СТРУКТУРА ТА ВЛАСТИВОСТІ

STRUCTURE AND PROPERTIES

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RHEOLOGICAL PROPERTIES OF OLIGOISOPRENE LIQUIDS. PRESENTATION IN THE FRAMEWORK OF THE ANGELL'S CONCEPT

The work is devoted to the study of self-organization processes in disperse systems. The most relevant aspect of such self-organization is the relationship between structure and properties in polymer composites. In this paper, we are talking about dispersion media (matrices), namely, the mechanisms of phenomena and interactions that occur during the deformation of disperse systems. These interactions depend on the properties and processes of self-organization of dispersion media and determine the properties of future polymer composites. One of the most popular dispersion media are diene oligomers (liquid rubbers). In this work, the rheology of diene oligomers with terminal hydroxyl groups (HRD) was studied in a wide range of shear rates and temperatures. It was assumed that in the case of oligoisoprene, an increase in the activation energy of viscous flow (from 46 to 95 kJ/mol) with decreasing temperature is associated with an increase in the density of the fluctuation dynamic structure with an increase in the volume content of associates of polar OH groups (i.e., nonionic micelles) with a decrease in thermal energy kT (k is the Boltzmann constant). The results of rheological studies for the first time (for nonionic liquids) were presented within the framework of the Angell's concept, from which it followed that these systems are fragile, i.e. they are very promising in terms of studying structure formation in a shear field.

Keywords: rheology, viscosity, shear deformation, activation energy, fragility, fragile liquids.

Introduction

An important trend in the modern development of composite polymer materials is the conduct of theoretical and experimental studies, which make it possible to outline new ways of obtaining materials with new unique properties. One of the effective ways to obtain such materials is the creation of particulate-filled materials. Filled systems (suspensions) of various types occupy a huge place in wildlife, technology, and everyday life. This is due to the variety of phenomena and effects in suspensions of various nature, therefore, the first topical direction in terms of creating such materials is the

study of the processes of structural self-organization of dispersion media (matrices). It is also significant that currently filled systems (suspensions) are considered as a special case of a more general class of materials called soft media. This should be understood as a continuous transition in structure and properties from suspensions of solid (hard) particles to deformable dispersed particles and to emulsions. Indeed, the rheology of suspensions and emulsions has much in common [1, 2].

When considering the mechanisms of phenomena that occur during the deformation of dispersed systems, two determining factors should be taken into account: the nature of the distribution of dispersed particles in a limited volume (their packing) and the interaction between particles [3, 4]. These interactions can be of the most diverse physical nature, and they largely depend on the properties and processes of self-organization of dispersion media (matrices). That is why, first of all, it is especially important to study the processes of structural self-organization of dispersion media (matrices), and this is an important direction in terms of solving the problem of creating new composite polymer materials.

One of the most popular dispersion media, as is known, are diene oligomers (rubbers). Diene oligomers with terminal hydroxyl groups (HRD) can be obtained with different molecular weight, that is, different content of polar hydroxyl groups. The presence of polar groups in a non-polar hydrocarbon matrix (i.e., the amphiphilic nature of the molecules of a substance) leads to structure formation due to the formation of non-ionic micelles during the aggregation of hydroxyl groups. Aggregation is carried out mainly due to hydrogen bonds. Therefore, it should be emphasized that it is precisely amphiphilicity that predetermines the possibility of the formation of various structures, i.e. it is a generator of structural self-organization [5, 6].

Modification of the original ORD can be carried out by polymer-analogous transformations of terminal hydroxyl groups. Without changing the structure of the main chain, hydroxyl groups can be converted into urethane or isocyanate groups. The terminal isocyanate groups can then be treated with alcohols of varying length and branching to give the urethane group in the chain and the terminal alkyl radical. The nature of the radical will affect the structure formation of the oligomer in

solution. If the alcohol contains a second functional group that does not react with the isocyanate one, a series can be obtained in which structure formation in the oligomeric matrix will be different.

Wide variety of structures can be obtained by copolymerizing isoprene with other monomers, both containing and without functional groups. Structure formation will be determined by the ratio of the non-polar diene monomer and the polar one. It is also possible to obtain a block copolymer. The most promising is the preparation of various oligomers (polymers) through macrodiisocyanates, since the structure of the main initial chain will not change in this case.

To implement the rheological approach to the processes of structural self-organization, we chose diene oligomers with terminal hydroxyl groups, which can be obtained with different molecular weights, i.e. different content of polar hydroxyl groups. The presence of polar groups in a nonpolar hydrocarbon matrix leads to structure formation due to the formation of micelles during the aggregation of hydroxyl groups. Aggregation is carried out mainly due to hydrogen bonds.

