ISSN 1560-0904, Polymer Science, Ser. B, 2006, Vol. 48, Nos. 9–10, pp. 267–270. © Pleiades Publishing, Inc., 2006.
Original Russian Text © A.M. Lotonov, N.D. Gavrilova, E.Yu. Kramarenko, E.I. Alekseeva, P.Yu. Popov, G.V. Stepanov, 2006, published in Vysokomolekulyarnye Soedineniya, Ser. B, 2006, Vol. 48, No. 10, pp. 1898–1902.

Effect of Iron Particles on Dielectric Properties of Polydimethylsiloxane near Crystallization and Glass Transition Temperatures[1]

A. M. Lotonov[a], N. D. Gavrilova[a], E. Yu. Kramarenko[a], E. I. Alekseeva[b], P. Yu. Popov[a], and G. V. Stepanov[b]

[a] *Faculty of Physics, Moscow State University, Leninskie gory, Moscow, 119992 Russia*

[b] *State Scientific Center of the Russian Federation, State Research Institute of Chemistry and Technology of Organoelement Compounds, sh. Entuziastov 38, Moscow, 111123 Russia*

e-mail: lotonov@polly.phys.msu.ru

Received December 27, 2005;
Revised Manuscript Received April 17, 2006

Abstract—The properties of a pure PDMS and PDMS containing iron particles have been studied with dielectric spectroscopy. A Novocontrol broadband dielectric spectrometer was used to record frequency and temperature dependences of the conductivity and dielectric loss factor. The mechanisms of the observed behavior are discussed.

DOI: 10.1134/S1560090406090107

INTRODUCTION

PDMS is widely applied as a material that preserves its performance ability at temperatures ranging from −35 to +200°C.

In worldwide practice, PDMS is used, in particular, for the production of light-reflective, buffer, filter, and protective coatings for optical fibers. The structure of PDMS was studied by the methods of X-ray analysis at low temperatures and by the DTA method at high temperatures [1–3]. As was shown, the above polymers experience phase transitions between amorphous and crystalline phases at temperatures below ~–60°C. Temperatures below the crystallization temperature of PDMS correspond to the glass transition region. On passing through the temperature region of crystallization (from –60 to –90°C), one can observe hysteresis, which is associated with high relaxation times of the crystallization process.

It was found that the incorporation of iron nanoparticles and microparticles (2–10 nm) into PDMS exerts a marked effect on its elastic properties and can induce the development of a tremendous magnetically strained phenomenon under the action of external magnetic fields [4, 5].

[1] This work was supported by NATO Program "Science for Peace," grant SfP-977998.

The test samples under study were soft dark-colored rods based on PDMS containing 10–30 wt % iron particles. In this study, we examined the effect of a magnetic filler on the dielectric characteristics of PDMS.

EXPERIMENTAL

Relaxation methods and, in particular, the method of low-frequency dielectric spectroscopy (the frequency region from very low- to radio frequency) offer substantial advantages for studying the polymer structure and its phase transition behavior in a wide temperature range. The methods of dielectric characterization are based on the measurements of complex permittivity $\varepsilon^* = \varepsilon' + j\varepsilon''$, where ε' is estimated through capacity $C = \varepsilon' S/4\pi d$ (S is the area of the flat sample, and d is the thickness of a plate or film) and $\varepsilon'' = \varepsilon' \tan\delta$ is expressed through the dielectric loss factor $\tan\delta$. Conductivity is estimated from ε'' through the following formula: $\sigma = \varepsilon''\varepsilon_0\omega$ (ω is the cyclic frequency, and $\varepsilon_0 = 8.85 \times 10^{-12}$ F/m is the electric constant). Dielectric characteristics were recorded on a Novocontrol broadband dielectric spectrometer (Germany) with automatic recording and digital data processing.

In the experiments, the electric field frequency was varied from 10^{-1} to 10^6 Hz; temperatures ranged from −140 to +60°C. At each point, temperature was maintained to within ±0.01°C.

