Journal of Engineering Physics and Thermophysics, Vol. 78, No. 5, 2005

RHEOLOGY OF GELATING SYSTEMS

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UDC 557.1:543.422.27

Two different types of physical gels — thermoreversible gels based on ultrahigh-molecular-weight polyethylene and thixotropic ones based on cysteine and silver nitrate — have been investigated using viscosimetric methods. Structural methods (IR and Raman spectroscopy and dynamic light scattering) have been used in interpretation of the rheological data obtained.

Gels, including polymer ones, are widely used in creation of high-strength fibers, supersorbents, and highly filled materials, in immobilization of medicines, etc. Viscosimetric methods are fundamental in identifying and characterizing the gel state of a system. In this connection, the present work seeks to use the viscosimetry method for studying thermoreversible gels based on ultrahigh-molecular-weight polyethylene (UHMWPE) and thixotropic gels based on the aqueous solutions of cysteine silver and nitrate (they differ in the structural character of physical sites). To interpret the rheological data obtained we use such direct structural methods as IR Fourier spectroscopy, low-frequency Raman spectroscopy (LAM technique), and dynamic light scattering.

Thermoreversible UHMWPE Gels. Gels represent a space network formed by polymer molecules and filled with solvent. According to De Gennes [1], all polymer gels can be subdivided into physical gels and chemical ones. The presence of the space network imparts the specific properties of a solid body (strength, holding of the shape, and others) to the gel (Fig. 1). The growing interest in physical (thermoreversible) gels (i.e., in gels whose space-network sites have a physical nature) is primarily due to the possibility of producing superstrong fibers from them (gel-technology method).

In the rheological tests of UHMWPE physical gels (Carri-Med CSL 100 rotary viscosimeter), it has been established (Fig. 2) that, with a certain critical concentration of the polymer in the solution C^*, we have a significant growth of nearly five orders of magnitude (from 10 to 10^5 Pa) in the shear modulus of the polymer system. This, in turn, points to the process of gelation and the occurrence of a continuous space network in the polymer system. It has turned out that the value of C^* substantially depends on the molecular weight of the polymer (see Table 1) and decreases with its growth.

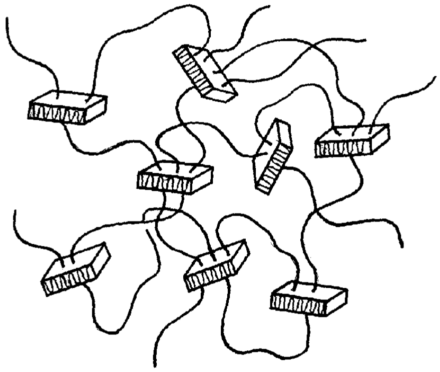
Using the IR-spectroscopy method we have been able to show (Fig. 3) [3] that the sites of the space network of a UHMWPE gel are crystalline in character. Beginning from very low concentrations, a characteristic 720/731 cm^{-1} "crystalline" doublet appears in the IR spectrum of the system. An increase in the gel temperature led to a significant reduction in the intensity of this doublet, which was attributable to the weakening of the crystalline sites and their fusion at 90°C, when the 731-cm^{-1} "crystalline" band disappeared, and the gel transformed into the state of a solution. In cooling of the solution, a reverse transition to the gel state occurred, and the IR spectrum regained its initial form.

An efficient method of studying the supermolecular structure of UHMWPE gels is low-frequency Raman spectroscopy (LAM technique) [4]. We recorded the spectra using a DILOR XY 800 triple monochromator equipped with a high-power NdYVO_4 laser (λ = 552 nm).

The position of the maximum of the LAM frequency (ν_{LAM}) is related by the formula

$$\nu_{\text{LAM}} = \frac{1}{2cL}\sqrt{\frac{E}{\rho}}$$

Tver' State University, 35 Sadovyi Lane, Tver', 170002, Russia. Translated from Inzhenerno-Fizicheskii Zhurnal, Vol. 78, No. 5, pp. 118–122, September–October, 2005. Original article submitted October 29, 2004.



