

UDC 538.9+537.3

DOI: 10.33910/2687-153X-2020-1-1-15-19

## Dielectric relaxation in nanocomposites based on thermoplastic polyimide and carbon nanofibres

H. T. Dao<sup>✉1</sup>, R. A. Castro Arata<sup>1</sup>, A. A. Kononov<sup>1</sup>, N. A. Nikonorova<sup>2</sup>

<sup>1</sup> Herzen State Pedagogical University of Russia, 48 Moika River Emb., Saint Petersburg 191186, Russia

<sup>2</sup> Institute of Macromolecular Compounds of Russian Academy of Sciences, 31 Bolshoy Pr., Saint Petersburg 199004, Russia

### Authors

Hong T. Dao, e-mail: [honghip2012@gmail.com](mailto:honghip2012@gmail.com)

Rene Alejandro Castro Arata, ORCID: [0000-0002-1902-5801](https://orcid.org/0000-0002-1902-5801)

Alexey A. Kononov, ORCID: [0000-0002-5553-3782](https://orcid.org/0000-0002-5553-3782)

Natalia N. Nikonorova, ORCID: [0000-0002-7928-9227](https://orcid.org/0000-0002-7928-9227)

**For citation:** Dao, H. T., Castro Arata, R. A., Kononov, A. A., Nikonorova, N. A. (2020) Dielectric relaxation in nanocomposites based on thermoplastic polyimide and carbon nanofibres. *Physics of Complex Systems*, 1 (1), 15–19. DOI: 10.33910/2687-153X-2020-1-1-15-19

**Received** 30 January 2020; reviewed 11 February 2020; accepted 11 February 2020.

**Funding:** This study was supported by the Ministry of Education and Science of the Russian Federation (project no. 3.5005.2017/BY).

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**Abstract.** The article presents the study of R-SOD 3% nanocomposite's molecular mobility based on thermoplastic PI (R-SOD) with 3% of carbon nanofibres by dielectric method. Dielectric spectrum shows two processes of dipole polarisation relaxation: in the glassy state (local  $\beta$  process) and in the highly elastic state (cooperative  $\alpha$  process) related to molecular mobility of phenyl rings with polar —O— groups in diamine and dianhydride parts of a macromolecule and to segmented motion, respectively.

**Keywords:** dielectric relaxation, polymeric composites, polyimide.

### Introduction

Recently, polymer nanocomposites have been in especially great demand, since they differ from conventional polymer composite materials by their greater impact and wear resistance, which allows their use in the military and aerospace developments. Polypropylene, polystyrene, polyamide and polyimide are used as a matrix, while particles of aluminium and titanium oxides, carbon as well as silicon nanotubes and fibres act as nanofillers. Introducing nano-additives of different nature and concentration makes it possible to change their mechanical, electrical, thermal, optical and other characteristics. Nanocomposite membranes based on thermoplastic polyimides PI (heat treatable), which are actively used as thermostable coatings resistant to water and chemical attack, are of special interest.

The properties of nanocomposites, studied by various methods, depend not only on the chemical structure of the matrix and the nature of nanoparticles, but also on interaction between them. The intramolecular and intermolecular interactions in a nanocomposite can be evaluated by molecular mobility (McCrum, Read, Williams 1967; Hedvig 1977). One of the traditional methods for studying molecular mobility is dielectric spectroscopy (DS). The DS method serves as a tool for discovering specific features of polarisation processes and their relationships with structural features of the studied material.

This work uses the dielectric method to investigate the molecular mobility of thermoplastic PI nanocomposite based on R-SOD (see Fig. 1) with 3% of carbon nanofibres. The objective of this study is to determine molecular mechanisms underlying the observed relaxation processes of the dipole polarisation.

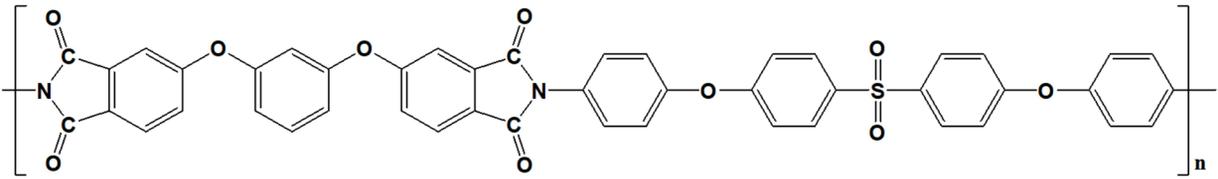


Fig. 1. Structure of R-SOD thermoplastic polyimide

Thermoplastic polyimide (P-SOD) was produced by a two-step synthesis of 1,3-bis(3,4-dicarboxyphenoxy) benzene and 4,4'-bis(4"-aminophenoxy)diphenyl sulfone as well as nanocomposites R-SOD 3% with carbon nanofibres ( $D \times L = 100 \text{ nm} \times 20\text{--}200 \text{ }\mu\text{m}$ ) (Nikonorova, Kononov, Dao, Castro 2019).

