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Low-temperature viscoelastic relaxation in PMA polyimide (Kapton)

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In the temperature range 4.2–350 K for the first time was studied the temperature dependence of the dynamic Young's modulus and acoustic absorption of the polyimide film PMA (Kapton). Two low-temperature relaxation processes on the temperature dependences of the acoustic properties of the PMDA/ODA polyimide are recorded: δ-relaxation at 45 K and β-relaxation at 185 K. A microscopic interpretation of the mechanisms is responsible for the occurrence of δ and β relaxation in the PMDA/ODA polyimide is proposed. Estimates of the activation energy for these relaxation processes are obtained: δ-relaxation — 0.05 eV, β-relaxation — 0.7 eV.

Keywords: viscoelastic relaxation, Young's modulus, kapton, PMDA/ODA, low-temperature.

В области температур 4.2–350 К впервые изучены температурные зависимости динамического модуля Юнга и логарифмического декремента колебаний промышленной полиимидной пленки марки ПМА. На температурных зависимостях акустических свойств PMDA/ODA полиимида зарегистрировано два низкотемпературных релаксационных процесса: δ-релаксация при 45 К и β-релаксация при 185 К. Предложена микроскопическая интерпретация механизмов, ответственных за возникновение δ и β релаксации в PMDA/ODA полиимиде. Получены оценки энергии активации для этих релаксационных процессов: δ-релаксация — ~ 0.05 эВ, β-релаксация — ~ 0.7 эВ.

Низькотемпературна в'язко-пружна релаксація у поліімідіПМА. *Ю.О.Семеренко.*
У області температур 4.2–350 К вперше вивчено температурні залежності динамічного модуля Юнга та логарифмічного декременту коливань промислової поліімідної плівки марки ПМА. На температурних залежностях акустичних властивостей PMDA/ODA поліміду зареєстровано два низькотемпературні релаксаційні процеси: δ-релаксація при 45 К та β-релаксація при 185 К. Запропоновано мікроскопічну інтерпретацію механізмів, відповідальних за виникнення δ та β релаксації у PMDA/ODA поліімідіі. Отримано оцінки енергії активації для цих релаксаційних процесів: δ-релаксація — ~ 0.05 еВ, β-релаксація — ~ 0.7 еВ.

1. Introduction

PMA (poly-oxydiphenylene-pyromellithymide, foreign analogues of Kapton HN, Apikal HN) is a transparent polymer of golden color. Kapton is a typical representative of an extensive class of heat-resistant polymers — polyimides [1]. Kapton was first synthesized in the USA by the famous chemist, inventor of teflon Roy J. Plankett in 1964 [2].

Kapton has excellent physical, chemical and electrical characteristics, is resistant to radiation, space environment, temperature extremes. It is stable in a wide range of

