Dielectric spectroscopy of thermoplastic polyimide R-SOD in the region of medium and high temperatures

T H Dao¹, N A Nikonorova² and R A Castro¹

¹Herzen State Pedagogical University of Russia, St. Petersburg, 191186 Russia.
²Institute of Macromolecular Compounds of Russian Academy of Sciences, St. Petersburg, Russia

Email: honghip2012@gmail.com

Abstract. Molecular mobility and charge transport in R-SOD aromatic thermoplastic polyimide were studied by dielectric method. Dielectric spectra of all samples in the examined temperature and frequency range revealed two regions of dipole polarization relaxation. The β-process is determined by local motion of the phenyl rings in the diamine and dianhydride moieties of the macromolecule with the adjacent groups. The α-process can be associated with crossing the glass transition temperature, i.e., with the segmental large-scale mobility of the main chains. The introduction of nano-additives (R-SOD 3%) does not change the relaxation times in the regions of β and α process, but leads to an increase in intensity compared to pure polyimide R-SOD.

1. Introduction

Recently, polymer nanocomposites are especially in demand, since they differ from ordinary polymer composite materials with lower weight, greater impact resistance and wear resistance, as well as good resistance to chemical influences, which allow them to be used in military and aircraft and space engineering. Polypropylene, polystyrene, polyamide are used as a matrix, and particles of aluminum or titanium oxides, or carbon, as well as silicon nanotubes and fibers act as nanofillers. The introduction of nano-additives of different nature and concentration allows us to change the mechanical, electrical, thermal, optical and other characteristics.

Nanocomposites based on thermoplastic polyimides (PI) are of particular interest where they are actively used as highly heat-resistant structural materials, thermostable coatings resistant to water and solvents, membranes for various purposes [1,2].

The properties of nanocomposites have been studied by various methods and depend not only on the chemical structure of the matrix and the nature of the nanoparticles, but also on their interaction. The intramolecular and intermolecular interactions in a nanocomposite can be determined by the molecular mobility. One of the traditional methods for studying molecular mobility is dielectric spectroscopy [3-5].

The aim of this work is to determine the molecular mechanisms of β and α relaxation processes, the relationship between molecular mobility and the chemical structure of polyimide R-SOD and the nanocomposite based on it.

2. Experimental details

Under this study, molecular mobility of the thermoplastic PI R-SOD (Figure 1) and the nanocomposite based on it with 3% of carbon nanofibers were examined by dielectric spectroscopy method.
The synthesis details and the method of producing PI films are described in [6,7]. Films of 25...40 μm thickness, compressed between brass electrodes (diameter of the upper electrode – 20 mm) at a temperature of ~30°C above the glass transition temperature, were taken as samples. Dielectric spectra were obtained with “Concept 81” broadband dielectric spectrometer (Novocontrol Technologies GmbH), with ALPHA-ANB automatic high-resolution frequency spectrum analyzer. Temperature-frequency dependences of dielectric permittivity ε', dielectric loss factor ε'', dielectric loss tangent tgδ were obtained for all PI samples in the frequency range 10¹Hz ...10⁶Hz and the temperature range 313K...613K.

The spectra of complex dielectric permittivity and complex conductivity were calculated from the impedance spectra. Dielectric spectra were analyzed with the Havriliak-Negami (HN) two-parametric empirical function using the Novocontrol Winfit software. Based on these approximations, positions of the dielectric loss maxima were identified and the HN parameters were determined for the studied relaxation processes:

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

where, ε∞ is the high-frequency limit of the real part of dielectric permittivity, Δε is the dielectric increment (the difference between the low- and high-frequency limits), ω = 2πf is the angular frequency (f - frequency of the outer electrical field), τ is the characteristic time of the HN equation, βHN and αHN are shape parameters that describe the symmetric (β = 1, the Cole-Cole distribution) and asymmetric (α = 1, the Cole-Davidson distribution) expansion of the relaxation function, respectively.