The dielectric spectra were obtained with a wideband dielectric spectrometer "Concept 22" and "Concept 81" by Novocontrol Technologies with an automatic high-resolution frequency analyser ALPHA-ANB. Films of 25...40  $\mu\text{m}$  thickness compressed between brass electrodes (the upper electrode diameter of 20 mm) at a temperature of approx. 300  $^{\circ}\text{C}$  above the glass transition temperature ( $T_g$ ) were taken as samples. The dielectric behaviour was obtained in the 0.1–2E6 Hz frequency range and the 20–3200  $^{\circ}\text{C}$  temperature range.

Dielectric spectra were analysed with the Havriliak-Negami (HN) empirical function (Havriliak, Negami 1967) using the Novocontrol Winfit software. These estimations were used to determine positions of the dielectric loss maxima and the HN parameters for the studied relaxation processes:

$$\varepsilon^*(\omega) = \varepsilon_{\infty} + \frac{\Delta\varepsilon}{[1 + (i\omega\tau)^{\alpha_{HN}}]^{\beta_{HN}}} \quad (1)$$

where  $\varepsilon_{\infty}$  is the high-frequency limit of the real part of dielectric permittivity,  $\Delta\varepsilon$  is the dielectric increment (the difference between the low- and high-frequency limits),  $\omega = 2\pi f$ ,  $\alpha_{HN}$  and  $\beta_{HN}$  are shape parameters that describe the symmetric and asymmetric expansion of the relaxation function, respectively. The most probable relaxation time corresponding to the dielectric loss maximum was evaluated by the formula:

$$\tau_{\max} = \tau_{HN} \left[ \frac{\sin\left(\frac{\pi(\alpha_{HN})\beta_{HN}}{2(\beta_{HN} + 1)}\right)}{\sin\left(\frac{\pi(\alpha_{HN})}{2(\beta_{HN} + 1)}\right)} \right]^{1/(\alpha_{HN})} \quad (2)$$

## Results and discussion

Two regions of the maximum on dielectric spectra resulting from the relaxation processes of the dipole polarization were observed (Fig. 2). These regions are indicated in the order of the temperature increase as  $\beta$  (in the glassy state) and  $\alpha$  (in the rubbery state). Another  $\text{tg}\delta_{\max}$  region was observed at temperatures above  $\alpha$  process, corresponding to the DC conductivity relaxation not displayed in the figure 1.

Fig. 3 and 4 show the dependence of dielectric loss factor in temperature regions on the  $\beta$  and  $\alpha$  relaxation processes, respectively, where symbols indicate experimental points.

Fig. 5 shows the values of relaxation times for  $\beta$  and  $\alpha$  processes calculated by formula 2 (symbols) and their temperature dependences (lines) calculated according to the formulas 3 and 4, curve 1 and 2, respectively.

Dependence  $-\log\tau_{\max} = \phi(1/T)$  for  $\beta$  process can be described by the Arrhenius equation:

$$\tau(T)_{\max} = \tau_0 \exp\left(\frac{E_a}{RT}\right) \quad (3)$$

Table 1. Parameters of the Arrhenius equation (3) for  $\beta$  process

Sample	$-\log\tau_0, s$	$E_a, kcal/mol$
R-SOD 3% fibres	19.8	29
Error ( $\pm$ )	0.1	3

Table 2. Parameters of the equation (4) in  $\alpha$  process region for R-SOD 3%

Sample	$-\log\tau_0, s$	B, K	$T_0, K$	$T_g, ^\circ C$
P-CO $\Delta$ 3%	11.7	1317	441	222
Error ( $\pm$ )	0.3	46	13	8