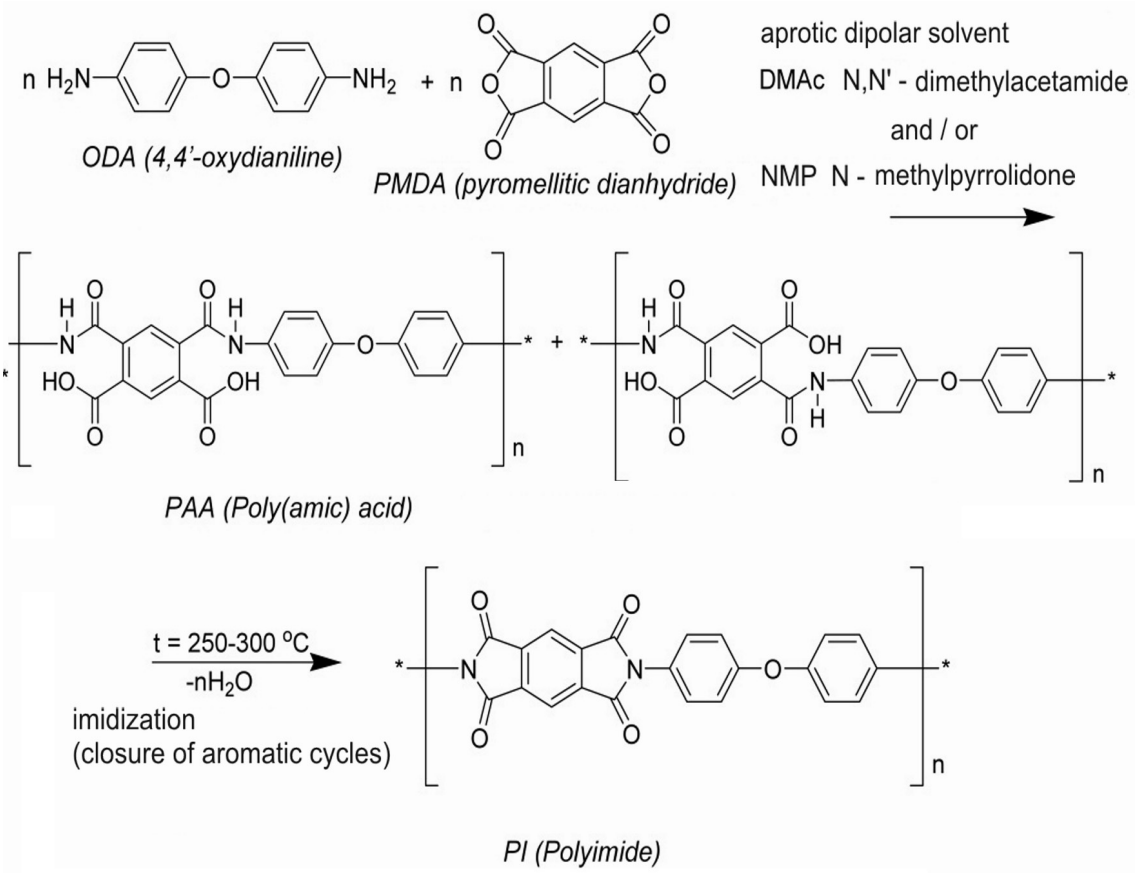

Fig. 1. Synthesis of PMDA/ODA polyimide [1].

temperatures from 4.2 K to 700 K [3], does not dissolve and does not swell in known organic solvents even with prolonged heating, does not burn, does not melt and does not soften up to the decomposition temperature [3]. It is used as high-temperature insulation in electrical equipment. Due to a lower specific weight than other dielectrics it is often used as insulation for on-board wires and cables for aviation and astronautics. Polyimide film is well metallized, so it is widely used in the manufacture of flexible printed circuit boards. Polyamide PMA has a high transmittance for X-rays and it is highly resistant to them. So it is widely used as a material for the manufacture of "windows" (instead of beryllium) in devices with X-ray sources and X-ray detectors. Good thermal conductivity, mechanical and thermal stability along with good dielectric properties and availability in the form of thin sheets make it one of the main materials in cryogenic and superconducting technology. Kapton is widely used as an insulator in ultra-high vacuum. An important property of this material is the absence of heat shrinkage. Therefore, thermal stresses arising in fixed fibers from Kapton are significantly lower than in highly oriented fibers from other linear polymers. So that products reinforced with fibers from Kapton retain their shape with temperature.

Currently, Kapton is manufactured using the two-step method patented by DuPont: 1. polyamic acid production by pyromelite dianhydride polycondensation (dianhydride, PMDA) and 4, 4′ — oxydianine (diamine, ODA) in a strong dipolar aprotic solvent (N, N′ — dimethylacetamide — DMAc and / or methylpyrrolidone — NMP) at a temperature from −20°C to +70°C followed by pouring onto the forming surface; 2. thermoimidization (cyclization) of amic acid at a temperature 250–300°C (see Fig. 1) [4]. The physicochemical properties of the final product are largely determined by the molecular weight of the polyamic acid, the residual solvent content [5] and the degree of imidization [6, 7]. In this case, the molecular weight of the polyamic acid depends on the temperature at which the polycondensation is carried out. The color of the final product depends on the degree of purification of ODA and changes as the purity increases from brown-red to light yellow. Ori-

entational stretching significantly (by 100–150 %) increases the strength and elasticity modulus of PMDA/ODA polyimide.

Practical importance as well as the simplicity of obtaining samples with desired and controlled properties (purity of the initial components, solvent composition, mode of polycondensation and imidization, etc.) makes this material one of the most studied polymers. It is now well understood its physical and mechanical characteristics. However, at low temperatures have been studied only the basic mechanical properties [8–10], while the relaxation properties were not studied.

2. Experimental

It was studied thin (80 microns thick) industrial PMDA/ODA films of polyamide PMA. The density of the samples was determined by the gravimetric method. The obtained value 1.390 g/cm^3 differs from the values 1.420 g/cm^3 known in the literature [1], which can be explained by the well-known dependence of the density of the final polymer on the conditions of imidization [11, 12].

The glass transition temperature of the studied polymer ranges from 320–370°C [11, 12]. There is evidence that under certain conditions partial crystallization of this material is possible [13]. X-ray structural method was found that deformation can lead to the appearance of structurally ordered inclusions [14].