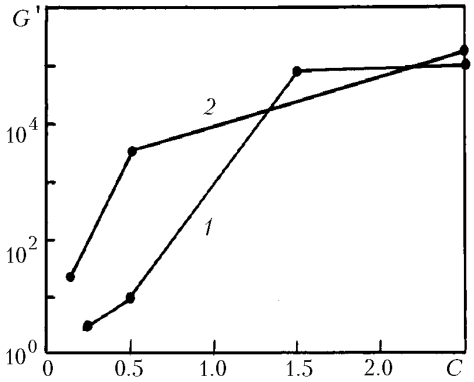
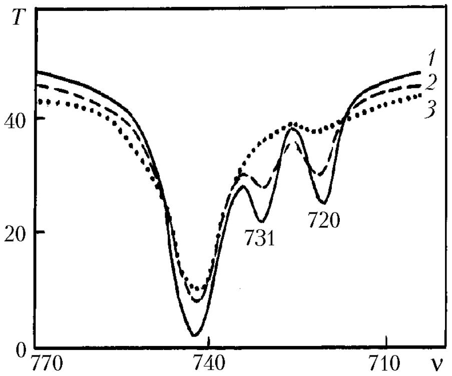


Fig. 1. Model of the ideal structure of a thermoreversible UHMWPE gel (Keller model) [2].

Fig. 2. Shear modulus vs. concentration of the UHMWPE solution in vaseline oil for $M_w = 1.7 \cdot 10^6$ (1) and $5.0 \cdot 10^6$ (2) at $t = 25°C$. G', Pa; C, %.

TABLE 1. Minimum Concentrations of UHMWPE Solutions That Contribute to the Formation of a Gel Network

$M_w \cdot 10^{-6}$	Solvent	C^*, wt. %
1.7	Vaseline oil	1.5
2.4	*n*-Xylol	0.5
2.4	Decalin	0.5
7.5	»	0.3
14.2	»	0.1



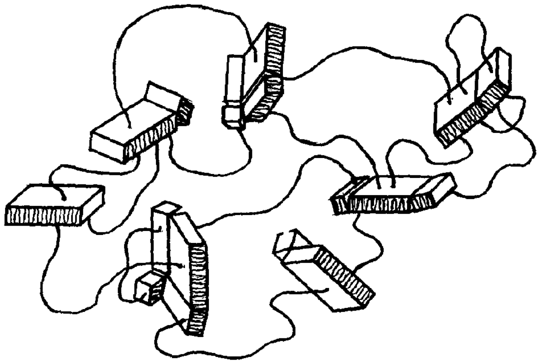


Fig. 3. IR spectra of transmission of the UHMWPE–decalin gel at different temperatures: 1) 20; 2) 80; 3) 90°C. T, %; ν, cm^{-1}.

Fig. 4. Modified structural model of the UHMWPE gel.

to the length L (straight transportions of macromolecules). In the UHMWPE gels, L represents a lamella thickness of 3 to 6 nm.

In accordance with Snyder [5], the LAM form characterizes the distribution function of straight-chain segments by length $F(L)$.

Raman data have shown [6] that crystallites of thickness from 3 to 6 nm are present in UHMWPE gels and it appreciably depends on the quality of the solvent and is virtually not related to the molecular weight in the range $1.7–14.2 \cdot 10^6$ in question and to the polymer concentration in the solution in the range 0.3–2.0%.

The function $F(L)$ substantially changes in gel → xerogel transition (i.e., when the solvent is removed from the gel). An additional narrow band appears in the Raman spectrum, and the spectrum with two bands transforms into the bimodal length-distribution function of straight-chain segments.

