INFLUENCE OF THE ELASTICITY OF POLYMER SOLUTIONS ON THE REDUCTION OF RESISTANCE

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The Toms effect is examined from the point of view of the viscoelastic properties of solutions of polymers. It is shown that the magnitude of the reduction of resistance depends on the set of the relaxation times of the macromolecules and the scales of the turbulent vortices.

Recently investigations have appeared with a view to building a model which would explain the reduction of the resistance when small quantities of soluble polymers are introduced into a turbulent flow of liquid (Toms effect [1]) and which confirmed it quantitatively. In the works [2, 3] the Toms effect is bound up with the influence of several particles-associates, formed due to the immobilization of part of the solvent by molecules of polymers, on the turbulence. G. F. Kobets [4] examines the flow of solution, containing very simple lengthened particles - dumb-bells, and introduces the coefficient of dynamic anisotropy of the viscosity of the solution in order to explain the phenomenon of reduction of resistance. The semiempirical theory of turbulence of weak solutions of polymers is presented in [5], in which a hypothesis about the existence of a universal relationship between the maximum magnitude of reduction of resistance and a certain combination of the concentration of the polymer and its molecular weight is stated on the basis of experimental data. In the work [6] it is assumed that a considerable part of the turbulent energy is stored in deformed polymer molecules. For quantitative evaluation of the influence of polymer additions on the reduction of the resistance a relationship is proposed between two dimensionless parameters. Treatment of experimental data by using these parameters enables it to be concluded that in the case of the given Reynolds number and the form of the surface surrounded by liquid there is a single relationship between the parameters.

It is known that in solutions of polymers the viscoelastic properties are already observed at small measured concentrations, when the individual molecules or particles are kinetically independent of one another [7]. In the presence of viscoelasticity, a complex viscosity $\eta_* = \eta_1 + j\eta_2$ is introduced into the examination, where the magnitude η_1 is associated with the energy scattered in the form of heat, and η_2 is associated with the accumulation of energy and its liberation during the deformation process.

When the kinetics of the macromolecules in the solution are examined by the authors of [8], a model of a macromolecule, consisting of N segments, subjected to the Brownian movement is introduced. As a result of the fact that although the segments can rotate one relative to the other, they are connected among themselves, and the movement of each of them is determined by all N segments of the molecular chain. Rouse [9] calculated this cooperative type of movement and showed that the viscosity of the solution depends on the set of the relaxation times of the macromolecules λ_p and the frequency of the outside disturbing influence ω . The distribution of the relaxation times is introduced on the strength of the fact that the molecule consists of N segments. Each segment introduces a certain discrete contribution into the spectrum of relaxation, which is limited as a result of the fact that the molecule has N segments. The relaxation times are associated with the equation $\lambda_p = \lambda_1/p^2$, where λ_p is the p-e time of relaxation of the macromolecule, λ_1 is the first (limiting) relaxation time, p is the number of segments in the molecular chain. On examining the macroscopic properties of the solution the most important parameter is the relaxation

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© 1974 Consultants Bureau, a division of Plenum Publishing Corporation, 227 West 17th Street, New York, N. Y. 10011. No part of this publication may be reproduced, stored in a retrieval system, or transmitted, in any form or by any means, electronic, mechanical, photocopying, microfilming, recording or otherwise, without written permission of the publisher. A copy of this article is available from the publisher for \$15.00. time for the first (slowest) mechanism or the "limit time of relaxation," λ_1 , which can be determined according to the formula [10]

$$\lambda_1 = \frac{6}{\pi^2} \frac{M}{RT} \eta_0 [\eta]_0$$

Here M is the molecular weight of the polymer, η_0 is the viscosity of the solvent, $[\eta_0]$ is the characteristic viscosity for a steady flow in the case of small gradients of medium velocity for a steady flow in the case of small gradients of medium velocity, R is the universal gas constant, T is the temperature.

From the Rouse theory for the characteristic viscosity $[\eta]_2$ it follows:

$$[\eta]_{2} = 0.608 [\eta]_{0} \sum_{p=1}^{N} \frac{\omega \lambda_{1}}{p^{2} + \omega^{2} \lambda_{1}^{2}}$$
(0.1)

The formula (0.1) gives a maximum where $\omega \lambda_1 \sim 1$, and hence the greatest quantity of energy is accumulated in the macromolecule. With increase of the number of segments p, which corresponds to increase of the set of relaxation times, the magnitude of the characteristic viscosity increases. Hence the presence of a viscoelastic property in the solutions of polymers is associated with the presence of different types of movement of flexible macromolecules. For the varying stresses, the quantity of potential (accumulated) energy depends on to what extent the Brownian movement is associated with the varying external forces.