Possible conformations of PMDA/ODA monomer are shown in Fig. 2 [15, 16]. The valence angles in the polymer chain have a well-defined value and the thermodynamic rotation of the links occurs without changing the valence angles. Therefore, chain links are not arranged arbitrarily, but the position of each subsequent link is dependent on the previous one. The measure of the flexibility of the polymer chain is the length of the Kuhn segment (statistically independent element or segment of the chain, the position of which does not depend on the position of neighboring elements) [17]. For PMDA/ODA polyimide number of links in the Kuhn segment ≈ 320 [18]. However, the degree of polymerization of an industrial polyimide film PMA ≈26÷260, i.e. within a single molecular chain there is only one statistically independent segment. Therefore, PMDA/ODA polyimide refers to the so-called rigid-chain polymers for which the turns of one part of the chain relative to the other are very difficult. Unlike flexible-chain polymers where the equilibrium state is a folded conformations (statistical

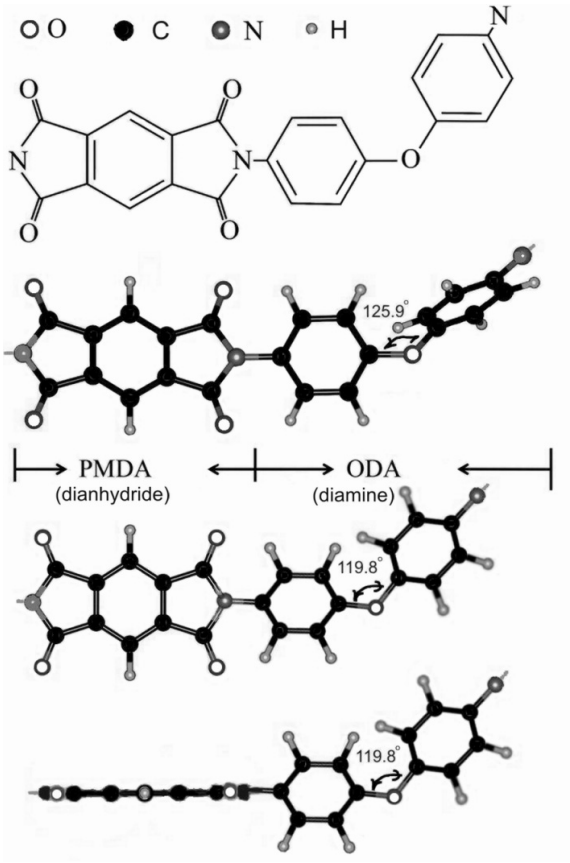

Fig. 2. Possible conformations of PMDA/ODA monomer according to nuclear magnetic resonance data [15], theoretical modeling by the DFT method (density functional) and scanning electron microscopy [16].

tangle), rigid-chain polymers are characterized by straightened conformations tending to certain orderliness (state with a minimum volume). The stable conformation of the PMDA/ODA polyimide is a crankshaft. According to molecular modeling data [19], only small conformational bends are possible on the molecular chain, see Fig. 3.

The temperature dependences of the dynamic elastic modulus $E_D(T)$ and acoustic absorption of PMDA/ODA polyimide are studied in the temperature range 4.2–350 K. Acoustic properties were studied by dynamic resonance mechanical spectroscopy. The studied samples were in the form of thin plates (4×20×0.08 mm^3). Electrostatic methods were used to excite and record forced resonant flexural vibrations in the cantilever specimen. The measurements were carried out at a frequency of about 20 Hz in an amplitude-independent region of deformation $\varepsilon_0 \sim 10^{-7}$. The surface of the studied samples was covered with a thin (0.03 μm) electrically conductive aluminum layer to ensure electrostatic excitation and registration of vibrations.

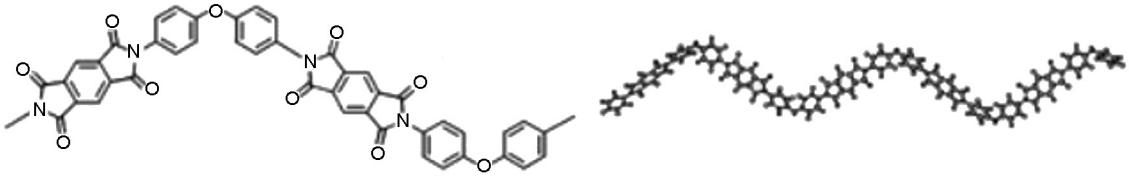

Fig. 3. One of the possible conformational configurations of the polymer chain of PMDA/ODA polyimide (molecular modeling) [19].