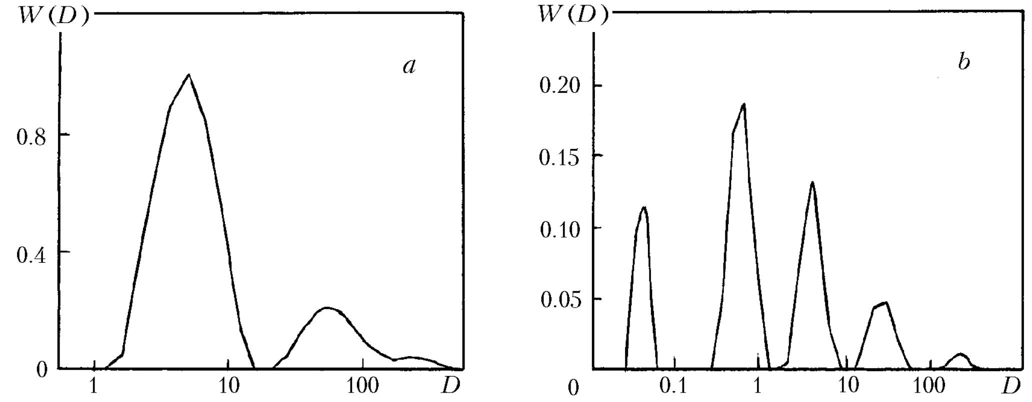


Fig. 5. Curves of distribution of the diffusion coefficient $W(D)$ for the aqueous solution with a concentration of cysteine of $2.15\cdot10^{-3}$ M and of silver nitrate of $6.23\cdot10^{-3}$ M and with a concentration of cysteine of $6.92\cdot10^{-3}$ and of silver nitrate of $19.8\cdot10^{-3}$ M (b). D, μm^2/sec.

Simple evaluations show that we have the formation of a certain number of straight-chain segments whose lengths are several times larger than the thickness or longitudinal dimension of a crystallite, i.e., a certain fraction of straight-chain segments threads and binds neighboring crystallites together.

Based on the viscosimetric, IR-spectral, and Raman data obtained, we proposed a modified Keller model for UHMWPE gels (Fig. 4) [6].

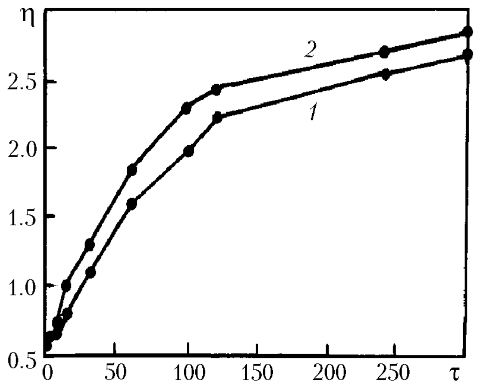
The quasimosaic structure of primary microcrystallites in the gel is an additional factor facilitating the rearrangement of the crystalline phase in transition to a highly oriented state in the process of production of high-strength fibers.

Thus, a combined use of viscosimetric and structural methods sheds light on the mechanism of gelation in the system in question.

Thixotropic Gels Based on the Aqueous Solutions of Cysteine and Silver Nitrate. Among the gelating systems, of particular interest are such systems in which structurization occurs with a low content of the dispersed phase. A search for such gelating systems and their study are important for development of the theory of self-organization in solutions and, in the practical aspect, for designing of original nanostructures. We have discovered such a system recently. A transparent stable gel with thixotropic properties was formed in pouring together of the aqueous solutions of cysteine and silver nitrate. The process of gelation in such a system was observed with a total concentration of the components of no higher than 0.06% (60 mg of the substance structurized 100 g of water) and even with a concentration of 0.02% in acidified solutions. Such gels provide a promising basis for the development of new biologically active substances and pharmaceutical preparations.

Since the molecular structure of a system determines its rheological characteristics, the thixotropic gels produced were investigated by the methods of optical spectroscopy and dynamic light scattering [7]. Study of the processes of structure formation at the stage to the gelation point by the method of dynamic light scattering has shown that clusters of different size are formed in the solution. A characteristic feature of cluster formation is the discreteness of the average size of cluster groups; the higher the concentration of the initial components, the larger the number of cluster groups formed in the solution (Fig. 5). Small clusters, judging by their hydrodynamic radii (1 to 4 nm), represent particles consisting of several silver-mercaptide molecules and silver ions. Clusters of larger size may contain hundreds or thousands of the initial molecules. According to the data of the dynamic light scattering, the average hydrodynamic radius of clusters increases with time. Upon the attainment of a certain size, the clusters interact by the surface groups to form weak donor–acceptor and hydrogen bonds [8].

