

# Determination of relaxation characteristics complex for penton — AgI matrix-disperse system

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It has been shown that calorimetric method of analysis of relaxation processes can be used to matrix-disperse systems which includes polymers able to crystallization, namely, high-molecular polyesters and disperse fillers. Using penton — AgI system as an example, the analysis of composites  $dC_p/dT$  multiplet dependence, whose shape is caused by structure-active silver iodide particles occurrence, have been carried out in glass transition temperature range, and the relaxation characteristics complex of composites have been determined.

Показано, что калориметрический метод анализа релаксационных процессов может быть применен и к матрично-дисперсным системам, в состав которых входят полимеры, способные к кристаллизации, а именно высокомолекулярные полиэферы и дисперсные наполнители. На примере системы пентапласт — AgI проведен анализ мультиплетной зависимости  $dC_p/dT$  композитов в температурном интервале стеклования, форма которой вызвана присутствием структурно-активных частиц йодида серебра, и определен комплекс их релаксационных характеристик.

## 1. Introduction

Current development of science and technology including space area requires continuous improvement and miniaturization of the equipment used. In this regard, there is a need to study and use new structural materials with completely new properties. Prominent representatives of such materials, which are intensively studied and widely used, are solid electrolytes — superionic conductors. Among solid electrolytes special attention attracts Silver Iodide — AgI, which in addition to the phase transition insulator — superionic type is characterized by abnormal dilatometer behavior that leads to hopping of its volume.

With all the complex of positive characteristics inherent to solid electrolytes their

operational characteristics, in the most cases, do not allow to use them in difficult weather conditions and corrosive environments. In this regard, it is urgent to develop new materials that would be resistant to the external environment and not lose superionic conductivity properties. These materials can be polymeric composite materials, in which solid electrolytes are used as particulate filler, and chemically resistant polymers used as polymer matrixes.

Thus, special interest exists to study of matrix-disperse systems (MDS) containing dispersed fillers that are characterized by phase instability in neighborhood of phase transitions temperatures of the polymer matrix. This feature of fillers allows to reveal and assess not only an influence of the dispersed component of MDS on the properties

and structure of the polymer matrix, but also an influence of the polymer on the filler, which can be regarded as a qualitative and quantitative assessment of such systems components interaction.

As a polymer matrix in investigation of the systems with active interaction of components it is advisable to use polymers that are capable of crystallization and contain polar groups. Good representative of such polymers can be macromolecular polyester — penton. Such composite systems are advantageously distinguished by the presence of two phase instabilities in the investigated temperature interval melting and glass transition of the amorphous component of the polymer matrix, which in the future allow to get a full and deep information about the interaction of such systems components.

An analysis of changes of polymer materials specific heat capacity allows to receive the information about molecules heat motion and intermolecular interaction. It is the most easily from the results of heat capacity measurements to determine the melting temperature, specific melting heat, beginning  $T_1$  and ending  $T_2$  temperatures of glass transition relaxation process, and the most probable transition temperature  $T_g$ , these are parameters of the processes which are characterized by simultaneous sharing a number of macromolecules and related with polymer molecules cooperative movement.

In spite of somewhat lower accuracy of determination of glass transition process parameters from the results of calorimetric investigations comparing with other methods, such measurements advantageously differ by the fact that, besides thermodynamics aspects they allow to analyze the relaxation character of the molecular processes. The above mentioned allows to determine the polymer materials relaxation characteristics complex (RCC) using the data of heat-physical researches without additional measurements by the methods of mechanical, dielectric, nuclear magnetic relaxations.

In spite of the method advantage there is insignificant amount of works dedicated to determination of RCC: activation energy of  $\alpha$ -relaxation process  $U_\alpha$ , pre-exponential factor  $B_\alpha$ , glass transition temperature  $T_\alpha$ , half-width of relaxation transition temperature interval  $C_0$ , glass transition process cooperativity level  $W$ , segments cooperative activation energy of  $\alpha$ -relaxation process  $U_{\alpha \text{ coop}}$ .

The earlier works [1, 2] have determined the parameters of glass transition process and RCC of a number of polymer materials by analysis of temperature dependences of the specific heat capacity.

