$$\Omega(\theta, \psi) = \frac{1}{4\pi} \left\{ \left[1 + \gamma \left(\gamma - \sqrt{\gamma^2 + 4} \right) \right] \sin^2 \theta \cos^2 (\psi - \chi) + \left[1 + \gamma \left(\gamma^2 + 4 \right) \right] \sin^2 \theta \sin^2 (\psi - \chi) + \cos^2 \theta \right\}^{-3/2} \tag{23}$$

where: χ — rotation angle of the axis under shear.

Value of χ is given as:

$$\chi = \tan^{-1} \left(\frac{\gamma}{2} + \sqrt{1 + \frac{\gamma^2}{4}} \right) \tag{24}$$

When three-dimensionally oriented fibre assembly is deformed in the elongation ratios of λ_1, λ_2 and λ_3 , then $V, \Omega(\theta, \psi)$ and Γ in eq. (12) are changed and must be presented as functions of λ_1, λ_2 and λ_3 . For V it means:

$$V = V_0 \lambda_1 \lambda_2 \lambda_3 \tag{25}$$

where: V_0 — volume of the fibre assembly at the initial state.

When the initial orientation distribution is homogeneous, the fibres are randomly oriented and $\Omega_0 = 1/4 \pi$, the fibre orientation function in eq. (17) can be written as $\Omega(\theta, \psi) = \Omega_0 (\lambda_1 \lambda_2 \lambda_3)^2 \left[(\lambda_2 \lambda_3 \sin \theta \cos \psi)^2 + (\lambda_3 \lambda_1 \sin \theta \cos \psi)^2 + (\lambda_1 \lambda_2 \sin \theta)^2 \right]^{-3/2}$

$$\tag{26}$$

Further, the volume fraction after deformation is a function of the initial fibre volume fraction, Φ_0 :

$$\Phi = \frac{\Phi_0}{\lambda_1 \lambda_2 \lambda_3} \tag{27}$$

and the shear modulus under deformation will be:

$$G = \frac{N_f I^2 E \Gamma}{V} \int_0^{2\pi} \int_0^\pi \sin^4 \theta \cos^2 \psi \sin^2 \psi \Omega(\theta, \psi) \sin \theta d\theta d\psi \tag{28}$$

Simple shear deformation of two-dimensionally oriented fibre assembly

The relation among shear modulus G_{ij} , stress σ_{ij} and shear strain ε_{ij} (where $i \neq j$) can be presented as

$$G_{ij} = \frac{\sigma_{ij}}{2\varepsilon_{ij}} \tag{29}$$

If the volume of fibre assembly does not change under deformation and is kept constant (Poisson ratio is 0.5), the same as in the initial state (V_0), the modulus decreases with the decrease in aspect ratio of fibres due to the reduction of Γ .

For simple shear deformation of two-dimensionally oriented fibre assembly, when the elongation ratio along X and Y axes is λ_1 and λ_2 , respectively, and shear deformation is γ , the rotation angle of axis (χ) is given by eq. (24).

Elongation ratios along the main axes after rotation are:

$$\lambda_1 = 1 + \frac{\gamma}{2} \left(\gamma + \sqrt{\gamma^2 + 4} \right) \tag{30a}$$

$$\lambda_2 = 1 + \frac{\gamma}{2} \left(\gamma - \sqrt{\gamma^2 + 4} \right) \tag{30b}$$

Then, the probability density function of fibre orientation angle is given as

$$q(\psi) = \left\{ 2\pi \left[\left(1 + \frac{\gamma \left(\gamma - \sqrt{\lambda^2 + 4} \right)}{2} \right) \cos^2 (\psi - \chi) + \left(1 + \frac{\gamma \left(\gamma - \sqrt{\lambda^2 + 4} \right)}{2} \right) \sin^2 (\psi - \chi) \right] \right\}^{-1} \tag{31}$$

The axis of each fibre may be thought to exist in the plane of two-dimensionally oriented fibre assembly. The orientation angle distribution can be presented in the following form:

$$\Omega(\theta, \psi) = \delta \left(\theta - \frac{\pi}{2} \right) q(\psi) \tag{32}$$

where: $\delta \left(\theta - \frac{\pi}{2} \right) = 1$ when $\theta = \frac{\pi}{2}$ and $\delta \left(\theta - \frac{\pi}{2} \right) = 0$ when $\theta \neq \frac{\pi}{2}$;

i.e. we consider here the case in which all fibres are oriented two-dimensionally.

$$G = \frac{N_f \ell^2 E \Gamma}{V} \int_0^{2\pi} \cos^2 \psi \sin^2 \psi q(\psi) d\psi = \frac{N_f \ell^2 E \Gamma}{8V} [1 - A_\psi(4)] \tag{33}$$

where: $A_\psi(2k)$ — Fourier cosine transformation of $q(\psi)$.