The fact of aggregation of the clusters is experimentally confirmed by the decrease in the intensity of light scattering in the solution after a certain period. At the final stage of evolution of the system, a space network, i.e., a gel, is formed in it. The conclusion on the fractal structure of the clusters formed may be drawn from the fact of gelation with a low content of the reagents. Indeed, to entirely fill the space, occupied by the solvent, with the set of



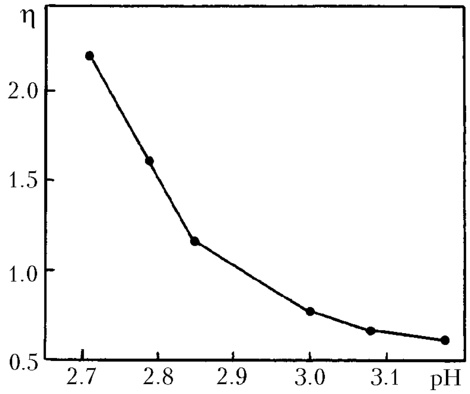


Fig. 6. Viscosity of the solution η vs. time: 1) aqueous solution of cysteine and silver nitrate; 2) the same, modified by polyvinyl pyrrolidone. τ, min.

Fig. 7. Viscosity of the gel η vs. pH.

interacting clusters and thereby to structurize the solution the weight of an individual cluster m must be expressed by the formula

$$m = m_0 (R/r_0)^{\Phi} ,$$

i.e., the cluster represents a fractal structure [9].

Testing of the system has shown that its rheological characteristics strongly depend on the regimes of strain. Thus, the gel formed may be diluted by intensely shaking the solution, but it sets to a gel again in storage; a "destructurized hole" that is healed with time is formed in the gel when a sphere rapidly falls. Also, the effective viscosity of the gel-like solution substantially changes when it is allowed to pass through the viscosimetric capillary. These regularities are probably attributed to the breaking of bonds between the clusters for certain rates of shear, whereas the cessation of mechanical action leads to a restoration of the bonds. By virtue of the above circumstances, we studied the effective viscosity of the solution only at the initial stage of evolution immediately after the mixing of the reagents. To evaluate the viscosity we used a thermostatted capillary viscosimeter and the method of a falling sphere in the solution (the density and size of the sphere were selected so as to avoid substantial disturbances in the system's structure). The effective viscosity η was determined from the formula

$$\eta = (\tau_{\text{ð}} — \tau_{\text{à}})/\tau_{\text{à}} .$$

The rheological investigations have shown (Fig. 6) a monotonic growth in the system's viscosity with time, which correlates with the increase in the cluster size, according to the data of the dynamic light scattering.

It has been shown that a number of water-soluble polymers, for example, low-molecular-weight polyvinyl pyrrolidone in small additions, increase the solution's viscosity (Fig. 6). This may be due to the fact that polymeric molecules bind different clusters together, thus contributing to the structurization of the system.

Also, it has been found that acidification of the solution with sulfuric and perchloric acids leads to a significant growth in the viscosity and to an acceleration of gelation (Fig. 7). If the system is characterized by the mechanical strength of the gel, the highest strength was observed for a mole excess of the silver ions of 1.5–2.0 times over the concentration of cysteine. Investigations in the field of the supermolecular structure and rheological properties of thixotropic gels based on the aqueous solutions of cysteine are being continued.

NOTATION

C, concentration of a polymer (weight %) or a low-molecular-weight substance (mole/liter) in the solution; C^*, critical concentration of the polymer in the solution, with which it becomes a gel; c, velocity of light, km/sec; D, diffusion coefficient, μm^2/sec; E, elastic modulus of a straight polymer chain, GPa; $F(L)$, length-distribution function of straight chains (it is normalized to unity); G', shear modulus in a polymer solution or a gel, Pa; L, length of a straight transportion of a polymer chain, nm; M_w, weight-mean or mass-mean molecular weight of the polymer, g; m, mass of an individual cluster, g; m_0, mass of an elementary structural fragment of a cluster, g; R, radius of a cluster, nm; r_0, radius of a structural fragment, nm; T, transmission of IR radiation, %; t, temperature, ^oC; $W(D)$, diffusion-coefficient distribution; it is normalized to unity; η, effective viscosity of the polymer solution, rel. units; ν, wave number, cm^{-1}; ν_{LAM}, frequency of the maximum of the longitudinal acoustic mode (LAM) in the Raman spectrum of a polymer, cm^{-1}; Φ, fractal dimension of a cluster, dimensionless quantity; ρ, density of a polymer, g/cm^3; τ_p, time of outflow or fall of a sphere in the polymer solution, sec; τ_a, time of outflow or fall of a sphere in water, sec. Subscripts: a, water (aqua); p, polymer; w, weight averaging.

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