1. In the turbulent flow there are disturbances with a continuous spectrum of frequencies [11]. Consequently, it is possible to imagine a turbulent movement in the form of a set of Fourier components, and it is possible to use for its examination the expression (0.1) obtained by Rouse, for disturbances of a periodic nature.

We will assume that the absorption of energy of high frequency pulsations is associated mainly with the accumulation of energy in the macromolecules. The energy is accumulated in the individual macromolecule in the case of elastic deformation, and then it is obviously dissipated into heat or it is radiated owing to the formation of displacement waves in the liquid. We will therefore examine the viscosity $[\eta]_2$, which determines the extent of accumulation of elastic energy in the macromolecule. Moreover, taking into account that in the turbulent flow in the case of high Reynolds numbers the macromolecule of the polymer can interact with the turbulent disturbances of different frequencies, for the characteristic viscosity $[\eta]_2$ we will write

$$[\eta]_{2} = 0.608 \ [\eta]_{0} \sum_{\omega_{k}, p=1}^{N} \frac{\omega_{k} \lambda_{1}}{p^{2} + \omega_{k}^{2} \lambda_{1}^{2}}$$
(1.1)

where the summing is carried out over the region of frequencies ω_k of the external disturbances with which the macromolecule interacts.

The pure solvent has a viscosity η_0 , and the viscoelastic polymer introduces an additional contribution. By using expression [12] for the viscosity of strongly diluted solutions of polymers, it is possible to write

$$\eta_2 = \eta_0 (1 + c [\eta]_2) \tag{1.2}$$

From (1.2), taking into account (1.1), it is seen that the viscosity η_2 depends on the concentration of the polymer c, the limiting relaxation time λ_1 , the number of segments p, and the region of frequencies of the external disturbing field ω_k .

We will examine a turbulent flow with a lateral displacement. Under the influence of the gradient of the average velocity the macromolecules will be orientated by the major axis in the direction of the flow. However, in every real liquid the predominant orientation created by the flow is weakened by the thermal movement of the particles. Under the influence of these factors in the flow a certain more probable angle of orientation is established between the direction of the flow and the major axis of the macromolecule [12]. As a result of the predominant orientation of the macromolecules in the flow, an uneven absorption of the turbulent energy along different directions takes place. The viscosity η_2 will then be different according to the different directions in the solution of the polymer.

Since the flow of liquid around the wall in a rectangular system of coordinates will be examined, then for further flow it is convenient to introduce the viscosity of the solution in two directions into the examination: the coefficient of viscosity η_{21} in the direction of the flow and the coefficient η_{22} in the perpendicular direction. The relationship $A = \eta_{22}/\eta_{21}$ will be known as the coefficient of anisotropy of the dynamic viscosity.

We note that as a result of the almost isotropic nature of the movement of the small scale vortices (at least in the case of large Reynolds numbers) complete absorption of energy by the macromolecule will not depend on the angle of orientation φ , but will be determined by its molecular properties, at the same time that the absorption of energy in the longitudinal and lateral directions is proportional to $\sin^2 \varphi$ and $\cos^2 \varphi$ respectively. Then for the viscosities η_{21} , η_{22} it is possible to write

$$\eta_{21} = \eta_0 \left(1 + c \left[\eta \right]_2 \sin^2 \varphi \right), \quad \eta_{22} = \eta_0 \left(1 + c \left[\eta \right]_2 \cos^2 \varphi \right)$$
(1.3)

In the case of large Reynolds numbers, the angle of the predominant orientation $\varphi \approx 0$ and the coefficient of anisotropy of the dynamic viscosity assumes the form

$$A_{0} = (\eta_{22} / \eta_{21})_{\omega=0} = 1 + c [\eta]_{2}$$
(1.4)

It is seen that for each p-th time of relaxation of the macromolecule (or natural frequency) there is an outside disturbing influence of the frequency $\omega = p \lambda_1^{-1}$, which is more intensively absorbed by the macromolecule. Hence the maximum absorption of the turbulent energy takes place for a limiting time of relaxation λ_1 . The upper limit of the frequencies of the turbulent disturbances ω_2 , with which the flexible macromolecule interacts, is determined by the dimensions of the minimum (dissipated) vortices, which are present in the flow; the lower limit of frequencies ω_1 corresponds to the limiting time of relaxation λ_1 . Then for the coefficient of anisotropy of the dynamic viscosity (1.4), taking into account (1.1), we will obtain the expression

$$A_{0} = 1 + 0.608c \, [\eta]_{0} \sum_{\omega = \omega_{1}}^{\omega_{2}} \sum_{p=1}^{N} \frac{\omega \lambda_{1}}{p^{2} + \omega^{2} \lambda_{1}^{2}}$$
(1.5)

