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DETERMINATION OF THE GLASS TRANSITION TEMPERATURE IN POLYMER COMPOSITES AND SYSTEMS

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ОПРЕДЕЛЕНИЕ ТЕМПЕРАТУРЫ СТЕКЛОВАНИЯ ПОЛИМЕРНЫХ КОМПОЗИЦИОННЫХ МАТЕРИАЛОВ И СИСТЕМ

The results of the study of the frequency dependence of the dielectric constant in a wide range of temperature in tetrazole polymers are presented. It has been found that the temperature at which the dielectric constant changes sharply in all systems is the glass transition temperature.

TETRAZOLE POLYMERS, GLASS TRANSITION TEMPERATURE, DIELECTRIC RELAXATION.

Представлены результаты исследования частотной зависимости диэлектрической проницаемости в широком интервале температур в тетразолсодержащих полимерах. Обнаружено, что температура, при которой происходит смена характера зависимости обратной величины диэлектрической проницаемости от температуры, для всех изученных нами систем совпадает с их температурой стеклования.

ТЕТРАЗОЛСОДЕРЖАЩИЕ ПОЛИМЕРЫ, ТЕМПЕРАТУРА СТЕКЛОВАНИЯ, ДИЭЛЕКТРИЧЕСКАЯ РЕЛАКСАЦИЯ.

The physical properties of the polymer in glass state are significantly different from the same properties in rubbery state. The conventional boundary between these two states is the glass transition temperature T_g , which is the most important characteristic of amorphous polymers introduced by Ubberrichter. Under the glass transition temperature we mean the temperature under which the viscosity of the polymer is no less than 10^{12} Pa·s. This temperature is also understood as the temperature below which the motion of chain segments of polymer molecules is «frozen» [1].

There are many methods of experimental determination of glass transition temperature. The measurement of mechanical and dielectric loss is among them. The use of the dielectric method can be sometimes difficult because measuring the temperature-frequency dependence of the dielectric loss in low-frequency region can cause certain problems. That is why

it is important to expand the possibilities of dielectric spectroscopy method to determine T_g . This paper suggests using the temperature dependence of the inverse value of the dielectric permeability ($1/\epsilon_1$) as a criterion to estimate the value of T_g .