Experimental part

We measured the rheological characteristics of three diene oligoisoprenes obtained by radical polymerization (RDP), obtained under different conditions, but having almost the same molecular weights: 2037 (sample 1), 2212 (sample 2) and 1731 (sample 3) . The molecular weight was determined by intrinsic viscosity (solvent was benzene) at 25°C using the known formula:

$$[\eta] = 5.02 \cdot 10^{-4} \, M^{0.67} . \qquad (1)$$

The initial isoprene was modified with various alcohols: n-butanol (samples 1 and 2) and iso-butanol (sample 3).

Rheological studies were carried out in a wide range of shear rates from 10^{-1} to 10^{3} s^{-1} and temperatures from 15 to 80 °C on a PIRSP-03 rheometer.

Research results and discussion

The flow curves (viscosity η versus shear rate γ) of the studied oligoisoprenes at different temperatures are shown in Fig. 1. It follows from this figure that, in the studied range of shear rate and temperature, ORDs behave like Newtonian fluids,
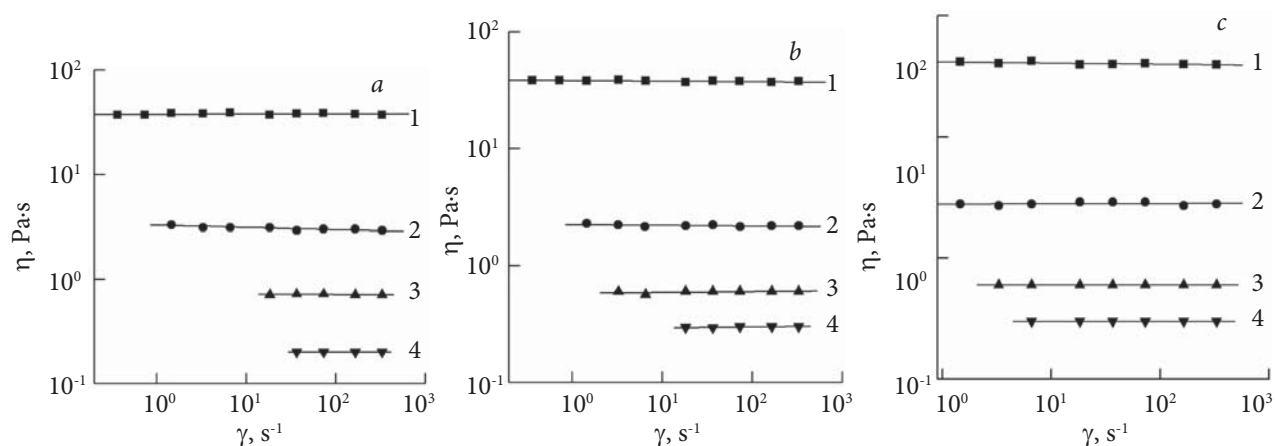
Fig. 1. Dependence of viscosity on shear rate of HPS at different temperatures: 15 (*1*), 40 (*2*), 60 (*3*), 80 (*4*, samples 2 and 3) and 85 °C (*4*, samples 1)

i.e. their viscosity does not depend on the mode of deformation. This result is consistent with literature data for other reactive oligomers.

The dependences of the shear stress τ and the effective viscosity η in the generalized coordinates $\tau - \gamma\eta_o$ and $\eta/\eta_o - \gamma\eta_o$ (η_o is the highest Newtonian viscosity) are presented in Fig. 2. Within the range of experimental error, all values of shear stress and the effective viscosity are described by single generalized curves. Possibly, this result is explained by the fact that the examined ORDs have close equivalent weights, that is, weights on one hydroxyl groups.

Despite the fact that the viscosity η of liquids, which reflects the transfer (transport) of the force impulse, viscous flow is not an activation process [7], and to describe the temperature dependence of viscosity, the Arrhenius equation is still used:

$$\eta = \eta_0 \exp\left(\frac{E_a}{RT}\right), \qquad (2)$$

where: η_o is the limiting (highest Newtonian) viscosity, E_a is the activation energy, R is the universal gas constant, and T is the temperature.

At the same time, the dependence of viscosity on temperature for room ionic liquids with an amphiphilic molecular structure (electrolytes) in the temperature range $T_g + (70 - 120 °C)$ (see, for example, [8]) is adequately described by the Vogel–Fulcher–Tammann equation [9–11]:

$$\eta = \eta_o \exp\left[\frac{B}{T - T_o}\right], \qquad (3)$$

where: η_o (Pa·s), B (K) and T_o (K) are empirical constants (fitting parameters) for a given substance.