On the basis of the above, we will assume that in a turbulent flow a resonance absorption of the turbulent energy by the macromolecules of the polymers takes place. With increase of the set (spectrum) of the relaxation times (which corresponds to an increase of the number of segments p of the macromolecule). and also with increase of the region of overlapping frequencies $\omega_1-\omega_2$ the absorption of energy by the macromolecules increases. In other words, a large part of the turbulent spectrum is subjected to the damping influence of the macromolecules, as a result of which a stronger anisotropy of viscosity occurs in the flow. If the frequency of the turbulent disturbances is less than the natural frequencies of the macromolecule $\omega < p\lambda_1^{-1}$, then a significant absorption of energy of these disturbances does not take place, and the coefficient of anisotropy A=1. Hence the effect of reduction of the hydrodynamic resistance also does not take place. For a manifestation of the effect it is necessary that the maximum frequency of the turbulent disturbance is greater than the first natural frequency of the macromolecule determined by the limiting time of relaxation λ_1 . Consequently, the macromolecules interact only with the small turbulent vortices, damping the pulsations in the thin layer around the wall, which includes the viscous sublayer and the transition region. In the case of removal along the normal from the wall, the rate of the dissipative vortices is increased, and at a certain distance from the wall the interaction of the macromolecule with the vortices ceases, and hence $\omega < p\lambda_1^{-1}$. Experiments with solutions of polymers actually showed that in the core of the flow the profile of the average speed remains logarithmic [13], and the intensity of the turbulent pulsations is the same as in a pure solvent [14].

2. When examining the movement of the liquid around a solid wall, we will use a two layer system, in accordance with which the flow is divided into two regions: a thin region of purely viscous movement near the wall (viscous sublayer) and a region which does not depend on the viscosity of the fully turbulent movement (turbulent core of the flow [15]).

We will examine the flow in the viscous sublayer. In the case of Newtonian liquid (solvent) the movement in the viscous sublayer is characterized by the magnitudes of the friction stresses on the wall τ_0 and the physical properties of the liquid: the viscosity η_0 and the density ρ_0 . By using the theory of dimensions, it is possible to obtain an expression for the thickness of the viscous sublayer,

$$\delta_0 = \alpha_1 \frac{v_0}{\sqrt[4]{r_0/\rho_0}} \tag{2.1}$$



where ν_0 is the kinematic viscosity, α_1 is a certain dimensionless constant. Experiments with Newtonian liquids show that $\alpha_1 = 11.6$.

In the case of movement of a weak solution of polymer we have the following determining parameters: τ_1 is the friction stress on the wall; ν_2 and ν_1 are the kinematic viscosities in the lateral and longitudinal directions; ρ_1 is the density of the solution. It is possible to obtain by a method of dimensions the expression for the thickness of the viscous sublayer in the solution

$$\delta_1 = \alpha_2 \frac{\nu_1}{\sqrt{\tau_1/\rho_1}} f\left(\frac{\nu_2}{\nu_1}\right)$$
(2.2)

We assign the simplest form of the function

$$f\left(\frac{\mathbf{v}_2}{\mathbf{v}_1}\right) = \frac{\mathbf{v}_2}{\mathbf{v}_1} \tag{2.3}$$

Moreover, taking into account that for weak solutions of polymers and in the case of high Reynolds numbers $\tau_0 = \tau_1$ and $\nu_1 = \nu_0$, we will obtain for the relationship of the thicknesses of the viscous sublayer in the solution and the solvent

$$\frac{\delta_1}{\delta_0} = \frac{\alpha_2}{\alpha_1} \frac{\nu_2}{\nu_0} = \frac{\alpha_2}{\alpha_1} A_0$$
(2.4)

In the same way as the work [4] we will allow that $\alpha_2 = \alpha_1$. Then for the thickness of the viscous sublayer in the solutions it can be written

$$\delta_{1} = \left(1 + 0.608 c \left[\eta\right]_{0} \sum_{\omega=\omega_{1}}^{\omega_{2}} \sum_{p=1}^{N} \frac{\omega \lambda_{1}}{p^{2} + \omega^{2} \lambda_{1}^{2}}\right) \delta_{0}$$

$$(2.5)$$

It is seen that in the case of high Reynolds numbers the thickness of the viscous sublayer in the solution of polymer increases A_0 times in comparison with the solvent.

Using the relationship (2.5) it is possible to obtain the profile of the average velocity in the solution of polymer in the case of high Reynolds numbers. We will examine a plane turbulent flow in the absence of a longitudinal pressure gradient. Then the equation which describes the movement of a weak polymer solution will have the following form:

$$\eta_1 \frac{d^2 u}{dy^2} + \frac{d\tau_{11}}{dy} = 0$$
 (2.6)

where η_1 is the viscosity of the solution in the direction of movement of the liquid, $\tau_{11} = -\rho \langle u'v' \rangle$ is the turbulent stress, y is lateral to the direction of movement of the coordinate.