However, methods suggested in those papers can be used only for the polymer systems, whose structure does not take of different modification influences. If we have the plasticizers, curing agents and disperse fillers in the system composition then glass transition process acquires more complicated character and the theory of RCC determination, based on the results of the specific heat capacity temperature dependences analysis, demands more precise definitions and additions.

Thus, under polymer filling by disperse particles the glass transition process can be divided into several separate processes, that are caused by modifier action on the molecular mobility of different kinetic units of the polymer matrix [3, 4].

The peculiarity of an influence of such modifier factors, like stoichiometric imbalance of resins and curing agents on the glass transition process of thermoreactive polymers have been considered in the papers [5, 6], where method of analysis of maximums shape on  $dC_p/dT$  dependences has been suggested.

Thus, the analysis of the literature shows that a definition of the complex relaxation characteristics of the polymer composite materials, that include high-polyesters, by the results of calorimetric studies, were not conducted. Therefore, an assessment of the feasibility and applicability of the relaxation characteristics determination method of such systems is of interest both from scientific and practical points of view.

## 2. Experimental

To produce composites silver iodide of clear quality with particle size of  $1\div 6 \mu\text{m}$  and penton with particle size of  $45 \mu\text{m}$  were used.

For producing samples dispersed AgI and penton mixture were thoroughly homogenized and then pressed from polymer melt ( $T_{press} = 483 \text{ K}$ ) at the same temperature and pressure conditions ( $P = 20 \text{ MPa}$ ). Cooling rate of the samples was  $0.5 \text{ K/min}$ .

Investigation of specific heat in the temperature range  $74\text{—}493 \text{ K}$  was performed by a differential scanning Calvet calorimeter [7], modified for determination of polymer materials heat-physical and relaxation

parameters. Density and porosity were determined by hydrostatic weighing.

### 3. Results and discussion

It is known [3] that for  $\alpha$ -relaxation process, the activation energy depends on temperature and is expressed by the Fulcher-Tammann-Vogel equation:

$$U_\alpha = \frac{U_\infty}{1 - \frac{T'}{T}}, \quad (1)$$

where  $U_\infty$  and  $T'$  — polymers constants.

Taking into account that the typical  $U_\alpha$  and  $T$  values for  $\alpha$ -process correspond approximately to linear section dependence, we can assume that the activation energy of low-cooperative processes in the temperature range of the glass transition depends linearly on temperature [3] according to the law:

$$U_i = U_i^{(0)} - \alpha_i T_i, \quad (2)$$

where  $U_i$  — the real activation energy,  $U_i^{(0)}$  — extrapolated  $U_i$  value at the  $T = 0$  K point,  $T_i$  —  $i$ -th kinetic unit transition temperature.

Kinetic unit transition probability through the barrier at arbitrary temperature is defined as

$$\frac{N_1}{N_{0i}\omega_i\Delta t_0} = \exp\left(-\frac{U_i}{kT_i}\right), \quad (3)$$

where  $N_i$  is number of successful transition attempts during observation time  $\Delta t_0$  of the system from the moment  $T = 0$  K;  $N_{0i}$   $\omega_i$   $\Delta t_0$  is the total number of attempts ( $N_{0i}$  is the total number of  $i$ -th kinetic units,  $\omega_i$  is the natural frequency of  $i$ -th kinetic unit) [8].

The deviation from the equilibrium state of the system is determined by the number of particles that passed the barrier and were not relaxed to the equilibrium value of energy.

$N_2$  values are determined by  $N_i$  values and decreased with time according to the law  $\exp(-\Delta t/\tau_i)$ , where  $\Delta t$  is system observation time from transition moment  $T_1$  through the barrier under  $v$  heating rate,  $\tau_i$  is  $i$ -th kinetic unit relaxation time, and can be found by next equation

$$N_2 = N_1\omega_i\Delta t \exp\left(-\frac{\Delta t}{\tau_i}\right). \quad (4)$$