In terms of the theory of free volume, the parameter T_o is a certain critical temperature at which the free volume disappears. The same dependence is also valid for most other liquids at lower temperatures (up to the glass transition temperature). Figure 3 shows the temperature dependences of the viscosity for the ORD. As can be seen from this figure, such a dependence for the studied liquids is non-linear in the temperature range of 15–80 °C and is satisfactorily described by relation (3). In this case, this relationship is represented by a single solid curve calculated using the following fitted parameters: log η_o = -3.481 (η_o = 0.00033 Pa s),
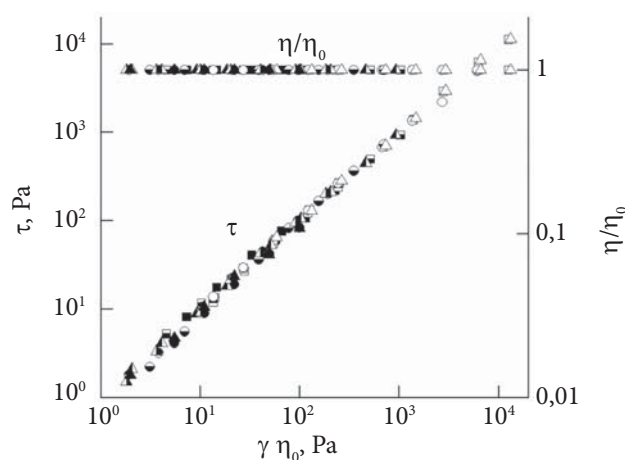
Fig. 2. Invariant dependences of the shear stress and viscosity of the ORD
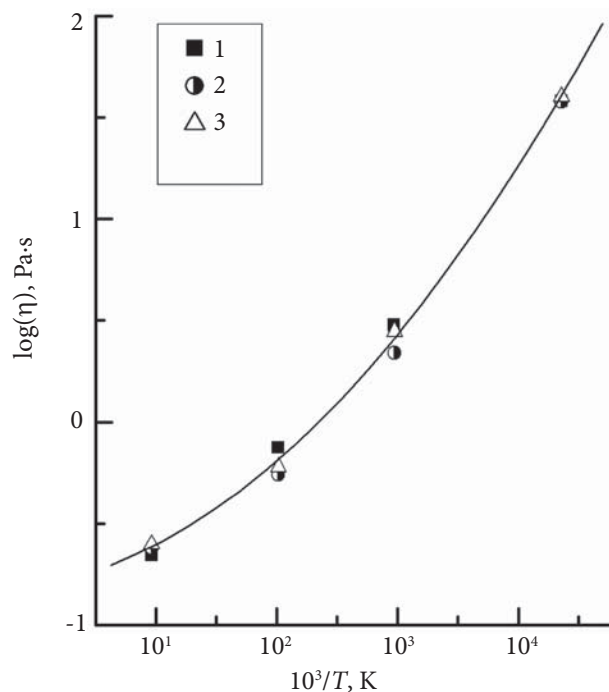
Fig. 3. Temperature dependences of the viscosity of the ORD: *1* (sample 1), *2* (sample 2), *3* (sample 3)

Fig. 4. Temperature dependence of the viscosity of the ORD: sample 1 (*1*), sample 2 (*2*) and sample 3 (*3*) in the coordinates of equation (2)

B = 995 K, T_o = 203 K (coefficient of determination R^2 = 0.9999). Using the values of these parameters and taking into account that the liquid passes into a glassy state at a temperature at which the viscosity becomes equal to 10^{12} Pa s (see below), the "viscous" glass transition temperature T_g^{η} = 217 K was calculated using equation (3).
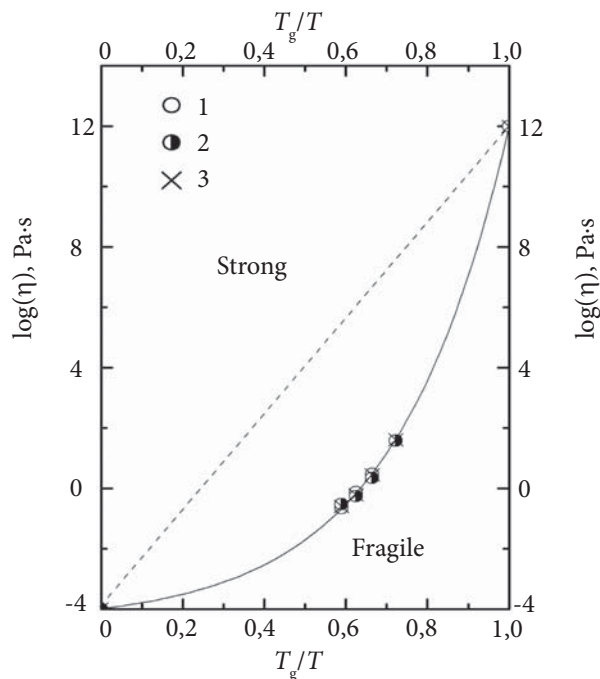
From the foregoing, it follows that the activation energy of the viscous flow of the ORD is an effective (depending on temperature) quantity. It is related to the parameters B and T_o by an equation [11, 12]:

