Dielectric spectroscopy of polymer nanocomposites based on tetrazol and KNO$_3$

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Abstract. For tetrazole polymers by dielectric spectroscopy the existence of three relaxation processes in the temperature range $T=273$–$423$ K is revealed, the values of relaxation and structural parameters are determined: activation energy $E_A$ and glass transition temperature $T_g$.

1. Introduction
Compounds based on tetrazole complex differ with complex of unique properties: low sensitivity to shock and friction, high thermal stability, low toxicity and great flatulence. These qualities determine the prospects of the use of polymers and copolymers based on vinyltetrazoles as components of condensed energy-systems for aerospace industry. Currently, there is information about the structure and physico-mechanical properties of this class of materials, but to date there had been no research of the electrical and dielectric properties and their relation to the structural features.

2. Experimental details
The detail analysis of influence of concentration of the modifier on relaxational properties of polymer composites based on tetrazole was aim of this work. The subject of research was poly-N-methylallyl-5-vinyl tetrazole (MPVT-A) having the following chemical structure:

\[
\text{\begin{tikzpicture}
\node at (0,0) (A) {\text{-CH$_2$-CH-}};
\node at (1,0) (B) {\text{-CH$_2$-CH-}};
\node at (2,0) (C) {\text{-CH$_2$-CH-}};
\node at (3,0) (D) {\text{-CH$_2$-CH-}};
\node at (4,0) (E) {\text{-CH$_2$-CH-}};
\node at (5,0) (F) {\text{CH-\(\Phi\)-CH$_2$}};
\node at (1,-0.5) (G) {\text{CN}};
\node at (2,-0.5) (H) {\text{N}};
\node at (3,-0.5) (I) {\text{N}};
\node at (4,-0.5) (J) {\text{N}};
\node at (5,-0.5) (K) {\text{N}};
\end{tikzpicture}}
\]

where $k = 5\%$, $n = 1\%$, $m = 90\%$, $z = 4\%$.

Dimethyl phthalate was used as plastifier.

As modifiers were used KNO$_3$ (55\%) and KNO$_3$ (70\%), which accounted for 65\% of the weight of the polymeric binder. The hardening of the samples was carried out by low-temperature hardening agent to di-N-oxide-1,3-dinitro-2,4,6-trietilenbenzol (TON-2).

The DSC (differential scanning calorimetry) curves of samples belonging to these three samples were recorded to detect the glass transition temperature $T_g$ (Fig. 1).
Measurements of dielectric spectra were performed on installation of "Concept 41" of the NOVOCONTROL Technologies GmbH Co, which consists of a frequency analyzer impedance measuring cell, temperature control system, automatic data collection system and Dewar vessel with system of evaporation and submission of gaseous nitrogen.

3. Result discussion

There have been revealed the existence of three relaxation processes in the temperature range \( T=273-423 \) K (\( \alpha, \beta \) and \( \gamma \)-processes), there have been determined the values of relaxation and structural parameters: the activation energy \( E_A \) (Fig. 2) and the glass transition temperature \( T_g \) (by the method, proposed in [1]) (Fig. 3) (See Table 1).

As can be seen from the table, the concentration change of KNO\(_3\) changes the value of the activation energy of \( \beta \)-process, whereas for \( \gamma \)-process the value of this parameter remains unchanged. With the increase of filler concentration, a slight decrease in the glass transition temperature occurs (associated with the transition to a glassy state). Since the position of the glass transition temperature is associated with the occurrence of macromolecular chains mobility, in such a case, the findings indicate that the formation of the adsorptive bonds between polymer...
Table 1. Glass transition temperature and activation energy of the nanocomposite: tetrazol + KNO$_3$.

| Concentration of KNO$_3$ (%) | $T_g$, K | Activation energy $\beta$, eV | Activation energy $\gamma$, eV |
|-----------------------------|----------|-------------------------------|-------------------------------|
| 70                          | 306      | 1.22                          | 0.39                          |
| 55                          | 312      | 1.06                          | 0.39                          |

molecules and the surface, as well as conformational changes at the phase boundary of polymer - filler, result in changes of the relaxation polymer properties [2]. Raising of the glass transition temperature indicates a noticeable restriction of chains mobility, equivalent to their flexibility decrease due to the additional bonds formation, or changes in the molecular conformation. This restriction of mobility (and hence, the raised glass transition temperature) should be the greater, the greater the number of polymer molecules is involved in the interaction with the surface.