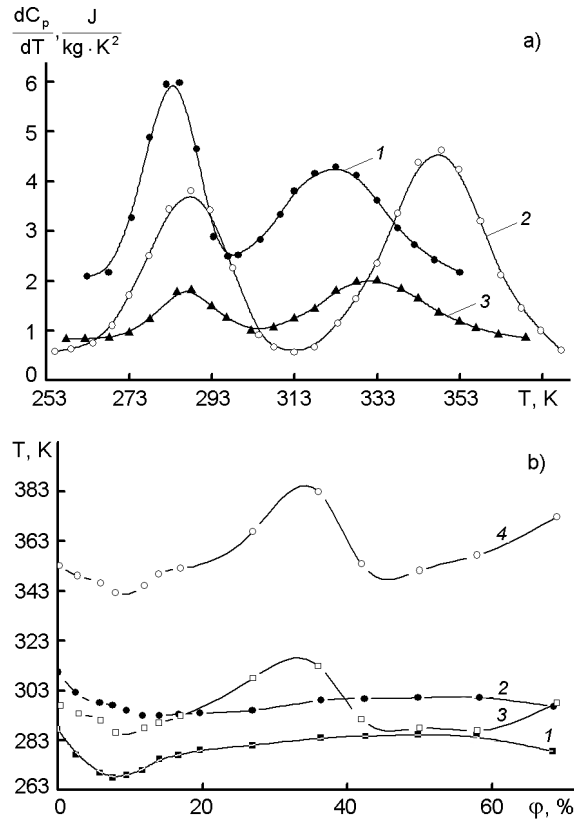


Fig. 1. (a). MDS composites temperature dependences  $dC_p/dT$ : 1 — 8 %, 2 — 36 %, 3 — 69 %. (b). Concentration dependences of the temperatures of the beginning  $T_{1\alpha}$  and the ending  $T_{2\alpha}$  of low-temperature component and the beginning  $T_{1\alpha'}$  and the ending  $T_{2\alpha'}$  of the glass transition process for MDS composites 1 —  $T_{1\alpha}$ ; 2 —  $T_{2\alpha}$ ; 3 —  $T_{1\alpha'}$ ; 4 —  $T_{2\alpha'}$ .

Let's find a number of transition attempts  $N_1$  from equation (3):

$$N_1 = N_{0i}\omega_i\Delta t_0 \exp\left(-\frac{U_i}{kT_i}\right). \quad (5)$$

$\tau_i$  can be found from the Boltzmann-Arrhenius equation:

$$\tau_i = B_i \exp\left(-\frac{U_i}{kT_i}\right), \quad (6)$$

where  $B_i = 1/\omega_i$  is pre-exponential factor.

Then, taking into account equations (5) and (6) the number of particles that passed the barrier  $U_i$

$$N_2 = N_{0i}\omega_i^2\Delta t_0\Delta t \exp\left(-\frac{U_i}{kT_i}\right) \exp\left(-\frac{\Delta t}{B_i \exp\left(-\frac{U_i}{kT_i}\right)}\right). \quad (7)$$

Table.

$\varphi$ , %	$T_{\alpha 1}$ , K	$T_{\alpha 2}$ , K	$C_{01}$ , K	$C_{02}$ , K	$B_{\alpha 1} \cdot 10^{-12}$ , sec	$B_{\alpha 2} \cdot 10^{-12}$ , sec	$U_{\alpha 1}$ , kJ/mole	$U_{\alpha 2}$ , kJ/mole	$w_1$	$w_2$
0	300	341	11	28	4.9599	5.648	77.213	87.925	4.941	5.627
3	293	338	12.5	27.5	4.8319	5.5839	75.221	86.931	4.814	5.563
6	289	335	14	27.5	4.7679	5.5359	74.227	86.183	4.750	5.515
8	288	331	14.5	28	4.7519	5.472	73.976	85.185	4.734	5.451
10	286	330	13	28	4.72	5.456	73.479	84.938	4.702	5.436
12	284	334	11	28.5	4.6879	5.5199	72.982	85.933	4.670	5.499
14	284	339	8,5	30	4.6879	5.600	72.982	87.178	4.670	5.579
17	285	343	8,5	29.5	4.7039	5.664	73.232	88.176	4.686	5.643
20	285	343	7.5	28.5	4.7039	5.664	73.232	88.176	4.686	5.643
27	286	356	7	29.5	4.703	5.8719	73.479	91.414	4.702	5.850
36	290	371	7.5	35	4.7839	6.1279	74.477	95.399	4.766	6.105
42	289	343	7	31	4.7679	5.664	74.227	88.176	4.750	5.643
50	288	340	7	31.5	4.7519	5.616	73.976	87.428	4.734	5.595
58	288	346	7,5	35	4.7519	5.691	73.976	88.924	4.734	5.691
69	288	361	10.5	37.5	4.7519	5.968	73.976	92.91	4.734	5.946