$T_g$  is determined at  $\tau_{max} = 0$

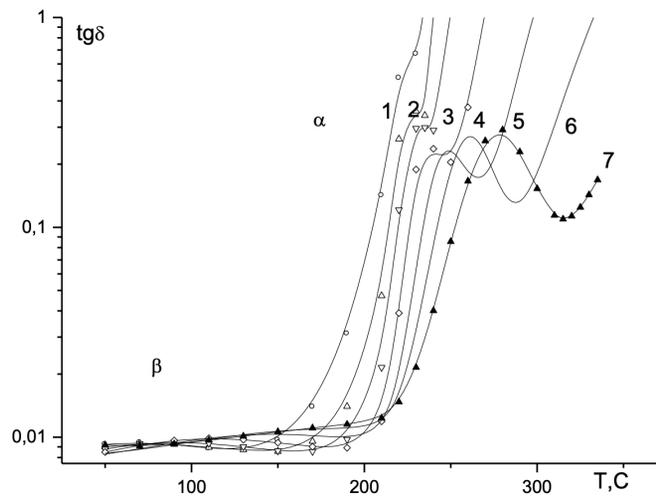


Fig. 2. Temperature dependence of  $tg\delta$  at 0.1(1), 1(2). 10(3), 100(4), 1000 (5) 10000 (6), and 100000 (7) Hz

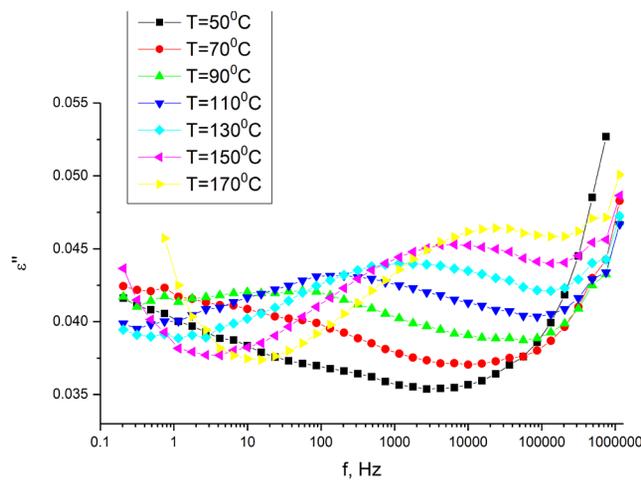


Fig. 3. Frequency dependences of dielectric loss factor process at different temperatures (T see in Figure) for  $\beta$  Symbols are experimental points. Solid lines are approximation by HN formula

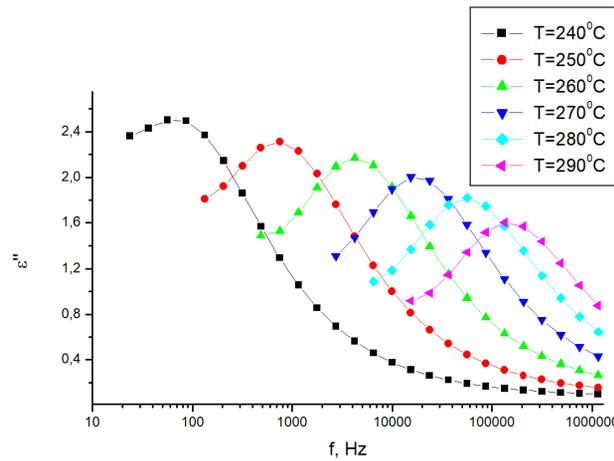


Fig. 4. Frequency dependences of dielectric a loss at different temperatures (T see in Figure) for  $\alpha$  process. Symbols are experimental points. Solid lines are approximation by HN formula

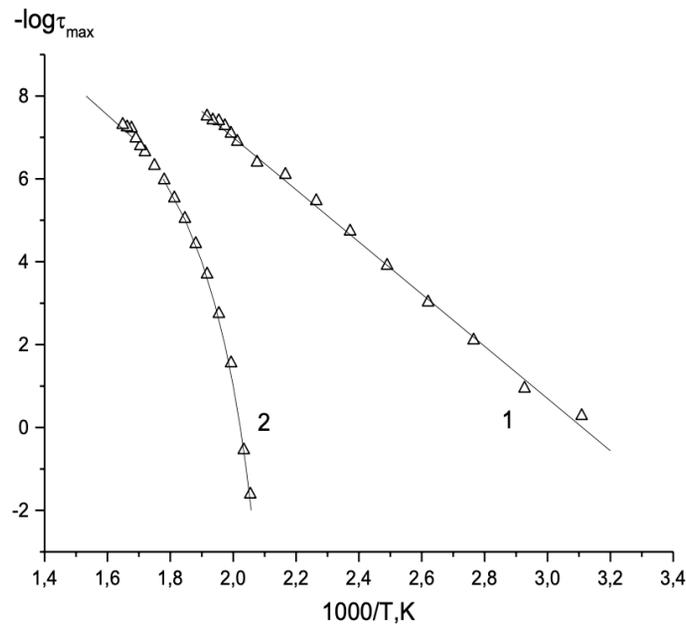


Fig. 5. Temperature dependence of the relaxation time calculated by the HN formula in the region of  $\beta$  (curve 1) and  $\alpha$  process (curve 2)

where  $\tau_0 = \tau_{\max}$  at  $T = \infty$ ,  $E_a$  is the activation energy and  $R$  is the universal gas constant ( $R = 8.314 \text{ J/mol.K}$ ). The linearity of  $-\log\tau_{\max} = \phi(1/T)$  dependence is typical for local forms of molecular mobility described by the Debye model. This model assumes the absence of intermolecular interactions, and the activation energy does not depend on temperature here. The equation parameters of formula (3) are presented in Table 1.