A common feature to all the amorphous semiconductors is that the ac conductivity $\sigma_{ac}(\omega)$ increases with frequency according to

$$\sigma_{ac}(\omega) = \sigma_i(\omega) - \sigma_{dc} = A\omega^s,$$  \hspace{1cm} (1)

where $\omega$ is the angular frequency, $s$ is the frequency exponent and $A$ is a constant independent of frequency [3]. Fig. 4 and Fig. 5 shows the frequency dependence of ac conductivity $\sigma_{ac}(\omega)$ for samples with different KNO$_3$ concentration. It is clear from the figure that $\sigma_{ac}(\omega)$ increases linearly with frequency. The same behavior of the frequency dependence of $\sigma_{ac}(\omega)$ was obtained for all the investigated films. Values of the frequency exponent $s$ were obtained from the slopes of these lines of the figure ($s=0.75-0.85$).

Figure 4. Frequency dependence of conductivity $\sigma_{ac}(\omega)$ for sample KNO$_3$(55%).

Figure 5. Frequency dependence of conductivity $\sigma_{ac}(\omega)$ for sample KNO$_3$(70%).

According to correlated barrier hopping (CBH) model, values of the frequency exponent $s$ is ranged from 0.7 to 1 at room temperature and is found to decrease with increasing temperature. This is in good agreement with the obtained results, so the frequency dependence of $\sigma_{ac}(\omega)$ can be explained in terms of CBH model. The expression for $s$ derived on the basis of this model is given by Elliott [4,5] as

$$s = 1 - \left(\frac{6 kT}{E_g}\right),$$  \hspace{1cm} (2)
where $k$ is the Boltzmann constant, $T$ is the temperature in Kelvin and $E_g$ is the optical band gap of the material.

According to the Austin-Mott formula [6], based on CBH model, ac conductivity $\sigma_{ac}(\omega)$ can be explained in terms of the hopping of electrons between pairs of localized states at the Fermi level. $\sigma_{ac}(\omega)$ is related to the density of states $N(E_F)$ at the Fermi level by

$$\sigma_{ac}(\omega) = (\pi/3)[N(E_F)]^{2}kTe^{2}\alpha^{-5}[\ln(\nu_{ph}/\omega)]^{4}, \quad (3)$$

where $\alpha$ is the exponential decay parameter of localized states wave functions, and $\nu_{ph}$ is the phonon frequency. By assuming $\nu_{ph} = 10^{12}$Hz and $\alpha^{-1} = 10\text{Å}[7]$, the density of states is calculated and it is found that $N(E_F)$ has values of the order $10^{22}$eV$^{-1}$ cm$^{-3}$, which increases with frequency and temperature.

The temperature dependence $\sigma_{ac}(\omega)$ at different frequencies for used composites is shown in Fig. 6.

It is clear from the figure that $\sigma_{ac}(\omega)$ decreases linearly with the reciprocal of absolute temperature in two temperature regions. This suggested that the ac conductivity is a thermally activated process from different localized states in the gap or its tails. The activation energy of conduction ($E_a$) is calculated at different frequencies from the slopes of lines of Fig. 5 using the well-known equation $\sigma = \sigma_0 \exp(E_a/kT)$. For 55% concentration the values ($E_a$): ($E_{a1}$) = 1.54 eV, ($E_{a2}$) = 0.41 eV, for 70% concentration the values ($E_a$): ($E_{a1}$) = 1.41 eV, ($E_{a2}$) = 0.40 eV.

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