Taking into account, that  $\omega_i = 1/B_i$ ,  $\Delta t_0 = (T_i - T_0)/v$ ,  $\Delta t = (T_i - T_1)/v$ , equation (7) can be rewritten as

$$N_2 = N_{0i} \frac{(T_i - T_0)(T_i - T_1)}{B_i^2 v^2} \exp\left(\frac{U_i}{kT_i} - \frac{T_i - T_1}{B_i v} \exp\left(\frac{U_i}{kT_i}\right)\right) \quad (8)$$

Taking into account equation (2), we obtain

$$N_2 = N_{0i} \frac{(T_i - T_0)(T_i - T_1)}{B_i^2 v^2} \times \exp\left(\frac{a_i}{k} - \frac{U_i^{(0)}}{kT_i} - \frac{T_i - T_1}{B_i v} \exp\left(\frac{a_i}{k} - \frac{U_i^{(0)}}{kT_i}\right)\right) \quad (9)$$

The content of the temperature  $T_1$  is the lowest temperature at which relaxation processes is possible. The structural relaxation processes being possible in the presence of molecular motion, we can take that  $T_0 = T_1 = 0$  K.

Then equation (9) takes the form

$$N_2 = N_{0i} \frac{T_i^2}{B_i^2 v^2} \exp\left(\frac{a_i}{k} - \frac{U_i^{(0)}}{kT_i} - \left(\frac{T_i}{B_i v} \exp\left(\frac{a_i}{k} - \frac{U_i^{(0)}}{kT_i}\right)\right)\right) \quad (10)$$

Also, the maximum deviation from the equilibrium state corresponds to the maximum value of  $dC_p/dT$  at  $T = T_i$ . Under the same temperature the value must match the

maximum, which at  $T = T_i$  corresponds to  $dN_2/dT = 0$  condition [1].

So, for analysis of  $dC_p/dT$  depending one can use the following equation

$$\frac{dC_p}{dT} = \gamma_i N_{0i} \frac{T_i^2}{B_i^2 v^2} \exp\left(\frac{a_i}{k} - \frac{U_i^{(0)}}{kT_i} - \frac{T_i}{B_i v} \exp\left(\frac{a_i}{k} - \frac{U_i^{(0)}}{kT_i}\right)\right) \quad (11)$$

with double set of fitting — parameters  $a_i$ ,  $\gamma_i \cdot N_{0i}$  and  $T_i$ , individual for each composite material and corresponding kinetics units (values of  $U_i$  and  $B_i$  separately calculated for each step of parameters refinement), where  $\gamma_i$  — individual contribution of  $i$ -th kinetic unit into a  $dC_p/dT$  "jump".

As can be seen from Fig. 1, a the temperature dependences  $dC_p/dT$  of the system composites are characterized by two clearly marked maximums, one of which is observed at the lower temperatures, and another — at the higher ones. Thus, glass transition of the polymer matrix is divided into two processes — the low-temperature ( $\alpha$ -relaxation) and the high-temperature ( $\alpha'$ -relaxation) glass transition.

As a result of the lower molecular mobility the structural elements, which take part in  $\alpha'$ -relaxation process, actively react on disperse filler presence that is manifested by significant increasing the glass transition temperatures at contents of AgI in the range of  $8 \leq \varphi \leq 36$  % and by existence of

the considerable glass transition temperature range (Fig. 1b).

RCC analysis (Table) shows that pentone — AgI MDS composites with the low content of filler particles ( $\varphi < 27\%$ ) are characterized by narrowing of the half-width of low-temperature glass transition interval  $C_{0\alpha}$  and decreasing of  $\alpha$ -relaxation activation energy  $U_\alpha$  values at simultaneous relative steadiness of the half-width interval  $C_{0\alpha'}$  and activation energy  $U_{\alpha'}$  of high-temperature  $\alpha'$ -relaxation. With concentration increasing up to  $\varphi \leq 69\%$ , an increasing of the half-width of  $\alpha'$ -relaxation interval  $C_{0\alpha'}$  and activation energy  $U_{\alpha'}$ , is observed that followed by practical constancy of  $C_{0\alpha}$  and  $U_\alpha$  parameters.