In the case of high Reynolds numbers the polymer molecules are oriented according to the flow and for qualitative calculations it is possible to assume that $\eta_1 = \eta_0$. Then, by integrating equation (2.6) and using the condition $\tau_{11} = 0$ on the wall, we will write

$$\eta_0 \frac{du}{dy} + \tau_{11} = \tau_1, \quad \tau_1 = \eta_0 \left(\frac{du}{dy}\right)_{y=0}$$
(2.7)

In the region which is at a distance from the wall, the term $\eta_0 du/dy$ is small in comparison with the turbulent friction τ_{11} , and equation (2.7) assumes the form

$$\tau_{11} = \tau_1 \tag{2.8}$$

In the above-mentioned region, the derivative du/dy is small, and the generation of turbulent pulsations is very slight, which leads to the formation of only large vortices of low intensity. The greatest frequency of pulsations in this region is less than the natural frequencies of the macromolecules, and as a result of this interaction of the macromolecules with the turbulent field does not take place. It is therefore possible to consider that the intensity of the pulsations of the velocity and correspondingly the mixing length l in this region is the same as in the pure solvent. This means that the stresses of the turbulent friction and the solution and the solvent will also be $\tau_{11} = \tau_{01}$. Then, using the Prandtl formula of turbulent friction [11] and integrating the equation (2.8), we will obtain

$$u = \frac{1}{\varkappa} \sqrt{\frac{\tau_1}{\rho_0}} \ln y + C$$
 (2.9)

The constant C can be determined by using the expression (2.5) for the thickness of a viscous sublayer in the solution, similar to the conclusion [15]:

$$C = u_* \left(\alpha_1 A_0 - \frac{1}{\kappa} \ln \alpha_1 A_0 \right) - \frac{1}{\kappa} u_* \ln \frac{\nu_0}{u_*}$$
(2.10)

Here $u_* = \sqrt{\tau_0/\rho_0}$ is the dynamic velocity and \varkappa is the universal constant. Substituting the value of the constant into (2.9) and taking into account that in the case of high Reynolds numbers $\tau_1 = \tau_0$, we will obtain a velocity profile in the polymer solution:

$$\frac{u}{u_{\star}} = \frac{1}{\varkappa} \ln \frac{u_{\star} y}{v_0} + \alpha_1 A_0 - \frac{1}{\varkappa} \ln \alpha_1 A_0$$
(2.11)

or

where

$$\frac{u}{u_{\star}} = 2.5 \ln \frac{u_{\star} y}{v_0} + B \tag{2.12}$$

$$B = 11.6 \left(1 + 0.608 c \left[\eta \right]_0 \sum_{\omega = \omega_1}^{\omega_2} \sum_{p=1}^{N} \frac{\omega \lambda_1}{p^2 + \omega^2 \lambda_1^2} \right) - 2.5 \ln \left[11.6 \left(1 + 0.608 c \left[\eta \right]_0 \sum_{\omega = \omega_1}^{\omega_2} \sum_{p=1}^{N} \frac{\omega \lambda_1}{p^2 + \omega^2 \lambda_1^2} \right) \right]$$

Figure 1 shows the results of calculation according to the formula (2.11) for different values of the coefficient of anisotropy. In formula (2.12) B = 5.5 corresponds to the case $A_0 = 1$. It is seen that with the increase of the coefficient A_0 displacement of the logarithmic velocity profile takes place, i.e., an increase of the discharge velocity.

We will again note factors which influence the magnitude of the coefficient of anisotropy and, correspondingly, the reduction of the resistance. Firstly, the increase of the set of the relaxation times of the macromolecules will lead to increase of the coefficient A; secondly, increase of the Reynolds number leads to decrease of the dissipative vortices in the flow and expansion of the region of the overlapping frequencies $\omega_1 - \omega_2$, which also leads to increase of the coefficient of anisotropy.

The expression (1.5) for the coefficient of anisotropy not only qualitatively reflects the interaction of the macromolecules with the turbulent field, but also yields quantitative magnitudes corresponding with concentration $c=3 \cdot 10^{-4}$ g/cm³, the magnitude of the complex $c[\eta]_0 \approx 1$. If it is assumed that the greatest frequencies of the turbulent disturbances $\omega_2 \approx 9\lambda_1^{-1}$, i.e., the frequencies of the dissipative vortices correspond to the third time of relaxation, then for the coefficient of anisotropy we will obtain $A_0 = 2.3$. In the case of this coefficient the discharge velocity is increased 1.6 times, which corresponds well with the experiments.

In conclusion it must be noted that the expression for the coefficient of anisotropy will be accurate also in the case when the agglomeration of particles takes place in the solution. Hence the times of relaxation of the enlarged particles—associates which are forming will be introduced into the formula for the coefficient.

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