RESULTS AND DISCUSSION

Figure 1 shows the 3D plots illustrating the permittivity of the pure PDMS and PDMS with admixtures, where temperature and frequency are variable parameters. The measurements of temperature dependences of ε', $\tan\delta$, and σ of PDMS in such a wide frequency range were performed for the first time. Comparing the temperature dependences of ε' at different frequencies during heating and cooling runs, one can observe the dielectric hysteresis with abnormal regions at about –40°C and in the temperature interval from –70 to –100°C.

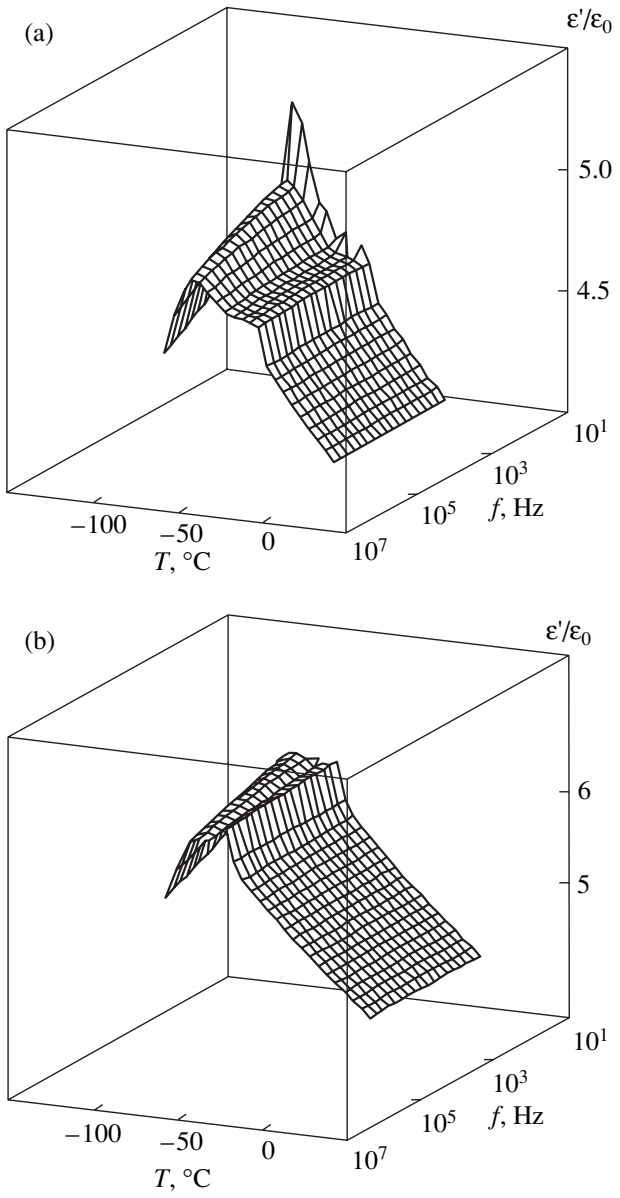

Fig. 1. Temperature–frequency dependence of permittivity for (a) the pure PDMS and (b) PDMS containing 10 wt % iron particles. The measurements were performed during cooling runs.

At all frequencies, the samples containing 10% magnetic particles show a single diffuse abnormal region of ε' at temperatures ranging from –70 to –100°C (Fig. 1b). Other samples containing 10–30% iron particles demonstrate a smeared maximum of ε' in the same temperature interval (Fig. 2). In this case, with an increase in the iron content in the samples, the absolute values of ε' tend to increase over the entire temperature range. As compared with the pure PDMS, owing to the introduction of 30% iron particles, ε' increases by a factor of 3–4. For the sample containing 30% iron particles, $\tan\delta$ increases by a factor of 20 at 100 Hz and by a factor of 5–6 at 10^5 Hz (Fig. 3). In this case, the maximum of $\tan\delta$ is observed at the same frequency regardless of the temperature. This fact suggests a weakly pronounced relaxation.

Complex systems of solid-state oscillation continua should possess a wide spectrum of connected oscillators. This is the reason behind the fractal nature of dielectric response, especially in the region of very low and audio frequencies. The fractal approach is widely used for studying the conductivity and nucleation at phase transitions in crystals and polymers [6, 7].