$$E_T = RB\left(\frac{T}{T - T_0}\right)^2, \qquad (4)$$

where: R is the gas constant.

Calculation of E_T for oligoisoprenes according to equation (4) using the parameters and gave the following activation energies of the studied liquids at different temperatures: 95 (15 °C), 67 (40 °C), 54 (60 °C), 46 kJ/mol (80 °C).

It is known that the activation energy of viscous flow strongly depends on the structure of polymers [13]. So, for example, if the activation energy of the linear polyethylene melt flow is 25 kJ/mol, then for branched PE it exceeds 50 kJ/mol. Therefore, it can be assumed that in the case of oligoisoprene, the marked increase in the activation

energy with decreasing temperature is associated with an increase in the density of the fluctuation dynamic structure with an increase in the volume content of associates of polar OH groups (i.e., nonionic micelles) with a decrease in thermal energy kT (k is the Boltzmann constant).

Now it is expedient to present these rheological data in terms of the Angell concept [14]. This concept was developed for amorphous substances. It is known that the most studied characteristic of liquids is viscosity and its dependence on temperature. The equilibrium glass transition temperature is usually defined as the temperature at which the viscosity is 10^{12} Pa s [15]. Another generally accepted result of the observation is that at "infinitely" high temperatures the limiting viscosity is $\eta_o \approx 10^{-4}$ Pa·s. Therefore, in the temperature range between T → ∞ and T_g, the viscosity changes by 16 orders of magnitude. It was this data that Angell used to classify liquids by scaling and plotting their state diagram. The diagram is a semi-logarithmic dependence of viscosity on temperature, normalized to T_g, i.e. log η_o – T_g / T. Such a diagram for the investigated oligoisoprene liquids is shown in Fig. 4.

Here, the straight dotted line represents the interface between two classes of liquids: "strong" and "fragile" according to [14].

The general concept of "fragility" (instability) was first proposed by Angell [14] to classify liquids according to their dependence of viscosity versus temperature. Fragility m was determined as the limiting slope of log η versus T_g/T at the glass transition temperature T_g. This made possible to avoid measuring the temperature dependence of viscosity at the glass transition temperature. The larger the value of m, the higher the fragility and the stronger the viscosity change for the temperature increment at T_g. Thus, m can be represented by the following expression [16]:

$$m = \frac{d(\log \eta)}{d(T_g/T)^{T=T_g}} .$$ (5)

Applying this expression to the Vogel–Tammann equation with the energy parameter $D = B/T_o$ (B is the constant of this equation), leads to a simple relationship between m and D:

$$m = \frac{DT_0}{\ln 10} * \frac{T_g}{(T_g - T_0)^2} .$$ (6)

Thus, the equilibrium glass transition temperature is usually defined as the temperature at which the viscosity exceeds 10^{15} mPa·s (10^{12} Pa·s) [15, 17]. Since at the glass transition temperature the viscosity changes by many orders of magnitude within a very small temperature range, its actual value used in this approach is not so critical (decisive) for the final results, therefore, in accordance with the literature, $\eta(T_g) \equiv 10^{15}$ mPa·s is also used. And since the limiting viscosity is $\eta_o \approx 10^{-1}$ mPa·s at "infinitely" high temperatures, this leads to the conclusion that the viscosity typically spans a range of about 16 orders of magnitude between $T \to \infty$ and T_g.