Fourier cosine transformation is given by:

$$A_\psi(2k) = \int_0^{2\pi} \cos 2k\psi q(\psi) d\psi \tag{34}$$

For two-dimensional deformation (λ_1, λ_2) , $A_\psi(2k)$ is given from eqs. (30), (31) and (34) as:

$$A_\psi(2k) = \left(\frac{\lambda_1 - \lambda_2}{\lambda_1 + \lambda_2} \right)^k \quad (35)$$

From eqs. (33) and (35), the shear modulus is

$$G = \frac{N_f \ell^2 E \Gamma}{V} \frac{\lambda_1 \lambda_2}{2(\lambda_1 + \lambda_2)^2} \quad (36)$$

For the simplification of G relation, Hermanns's orientation coefficient (J) can be used. For two-dimensionally oriented fibre assembly it is defined by the following equation:

$$J = 2 \int_0^{2\pi} q(\psi) \cos^2 \psi d\psi - 1 \quad (37)$$

and also from eq. (35)

$$J = A_\psi(2) = \frac{\lambda_1 - \lambda_2}{\lambda_1 + \lambda_2} \quad (38)$$

So, the simplified formula of modulus for two-dimensional deformations is

$$G \equiv G_{1122} = \frac{N_f \ell^2 E \Gamma}{8V} (1 - J^2) \quad (39)$$

From the equation, G has a maximum at $J = 0$, i.e., fibres are in two-dimensional random orientation.

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REFERENCES

- Kaczmar J. W., Pach J., Kozłowski R.: *Polimery* 2006, **51**, 722.
- Liber-Kneć A., Kuciel S., Dziadur W.: *Polimery* 2006, **51**, 571.
- Siejka-Kulczyk J., Lewandowska M., Kurzydłowski K. J.: *Polimery* 2006, **51**, 742.
- Kijeński J., Osawaru O.: *Polimery* 2006, **51**, 115.
- Bledzki A. K., Faruk O., Kirschling H., Kuhn J., Jaszkievicz A.: *Polimery* 2007, **52**, 3.
- Gądek A., Kuciel S., Wojnar L., Dziadur W.: *Polimery* 2006, **51**, 206.
- Thomasset J., Carreau P. J., Sanschagrín B., Ausias G.: *J. Non-Newtonian Fluid Mech.* 2005, **125**, 25.
- Kitano T., Kataoka T.: *Rheol. Acta* 1981, **20**, 390.
- Kataoka T., Kitano T., Oyanagi Y., Sasahara M.: *Rheol. Acta* 1979, **18**, 635.
- Kitano T., Kataoka T.: *Rheol. Acta* 1981, **20**, 403.
- Sakai H., Kitano T., Nishimura T.: *Kobunshi Ronbunshu* 1988, **45**, 123.
- Nishitani Y., Sekiguchi I., Hausnerova B., Nagatsuka Y., Kitano T.: *Polym. Polym. Comp.* 2001, **9**, 199.
- Araki K., Kitano T., Hausnerova B.: *Appl. Rheol.* 2001, **11**, 188.
- Kitano T., Funabashi M., Klason C., Kubat J.: *Int. Polym. Proc.* 1988, **3**, 67.
- Kataoka T., Kitano T., Nishimura T.: *Rheol. Acta* 1978, **17**, 626.
- Nishitani Y., Sekiguti I., Nakamura K., Tai N., Nagatsuka Y., Kitano T.: *Reinf. Plast. Japan* 1998, **44**, 222.
- Chan Y., White J. L., Oyanagi Y.: *J. Rheol.* 1978, **22**, 507.
- Navickis L. L., Bagley E. B.: *J. Rheol.* 1983, **27**, 519.
- Wildemuth C. R., Williams M. C.: *Rheol. Acta* 1985, **24**, 75.
- White J. L.: *Rheol. Acta* 1981, **20**, 381.
- Prager W., Hodge P.: "Theory of Perfectly Plastic Solids", Wiley, New York 1951.
- Poslinski A. J., Ryan M. E., Gupta R. K., Seshadri S. G., Frechette F. J.: *J. Rheol.* 1988, **32**, 703.
- Munstedt H.: *Polym. Eng. Sci.* 1981, **21**, 259.
- Casson N. in: "Rheology of disperse systems" (Ed. Mill C. C.), Pergamon Press, New York 1959.
- Lobe V. M., White J. L.: *Polym. Eng. Sci.* 1979, **19**, 617.
- Carreau P. J., Malik T. M.: Proceedings of Xth International Congress on Rheology, Sydney 1988, **1**, 220.
- Shouche S. V., Chokappa D. K., Naik V. M., Khakhar D. V.: *J. Rheol.* 1994, **38**, 1871.
- Barnes H. A.: Proceedings of XIth International Congress on Rheology, Brussels 1992, 17.
- Barnes H. A., Walters K.: *Rheol. Acta* 1985, **24**, 323.
- Kataoka T., Kitano T., Sasahara M., Nishijima K.: *Rheol. Acta* 1978, **17**, 149.
- Mutel A. T., Kamal M. R.: *Polym. Comp.* 1986, **7**, 283.
- Onogi S., Mikami Y., Matsumoto T.: *Polym. Eng. Sci.* 1977, **17**, 1.
- Yamada K., Horikawa A.: *J. Text Eng. Japan* 1983, **36**, 51.
- Yamada K.: "Structure and mechanics of Fibres Aseemlies", PhD thesis, Osaka University 1986.

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