Such behavior of the parameters  $C_{0\alpha}$ ,  $C_{0\alpha'}$ ,  $U_{0\alpha}$  and  $U_{0\alpha'}$  are explained by the fact that, at insignificant concentrations the polymer matrix of system composites is also under transitional boundary and wall boundary layers states.

Thus, considerable decrease of the beginning and ending temperatures of  $\alpha'$ -relaxation process in penton — AgI system at concentrations from 36 up to 50% is caused by polymers staying in transitional boundary layers state, that, evidently, is characterized by less regulated, comparing with volume polymer, structure. Further increasing the temperatures of the beginning and ending of high-temperature glass transition at values  $\varphi > 0\%$  is caused by changes in structure of the polymer, which, at such concentrations, is under the wall boundary layer state and whose structure is characterized by the high degree of order [9], that is confirmed by high values of  $C_{0\alpha'}$  and  $U_{0\alpha'}$  parameters.

Numerical values of the cooperativity parameters  $W_\alpha$  and  $W_{\alpha'}$  show combined participation in  $\alpha$ - and  $\alpha'$ -relaxation processes of five and six kinetic units correspondingly.

Obtained  $B_\alpha$  and  $B_{\alpha'}$  values have order of  $5 \cdot 10^{-12}$  sec, which correlate well with the data obtained for the polymer composite systems by other methods [3, 4].

Thereby, the investigations of the temperature dependences of specific heat capacity of the system composites display multiplet character of glass transition of the polymer matrix and allowed to physically grounded execute the division of the observed data in  $\alpha$ - and  $\alpha'$ -relaxation transitions range, and separately determine their RCC.

#### 4. Conclusions

Thus, one could argue that the above described method of determining the relaxation characteristics complex, basing on the results of calorimetric studies, can be applied to the MDS comprising polymers capable of crystallization, in particular filled high-molecular polyesters.

#### References

1. L.K.Yanchevsky, M.I.Shut, M.V.Lazorenko, V.V.Levandovsky, *High-molecular Comp., Ser. A*, **32**, 307 (1990).
2. L.K.Yanchevsky, V.V.Levandovsky, *Acta Polymer*, **44**, 29 (1993).
3. G.M.Bartenev, V.G.Barteneva, *Polymers Relaxation Properties*, Khimiya, Moscow (1992) [in Russian].
4. G.M.Bartenev, D.S.Sanditov, *Relaxation Processes in Glassy Systems*, Nauka, Novosibirsk (1986) [in Russian].
5. T.G.Sichkar, L.K.Yanchevsky, O.V.Gorshunov, M.I.Shut, *Prob. Chem. Appl. Chem.*, **1**, 227 (2004).
6. O.V.Gorshunov, M.I.Shut, T.G.Sichkar, M.A.Rokitskiy, in: *Abstr. All-Ukrainian Cong. "Physics in Ukraine"*, Astroprint, Odessa (2005), p.92.
7. N.I.Shut, T.G.Sichkar, L.K.Yanchevsky et al., in: *Abstr. IV Int. Conf. "Problems of Industrial Heat Engineering"*, Kiev (2005), p.368.
8. L.D.Landau, I.M.Livshits, *Statistical Physics*, Moscow (1964) [in Russian].
9. M.A.Rokitskiy, M.I.Shut, *Phys. Aerodisperse Systems*, **44**, 37 (2007).

## **Визначення комплексу релаксаційних характеристик матрично-дисперсної системи пентапласт — AgI**

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Показано, що калориметричний метод аналізу релаксаційних процесів може бути застосований і до матрично-дисперсних систем, до складу яких входять полімери, здатні до кристалізації, а саме високомолекулярні поліефіри та дисперсні наповнювачі. На прикладі системи пентапласт — AgI виконано аналіз мультиплетної залежності  $dC_p/dT$  композитів у температурному інтервалі склування, форма якої спричинена присутністю структурно-активних частинок йодиду срібла, та визначено комплекс їх релаксаційних характеристик.