The frequency dependence of specific conductivity for PDMS is described by a power law. This observation is confirmed by virtually linear changes in the above parameters in the logarithmic plots (Fig. 4). Figure 4 presents the family of the frequency dependences of conductivity σ for the sample containing 30% iron particles at different temperatures. All plots show that the specific conductivity σ increases with an increase in frequency. At different frequencies, the values of the specific conductivity σ at –40 and –100°C differ by more than an order of magnitude.

The linear character of the $\log\sigma - \log\omega$ dependence attests to the fractal relations in a wide range of frequencies and temperatures beyond crystallization and

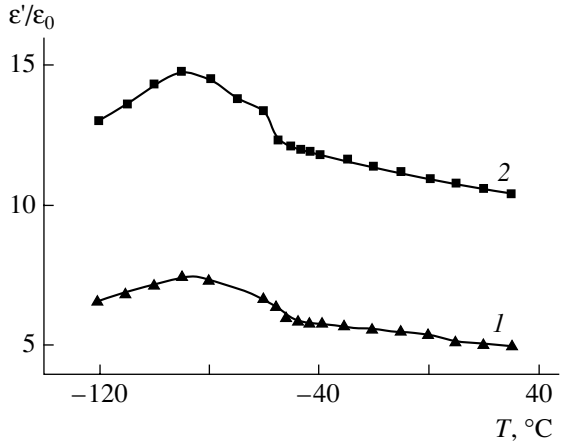

Fig. 2. Temperature dependence of permittivity at a frequency of 1.34 kHz for the PDMS sample containing (*1*) 16 and (*2*) 30 wt % iron particles.

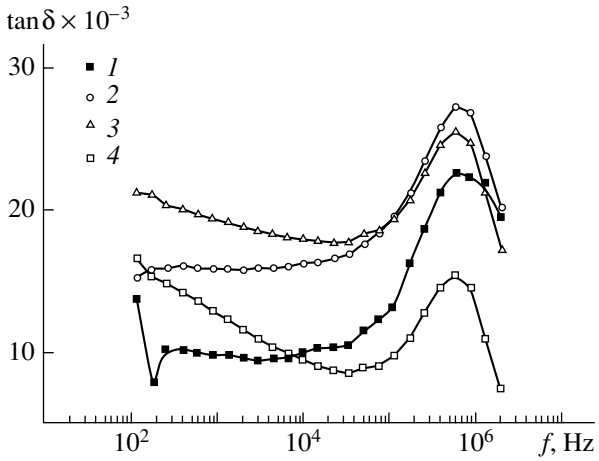

Fig. 3. Frequency dependence of the dielectric loss factor for the PDMS sample containing 30% iron particles at (*1*) –80, (*2*) –90, (*3*) –100, and (*4*) –120°C.

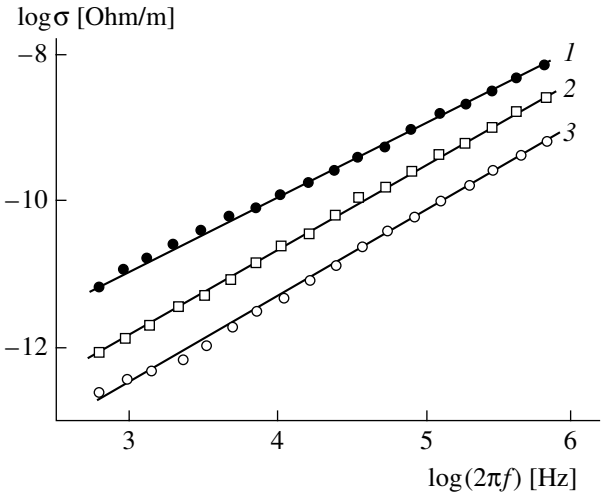

Fig. 4. Frequency dependence of conductivity for the pure PDMS at (*1*) –40, (*2*) –70, and (*3*) –100°C.

glass-transition temperature intervals. The slopes of linear s ($\sigma \sim \omega^s$) dependences are shown in Fig. 5. As is seen, the parameter s shows abnormal behavior at about –55°C and drastically decreases at temperatures below –85°C. At maximum, the s value exceeds 1.2. This fact reflects the cooperative interaction upon hop diffusion [8]. Conductivity at a frequency of 1–5 MHz also shows abnormal behavior, which is related to the fact that, at very high frequencies, heavy carriers are excluded from hop transport.