For strict Arrhenius behavior (equation 2), fragility has its minimum value m_{min}, obtained by applying equation (5) to equation (2) [8]:

$$m_{min} = \log \left(\frac{\eta(T_g)}{\eta_o} \right) = 15,5 .$$ (7)

On the other hand, in the case of using the Vogel-Tammann equation (3), m_{min} can be determined from the following equation:

$$m_{min} = \frac{DT_0}{\ln 10} \frac{1}{(T_g - T_0)} .$$ (8)

And after some transformations, we get:

$$\frac{T_g}{T_0} = 1 + \frac{D}{m_{min} \ln 10}$$ (9)

and

$$m = m_{min} + \frac{\ln 10}{D} m_{min}^2 .$$ (10)

This shows the inverse proportionality between the fragility m and the energy parameter D. Taking $m_{min} \approx 15,5$, we find a simple expression by analogy to [18]:

$$m \approx 15,5 + \frac{535}{D} .$$ (11)

This is a very useful relationship between m and D, similar to the model relationship between D and the average coordination number z_o of molecules in the liquid phase (i.e., the average number of neighbors) and its variability (instability) Δz, derived by Vilgis [19]:

$$D = \frac{1}{4} \left(\frac{z_0}{\Delta z} \right)^2 .$$ (12)

Strong liquids (small fragility m and large value of the parameter D) have very low variability Δz of the average coordination number z_o. The prototypes of this class liquids are melts of glasses with a network structure, such as SiO_2, GeO_2, and B_2O_3, for which typical values of z_o are approximately 3–5. They are characterized by strong direct intermolecular interactions and high resistance to structural change upon heating (high thermal stability). Weak or fragile liquids, on the other hand, have weaker direction-independent intermolecular interactions with much higher variability Δz. Molecules form a disordered dense packing in a liquid with high fluctuations (instabilities). This results in a higher tendency towards structural change with temperature change, hence high fragility. For the lower D limit, $z_o \approx 14$ and $\Delta z \approx 4$, giving $D_{min} \approx 3.2$; this corresponds to the upper limit for fragility $m_{max} \approx 200$. Typical examples of highly fragile liquids are melts of organic glass formers such as o-terphenyl, propylene carbonate, and some polymers [8]. The transition between these classes of fluids is a nonergodic – ergodic transition by definition [14].

Thus, for the first time we apply the Angell's concept to non-ionic liquids in the entire temperature range of their state. As we expected, the liquids studied by us belong to the most interesting

temperature region of the transition of a liquid with low viscosity and its weak dependence on temperature to a region with high viscosity and a stronger dependence on temperature. Based on the obtained experimental results and calculations of some characteristic parameters of oligoisoprene liquids (η_o = 3.3 x 10^{-4} Pa s, B = 995 K, T_o = 203 K,

T_g = 213 K, T_g^{η} = 217 K, D = 4.9 , m = 128,4), we consider these liquids to be fragile liquids. Such substances are very promising in terms of studying structure formation in a shear field. The obtained results make it possible to further study controlled structure formation in fluid systems, when the shear field is the main structure-forming factor.

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РЕОЛОГІЧНІ ВЛАСТИВОСТІ ОЛІГОІЗОПРЕНОВИХ РІДИН. ПРЕДСТАВЛЕННЯ В РАМКАХ КОНЦЕПЦІЇ АНЖЕЛЛА

Робота присвячена дослідженню процесів самоорганізації у дисперсних системах. Найбільш актуальним аспектом такої самоорганізації є взаємозв›язок структури та властивостей у полімерних композитах. У цій роботі йдеться про дисперсійні середовища (матриці), а саме механізми явищ і взаємодії, що відбуваються при деформуванні дисперсних систем. Ці взаємодії залежать від властивостей та процесів самоорганізації дисперсійних середовищ і визначають властивості майбутніх полімерних композитів. Одним із найпопулярніших дисперсійних середовищ є дієнові олігомери (каучуки). Досліджено реологію дієнових олігомерів з кінцевими гідроксильними групами (ОРД) у широкому діапазоні швидкостей зсуву та температури. Припустили, що у разі олігоізопрену збільшення енергії активації в›язкої течії (від 46 до 95 кДж/моль) при зменшенні температури пов›язане зі збільшенням щільності флуктуаційної динамічної структури зі зростанням об'ємного вмісту асоціатів полярних ОН-груп (тобто неіонних міцел) при зменшенні теплової енергії kT (k – константа Больцмана). Результати реологічних досліджень вперше (для неіонних рідин) було подано у рамках концепції Анжела, звідки випливало, що ці системи належать до "крихких" ("fragile") рідин, тобто вони дуже перспективні щодо дослідження структуроутворення в зсувному полі.

Ключові слова: реологія, в'язкість, деформація зсуву, енергія активації, крихкість, крихкі рідини.