The value of the dynamic modulus of elasticity E_D was calculated from the resonant frequency f of oscillation of the sample [20]:

$$E_D = 12 f^2 l^4 \rho (0.55966 h)^{-2}, \quad (1)$$

l, h — sample length and thickness, respectively and ρ — density.

And the acoustic absorption $\delta(T)$ is proportional to the electrostatic driving force [21, 22].

Since the literature data for the linear thermal expansion coefficient of PMDA/ODA polyimide in the temperature range of 4.2–350 K are not available, an empirical Barker relation was used to calculate the linear dimensions of the sample at temperatures different from room temperature [23]:

$$\alpha^2 E_S \sim 15 \cdot [N \cdot m^{-2} \cdot K^{-2}], \quad (2)$$

E_S — static elastic modulus.

This ratio holds true for most glassy linear and crosslinked polymers. Since $E_S \leq E_D$, then the ratio (2) allows to estimate the possible error in determining the absolute value of the E_D due to a change in the linear dimensions of the sample as the temperature changes. Estimates show that this error is no more than 2 %.

Temperatures below room temperature were obtained by cooling with cryogenic liquids and their vapors (4.2 K – 77.4 K — liquid helium, 77.4 K – 300 K — liquid nitrogen). Before the start of acoustic measurements, the measuring cell with the sample placed in it was cooled to the temperature of liquid helium. Temperature dependences of acoustic characteristics were recorded with an increase in temperature from 4.2 K to 350 K. The rate of temperature change was ~ 0.7 K/min. The temperature was measured with an accuracy of 50 mK (in the temperature range 4.2 – 30 K using an AsGa thermometer, and in the temperature range 30–350 K using a copper-constantan thermocouple) and regulated by a resistive heater. Temperature change, registration of temperature dependences of the dynamic elastic modulus and acoustic absorption was carried out in automatic mode under the computer control [24, 25].

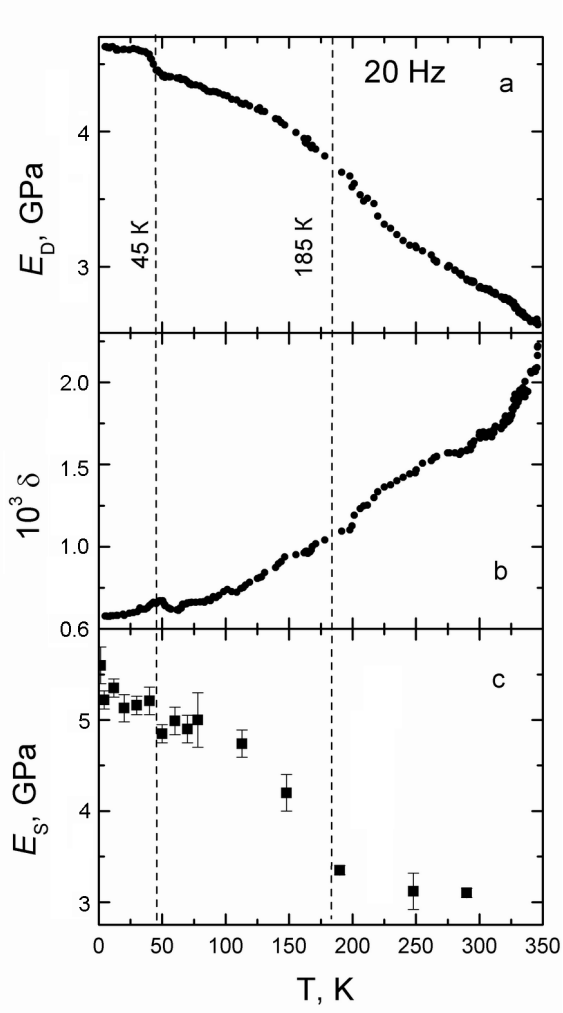

Fig. 4. Temperature dependences of the dynamic Young modulus (Fig. 4a) and the logarithmic damping decrement (Fig. 4b) as well as static Young's modulus [8–10] (Fig. 4c) of industrial polyimide film PMA.

The method of non-destructive mechanical spectroscopy used in this work combines high structural sensitivity, selectivity and accuracy. The temperature dependences of the dynamic elastic modulus $E_D(T)$ obtained in this work are compared with the temperature dependences of the quasistatic elastic modulus $E_S(T)$ obtained earlier [8–10]. In [8–10], the temperature depend-

ence of the quasistatic elastic modulus $E_S(T)$ was obtained from the data on uniaxial tension in the creep mode at a constant temperature [26]. In these experiments, the load on the sample was changed stepwise in small increments, and the value of the static elastic modulus $E_S(T)$ was calculated from the corresponding strain increase [8].