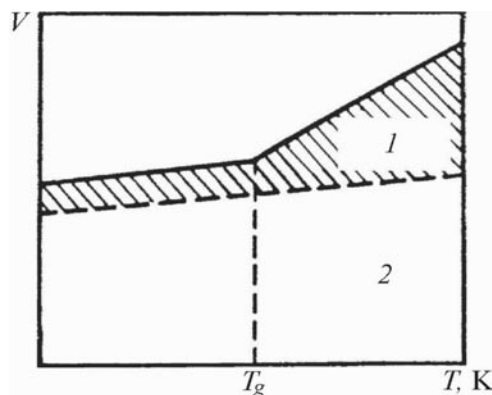


Fig. 1. The temperature dependence of the specific volume of amorphous solids

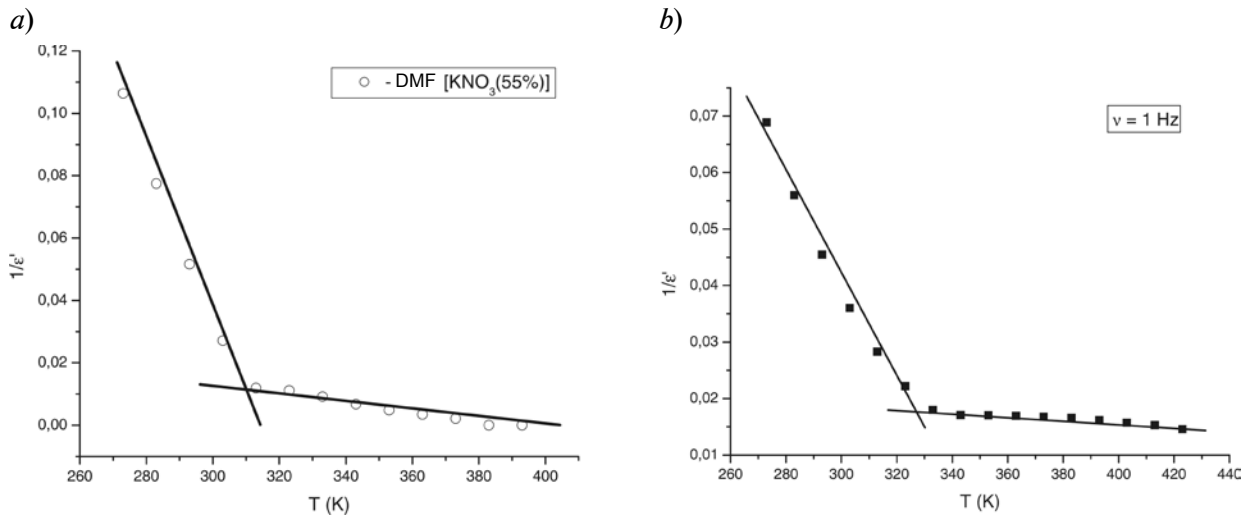


Fig. 2. Temperature dependences of the inverse of the dielectric constant of the sample #1 (a) and #3 (b)

According to the model suggested by the authors [2], the temperature dependence of the inverse value of dielectric permeability has a linear character. It is experimentally obtained that for many polymer systems in the dependence $(1/\varepsilon_1) = f(T)$ there are at least two regions which correspond to the system being in glass and rubbery state respectively. It means that on condition of certain critical temperature, there is a change in the character of the temperature dependence of $(1/\varepsilon_1)$. The same temperature dependence is also observed for

polymer density ($\rho \sim 1/V$) (Fig. 1). That is why the temperature dependence $1/\varepsilon'$ can be used to determine glass transition range.

The dielectric measurements were carried out using an impedance analyzer ALPHA-N Analyzer from Novocontrol Technologies, covering a frequency range from 0.1 Hz to 1 MHz and working at different increasing temperature steps from 173 up to 523 K. A drop of the polymer mixture with two silica spacers of 50 μm thickness was placed between two gold plated electrodes (20 mm of dia-

A comparison between experimental data of this work and from literature

Number of sample	Compound composition (Polymer-plasticizer- [modifier]- hardener)	T_g ($1/\varepsilon' = f(T)$)	T_g from literature
		K	
1	(MPVT-A) (DMF) [KNO ₃ (55%)] (TON-2)	310	310 [3]
2	(MPVT-A) (DMF) [KCl(70%)] (TON-2)	326	326 [4]
3	(MPVT-A) (DMFA) (MeO-TON)	328	329 [5]
4	(MPVT-A) (DMFA) (TON-2)	324	325 [5]
5	(MPVT-A) (DMFA) (Dur-TON)	327	—

(TON-2) – 2,4,6-triethylbenzene-1,3-dicyanobenzene-di-N-oxide

(MeO-TON) – 3,6-methoxy-1,4-dicyanobenzene-di-N-oxide

(Dur-TON) – 2,3,5,6-methyl-1,4-dicyanobenzene-di-N-oxide

(DMFA) – dimethylformamide C₃H₇NO

(DMF) – dimethylphthalate C₁₀H₁₀O₄

meter) of a parallel plate capacitor. The sample cell was mounted on a cryostat and exposed to a heated gas stream being evaporated from a liquid nitrogen Dewar. The temperature control was performed within ± 0.5 K, using the Novocontrol Cryosystem. Novocontrol GmbH supplied all these modules.

For polymer composite materials based on poly-N-methylalil-5-vinyltetrazol (MPVT-A) with the modifier KNO_3 (55 %), the glass transition temperature is $T_g = 310$ K (Fig. 2, a) (the critical temperature is 310 K); for MeO-TON, the glass transition temperature is $T_g = 328$ K (Fig. 2, b) (the critical temperature is 329 K). The experimental results we obtained can allow us to conclude that for a broad class of systems this critical temperature coincides with the glass transition temperature (see Table).

The first region is characterized by the abrupt

decrease of $1/\varepsilon'$. Such significant changes of the temperature dependence of the dielectric parameters are connected with the main thermal transition from glass state to rubber state (or vice versa). The second region corresponds to rubbery state. The analysis of the temperature dependence shows that this region is characterized by the smooth decrease of the value $1/\varepsilon'$ and the curve flattens out to the steady plateau.

The temperature under which there is a change in the character of the temperature dependence of the inverse value of dielectric permeability for all the systems we studied coincides with their glass transition temperature.

Thus, the measurement of $1/\varepsilon_1$ temperature dependence can be used as a new alternative method to determine T_g for polymer systems and composites.

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