3. Results and discussion

For the PIs under investigation, the dielectric spectra are qualitatively similar. To visualize the dielectric behaviors, the dielectric spectra ε' = ϕ(f) at different temperatures were transformed to dependences tgδ = ϕ(T). As an example dependences of tgδ = ϕ(T) for R-SOD samples are shown in Figure 2. These dependences indicate two ranges of tgδmax emerging due to the dipole polarization relaxation processes, as their position is shifted to high temperature with increasing frequency. These ranges of tgδmax in order of increasing temperature were referred as β (in the glassy state) and α (in the highly elastic state). At temperatures exceeding the α process, the sharp increase in dielectric losses due to conductivity was observed.
Figure 2. Temperature dependences of $\tan \delta$ at different temperatures. Symbols – experimental points. Solid lines are drawn as guides to the eyes.

Figure 3. Frequency dependence of dielectric loss factor in $\beta$-process region at different temperatures. Solid lines refer to the HN approximation of the experimental curves.

Figure 4. Frequency dependence of dielectric loss in $\alpha$ process region at different temperatures. Solid lines refer to the HN approximation of the experimental curves.

Figure 3 and Figure 4 demonstrate the dependences of dielectric loss factor in the temperature regions corresponding to $\beta$ and $\alpha$ relaxation processes.

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

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

where, $\tau_0 = \tau_{\text{max}}$ is the relaxation time at $T \to \infty$, $E_a$ is the activation energy, $R$ is the universal gas constant ($R = 8.314 \text{ J/mol-K}$). The linearity of $-\log \tau_{\text{max}} = f(1/T)$ dependence is typical for the local forms of molecular mobility described by the Debye model. This model assumes the absence of
intermolecular interactions and here the activation energy does not depend on temperature. The equation parameters (2) for these processes are presented in Table 1.

Table 1. Parameters of Equation (2) for β process (calculated values have uncertainties of less than 1%).

| Sample         | -log τ₀, c | Eₐ, kcal/mol | Eₐ, eV  |
|----------------|------------|--------------|---------|
| R-SOD          | 19.1       | 29.7         | 1.29    |
| R-SOD 3%       | 19.8       | 29           | 1.26    |
| Error (±)      | 0.09       | 0.07         | 0.003   |

Figure 5. Temperature dependence of the relaxation time calculated by the HN formula in β process region

(a) for pure R-SOD; b- for R-SOD with fibers 3%

Comparing the data obtained earlier for linear thermotropic polyesters and PIs of various structures, it can be assumed that the appearance of β process reflects limited rotations of the phenyl rings and the associated polar —O— groups. The values of -log τ₀ and Eₐ are larger than those for local processes, which can be explained by some influence of intermolecular interactions [8].

In the case of the α relaxation, the -log τₓₓ = φ(1/T) dependences are nonlinear (Figure 6). This pattern is typical for cooperative relaxation processes in molecular motion, which are characterized by a wide set of relaxation times and are implemented as a joint correlated movement of a large number of segments belonging to neighboring macromolecules (Table 1). The effect is that 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 τₓₓ = φ(1/T) dependences are well described by the empirical Vogel–Tammann–Fulcher (VTF) equation:

\[ \tau_{\max} = \tau_0 \exp \left( \frac{B}{T - T_0} \right) \]  

(3)
where, $\tau_0$, $B$ and $T_0$ are temperature-independent parameters. $T_0$ is the so-called Vogel temperature. $B$ parameter represents a measure of cooperativity of the relaxation process. The smaller $B$ is, the greater are distortion and deviation from linearity of $-\log \tau_{\text{max}} = \varphi(1/T)$ dependence, as well as the cooperativity of the process (parameters of the equation (3) for $\alpha$ process in the systems under study are presented in Table 2).

**Table 2. Parameters of Equation 3, $-\log \tau_0$, $B$, $T_0$, $T_g$ (calculated values have uncertainties of less than 3%).**

| PIs     | $-\log \tau_0$ [s] | $B$, K     | $T_0$, K | $T_g$, °C |
|---------|---------------------|------------|----------|----------|
| R-SOD   | 11.9                | 1903       | 428      | 223      |
| R-SOD 3%| 11.7                | 1317       | 441      | 222      |

The introduction of nano-additives (R-SOD 3%) does not change the relaxation times in the regions of $\beta$ and $\alpha$ process, but leads to an increase in intensity compared to pure polyimide R-SOD (Figure 6).