From the $\log(\sigma T) = f(1/T)$ dependence, activation energies are calculated to be 0.15–0.19 eV; as frequency is increased from 1.14 to 100 kHz, the above values decrease slightly. The above results lead us to conclude that carriers are protons, because the values of activation energy appear to be comparable with the activation energy of proton overbarrier hops in a hydrogen bond.

Let us analyze the temperature–frequency dependences of ε' and tanδ at positive temperatures (Fig. 6). At 34–37°C and 39–41°C (above 10 kHz), one can observe the smeared maxima of both ε' and tanδ and their temperature interval coincides with the temperature interval of the abnormal behavior of ε'(T) observed for some substances containing hydrogen bonds: crystals of triglycine sulfate [9]; Rochelle salt (prior to melting) [10]; triglycine tellurate [11]; vinylidene fluoride–trifluoroethylene copolymer (partial ordering of the amorphous phase) [12]; and lithium, yttrium, and holmium formates [13].

The abnormal behavior observed at about 40°C can be provided by structural rearrangements that are associated with the overoccupation of proton energy levels at hydrogen bonds or breakdown of bifurcate hydrogen bonds if they are involved in the framework of heavy metals [11].

One can expect the occurrence of short-scale relaxation processes provided by the rotation of atomic groups about different axes. The PDMS chain contains two such groups CH_3. The rotational degrees of freedom related to side groups are usually referred to as γ processes.

For PDMS, the temperature of the relaxation transition of α-methyl groups attached to a polymer chain is –100 ± 10°C and the activation energy is 0.15–0.20 eV for the pure and filled PDMSs. Note that similar values of the relaxation transition temperature (≅ –110°C) and

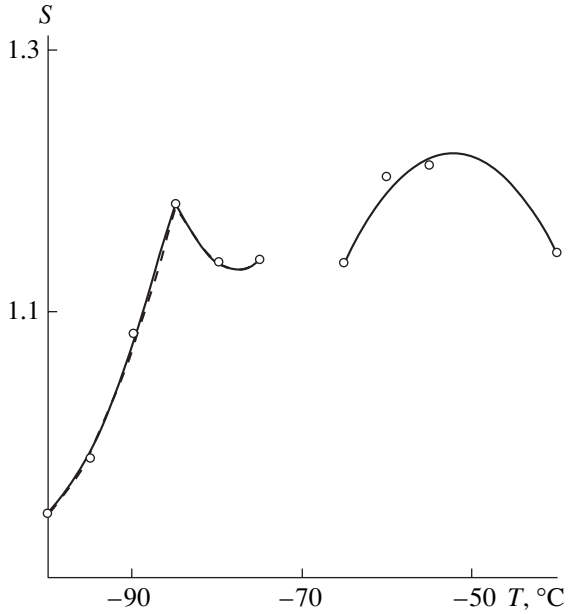

Fig. 5. Temperature dependence of the power index for the fractal power law $\sigma \sim \omega^s$ (according to the data presented in Fig. 4).