In the temperature region corresponding to  $\alpha$  relaxation process the values of relaxation time and temperature dependence  $-\log\tau_{\max} = \phi(1/T)$  reveal a nonlinear curve (Fig. 5, curve 2). This nonlinearity is typical for cooperative relaxation processes which are characterised by a wide set of relaxation times and can be considered as a joint correlated movement of a large number of segments belonging to neighbouring macromolecules. The molecular mobility of kinetic segments depends on the state of the immediate environment and is determined largely by intermolecular interactions. The activation energy of this cooperative process depends on the temperature, and  $-\log\tau_{\max} = \phi(1/T)$  dependences are well described by the empirical Vogel–Tammann–Fulcher (VTF) equation (Kremer, Schönhal 2012):

$$\tau_{\max} = \tau_o \exp\left(\frac{B}{T - T_0}\right) \quad (4)$$

where  $\tau_o$ ,  $B$ , and  $T_0$  are temperature-independent parameters.  $T_0$  is the so-called Vogel temperature.  $B$  parameter is a cooperativity measure of the relaxation process. The smaller  $B$  is, the greater distortion and deviation from linearity of  $-\log\tau_{\max} = \phi(1/T)$  dependence as well as the cooperativity of the process are. Parameters of the equation (4) for  $\alpha$  process are given in Table 2.

According to the data obtained earlier for linear thermoplastic PIs of various structures, it can be assumed that appearance of the  $\beta$  process reflects limited rotations of phenyl rings and associated —O— polar groups.

Regarding  $\alpha$  relaxation for thermoplastic PIs of various structures studied previously, this process can be explicitly associated with the glass transition temperature. The molecular source of  $\alpha$  process is the large-scale segmental mobility of the macromolecule ridge (Bryant 2006). The temperature-frequency coordinates of  $\alpha$  process (Fig. 5, curve 2), dependence  $-\log\tau_{\max} = \phi(1/T)$ , separate the glassy state region of the polymer (right) from the rubbery state region (left). The glass transition temperature,  $T_g$  (see Table 2), was determined by extrapolation of  $-\log\tau_{\max} = \phi(1/T)$  dependence described by the VTF equation to  $-\log\tau_{\max} = 0$ , ( $\tau_{\max} = 1$  s). For linear polymers,  $T_g$  is determined primarily by intermolecular and dipole-dipole interactions between macromolecules. In the case of PIs, the major contribution to intermolecular interactions is probably provided by dispersion forces between planar phenylene rings.

## Conclusion

The molecular mobility of the aromatic thermoplastic polyimide R-SOD with 3% of fibres was studied by the dielectric method. In the studied temperature-frequency range, the dielectric spectra showed two relaxation areas of dipole polarization:  $\alpha$  (in the glassy state) and  $\beta$  (in the rubbery state). The empirical formula of HN is used for the quantitative description of relaxation processes.

Comparing dielectric behaviour of polymers having similar structure and the given polyimide allows us to identify relaxation processes. The  $\beta$  process, which is the imposition of several molecular mobility modes with close relaxation times, is associated with the mobility of phenyl rings in the diamine and dianhydride parts of the macromolecule and the polar groups adjacent to them.

The temperature dependence  $-\log\tau_{\max} = \phi(1/T)$  in  $\alpha$  process region displays as a non-linear curve, which is typical for cooperative segmented molecular motion. In the case of the studied system, the major contribution to the intermolecular interactions could be provided by dispersion forces between planar phenylene rings.

This work is devoted to dielectric study of R-SOD 3%. However, in reality, we have in our disposition a series of nanocomposites R-SOD with 1, 3, 4 and 5% nanofibres, as well as pure R-SOD. Preliminary data show that R-SOD 1, 3, and 4% have the dielectric behaviour that differs slightly from pure R-SOD. The dielectric behaviour of R-SOD 5% changes dramatically, indicating the presence of pass-through conductivity (percolation). The next article will present results of a study concerning pure R-SOD and R-SOD 1, 4, and 5%.

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