**Figure 6. Temperature dependence of the relaxation time calculated by the HN formula in $\alpha$ process region**

(a) - for pure R-SOD; (b) - for R-SOD with fibers 3%

Considering the structure of the PIs under investigation, it can be assumed that a slower $\beta$ process is determined by local motion of the phenyl rings in the diamine and dianhydride moieties of the macromolecule with the adjacent ester, amide or sulphone groups. In other words, the $\beta$ process is the result of the superposition of several modes of molecular mobility with close relaxation times, which cannot be separated, unlike the results of [9]. For PIs investigated, temperature-frequency position and intensity of the $\beta$ process are practically independent of the chemical structure (the temperatures $T_{\text{g}_\delta}$ at 1 Hz are $\sim +75$ °C). Thus, for the $\beta$ relaxation process in the glassy state, the kinetic characteristics and, therefore, the molecular mobility do not depend on the chemical structure of PIs under study.

For the thermoplastic PIs under study, the $\alpha$ process can be uniquely associated with the transition through the glass transition temperature. The molecular source of the process is the large-scale segmental mobility of the macromolecule ridge. The temperature-frequency position of the $\alpha$ process (Figure 6), the $-\log \tau_{\text{max}} = \varphi(1/T)$ dependences, separate the region of the polymer’s glassy state (right) from the highly elastic state (left). The glass transition temperature of the investigated PIs (Table 2) was
determined by extrapolating the $-\log \tau_{\text{max}} = \varphi(1/T)$ dependence described by equation (3), to $\log \tau_{\text{max}} = 0$ ($\tau_{\text{max}} = 1s$).

4. Conclusion

Molecular mobility and charge transport in R-SOD aromatic thermoplastic polyimide were studied by dielectric method. Dielectric spectra of R-SOD samples in the examined temperature and frequency range revealed two regions of dipole polarization relaxation.

It can be assumed that a slower $\beta$ process is determined by local motion of the phenyl rings in the diamine and dianhydride moieties of the macromolecule with the adjacent ester, amide or sulphone groups. The observed $\alpha$-process can be associated with crossing the glass transition temperature, in other words, with the segmental large-scale mobility of the main chains. The introduction of nanoadditives (R-SOD 3%) was also observed in the studied temperature range and a conclusion can be made about its influence on the relaxation times in the regions of $\beta$ and $\alpha$ process, and it leads to an increase in intensity compared to pure polyimide R-SOD.

Acknowledgments

This study was supported by the Ministry of Education and Science of the Russian Federation (project № 3.5005.2017/VU).

References

[1] Bryant R G 2002 *Polyimides* John Wiley & Sons (New York)
[2] Sroog C E 1969 *Encyclopedia of Polymer Science and Technology* vol 11, ed John Wiley & Sons (New York) pp 247-72
[3] Kremer F and Schonhals A 2003 *Broadband Dielectric Spectroscopy* (Springer, Berlin)
[4] Nikonorova N A, Balakina M Y, Fominykh O D, Sharipova A V, Vakhonina T A, Nazmieva G N, Castro R A and Yakimansky A V 2016 Dielectric spectroscopy and molecular modeling of branched methacrylic (co)polymers containing nonlinear optical chromophores *Mater. Chem. Phys.* 181 217-26
[5] Nikonorova N A, Polotskaya G A, Kononov A A, Hinderliter B R, Levine K L and Castro R A 2018 Dielectric relaxation of fullerene C$_{60}$-containing nanocomposites based on poly(phenylene oxide) *J. Non-Cryst. Solids* 483 99-105
[6] Chisca S, Musteata V E, Sava I and Bruma M 2011 Dielectric behavior of some aromatic polyimide films *European Polymer Journal* 47 1176-97
[7] Bas C, Pascal T and Alberola N D 2003 On the dynamic mechanical behaviour of polyimides based on aromatic and alicyclic dianhydrides *Polymer Engineering & Science* 43 344-55
[8] Nikonorova N A et al. 2019 Molecular Mobility of Thermoplastic Aromatic Polyimides Studied By Dielectric Spectroscopy *J. Non-Cryst. Solids* 511 109-14
[9] Castro R A, Bordovsky V A and Grabko G I 2009 Investigation of the processes of charge transfer and charge accumulation in As$_2$Se$_3$ amorphous layers prepared by different methods *Glass Physics and Chemistry* 35(1) 43-46