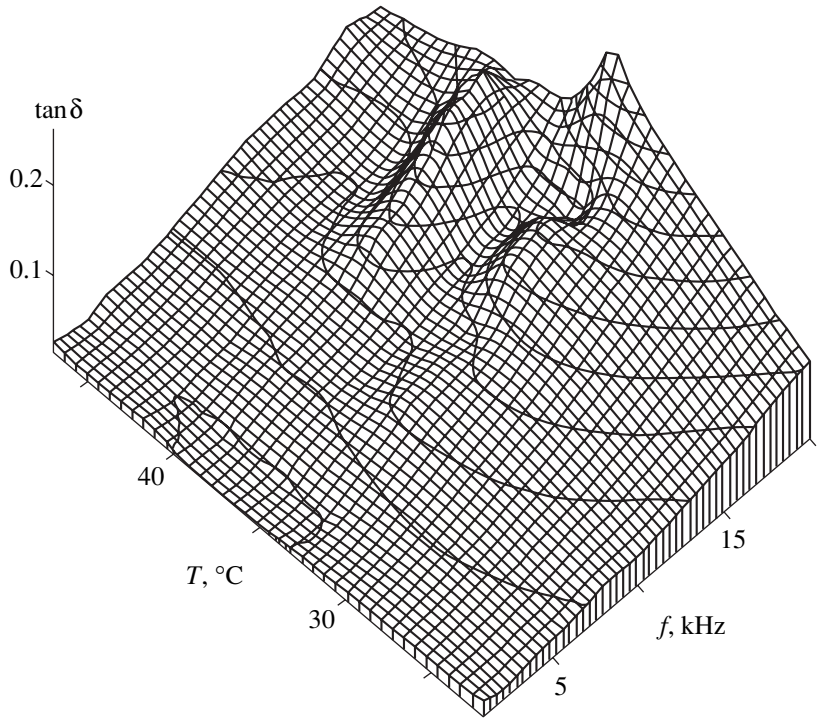

Fig. 6. Temperature–frequency dependence of dielectric loss factor for the pure PDMS.

the activation energy (~0.20 eV) were obtained for the α-methyl groups in PMMA [14] that are directly attached to the polymer chain.

REFERENCES

1. E. I. Alekseeva, A. I. Gusev, Yu. S. Milyavskii, et al., Preprint No. 8, IRE AN SSSR (Inst. of Radioelectronics, USSR Academy of Sciences, Moscow, 1985), p. 415.
2. E. I. Alekseeva, V. B. Kravchenko, Yu. S. Milyavskii, et al., Preprint No. 8, IRE AN SSSR (Inst. of Radioelectronics, USSR Academy of Sciences, Moscow, 1985), p. 426.
3. L. M. Averina, V. B. Kravchenko, Yu. S. Milyavskii, et al., Zh. Tekh. Fiz. **55**, 1605 (1985).
4. L. V. Nikitin, L. S. Mironova, G. V. Stepanov, and A. N. Samus', Polymer Science, Ser. A **43**, 443 (2001) [Vysokomol. Soedin., Ser. A **43**, 698 (2001)].
5. S. S. Abramchuk, D. A. Grishin, E. Yu. Kramarenko, et al., Polymer Science, Ser. A **48**, 138 (2006) [Vysokomol. Soedin., Ser. A **48**, 245 (2006)].
6. A. K. Jonscher, J. Mater. Sci. **16**, 2037 (1981).
7. N. D. Gavrilova, A. A. Zheleznyak, A. M. Lotonov, and V. K. Novik, Vestn. Mosk. Univ., Ser. 3: Fiz., Astron., No. 3, 61 (2001).
8. Z. D. Deng and K. A. Mauritz, Macromolecules **25**, 2369 (1992).
9. L. G. Bradulina, A. M. Lotonov, and N. D. Gavrilova, Neorg. Mater. **37**, 607 (2001).
10. I. A. Malyshkina, Neorg. Mater. **38**, 468 (2002).
11. N. D. Gavrilova, A. M. Lotonov, and I. N. Medvedev, Neorg. Mater. **29**, 403 (1993).
12. K. A. Verkhovskaya, N. D. Gavrilova, V. K. Novik, et al., Vestn. Mosk. Univ., Ser. 3: Fiz., Astron., No. 3, 41 (1997).
13. G. L. Slabkaya, A. M. Lotonov, and N. D. Gavrilova, Neorg. Mater. **40**, 323 (2004).
14. G. M. Bartenev and A. G. Barteneva, *Relaxation Properties of Polymers* (Khimiya, Moscow, 1992) [in Russian].