The samples studied in this work and in [8–10] were cut from one batch of industrial film of PMDA/ODA polyimide (PMA polyimide).

3. Results and discussion

It has been established that a change in temperature from 4.2 K to 350 K leads to a decrease in the dynamic elastic modulus $E_D(T)$ from 4.7 GPa to 2.6 GPa (in this case, the frequency of resonant oscillations of the sample varies from 25.71 Hz to 18.96 Hz). The experimental data for the dynamic $E_D(T)$ and quasistatic $E_S(T)$ [8–10] Young moduli are in good qualitative and (with allowance for experimental error) quantitative correspondence. On the temperature dependence of the elastic modulus, two anomalies ("steps") were found at 45 K and 185 K. The "step" of the modulus at 45 K corresponds to a peak of acoustic absorption $\delta(T)$. An increase in temperature from 4.2 K to 350 K leads to a significant (~ 1.8 times) change in the elasticity modulus which indicates that in this temperature interval there is a fairly intense mobility of large kinetic elements.

It is known that in an isotropic solid the speed of longitudinal c_l and transverse c_p sound waves is associated with the elastic characteristics by the relations [20]:

$$c_l^2 = \frac{E}{\rho} \cdot \frac{1-\nu}{(1+\nu)\cdot(1-2\nu)} \quad \text{and} \quad c_t^2 = \frac{G}{\rho} = \frac{E}{2\rho(1+\nu)}, \tag{3}$$

G — shear modulus and ν — Poisson's ratio.

The results of numerous experimental studies performed at both low and high frequencies show that the speed of sound in polymers linearly depends on temperature [27–29]. The temperature coefficient of sound velocity changes abruptly only at those points where the character of the molecular motion changes. Thus, the defrosting of one or another type of molecular motion is indicated by the peculiarities of the temperature dependence of the speed of sound or the corresponding elastic modulus.

It is known that in polyimides the relaxation process at 185 K is related to the so-called β-relaxation [30]. It is believed that the β-process is responsible for the movement of chain segments that include imide groups that are free from hydrogen bonds with similar groups of neighboring macromolecules [31, 32]. β-Relaxation occurs only in the amorphous regions of the polymer [33].

It is considered that in linear polymers that do not have side groups suspended from the main chain, the maxima of acoustic losses below 100 K (known as δ-peaks) can only be associated with the presence of ordered regions [27, 30]. For example, in [34] a peak of acoustic absorption was registered in polyethylene at 48 K. This peak is absent in the annealed samples and occurs when orientational stretching or under the influence of thermoelastic stresses. Temperature and mechanical effects can lead to structural changes in hard chain polymers [35, 36].

The existence of an amorphous halo on radiographs of an amorphous PMDA/ODA polyimide shows that it is not a completely disordered system, it contains local regions in which the short-range order is preserved [8, 14].

The δ-relaxation mechanism is associated with the interaction of conformational kink-like defects in the almost parallel folding of molecular chains [34, 38]. The hypothesis about the possible presence of such defects was put forward in [39–41] and then confirmed theoretically [42] and experimentally [43, 44]. The appearance of ordered regions in PMA polyimide under influence of thermoelastic stresses was experimentally recorded in [8]. The analogue of this process is the mechanism of the Bordoni peak in fcc metals [45, 46].

Analysis of the shape and temperature for the localization in the resonance experiment allowed us to estimate the energy of activation is responsible for their processes [47]: δ-relaxation ~ 0.05 eV; β-relaxation ~ 0.7 eV. These estimates are consistent with the characteristic values for relaxation processes of this type [27, 33].

It is known that a change in the degree of imidization can significantly change the mechanical properties of polyimide. In this work it was studied samples of industrial film PMA for which this parameter is not standardized. Perhaps this circumstance is connected with the fact that the values of the dynamic module registered in the presented work are less than the values of the static module obtained earlier [8–10]. It should be noted that a change in the degree of imidization should not significantly affect the temperature of localization of the registered acoustic properties.

5. Conclusions

For the first time the low-temperature acoustic properties of an industrial polyimide PMA film have been experimentally studied.

Two low-temperature relaxation processes on the temperature dependences of the acoustic properties of the PMDA/ODA polyimide are recorded: δ-relaxation at 45 K and β-relaxation at 185 K.

Estimates of the activation energy for low-temperature relaxation processes in kapton are obtained: δ-relaxation — ~0.05 eV, β-relaxation — ~0.7 eV.

A microscopic interpretation of the mechanisms which is responsible for the occurrence of δ and β relaxation in the PMDA/ODA polyimide is proposed.

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