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Characteristic Features of Relaxation Processes in Thermoplastic Heat-Resistant Polymers Related to their Structure

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The article presents an analysis of structure-property relations of thermoplastic heat-resistant polymers (HRP) polyimides and polybenzoxazole evaluating stress relaxation conditions. The main characteristic features of mechanical behavior of HRP, such as very high glass transition temperatures (250 – 500 °C) and existence of relaxation ss-transitions (solid-solid transitions) were considered in comparison to peculiarities of their chemical structure and morphology. The influence of of hinge-type groups in polymer macromolecules on glass transition and relaxation transition temperatures was assessed.

Keywords: heat–resistant polymer, stress relaxation, glassy-state transition, relaxation ss-transition, morphology, X-ray diffraction.

INTRODUCTION

Thermoplastic heat-resistant polymers (HRP) take very important place in a large variety of different structural materials [1, 2]. Aromatic structures of macromolecules define high glass transition temperatures of HRP (210 – 520 °C) and overall balance of their thermal-mechanical properties in a wide range of high and low temperatures [3 – 6]. The high values of glass transition temperatures enable HRP to be applied in the extreme loading conditions where mechanical relaxation processes are clearly expressed and have essential influence on mechanical behavior [5 – 8].

Structure of polymers is one of main factor, which governs the behavior of solid material being under action of external forces [3 – 6]. Relaxation processes and viscoelastic properties of HRP also depend on such very important factors as temperature, level of strains and stresses, loading type and deformation rate [7].

The mechanical behavior of some thermoplastic HRP under stress relaxation conditions was investigated in the range of high and low temperatures and analysed in [9 – 12]. On a basis of investigation results obtained, the main features of relaxation processes of HRP were determined and characterised.

Heat-resistant polymers have aromatic structure of macromolecules that lead to complicated conditions of supermolecular structure formation process [3, 13]. For evaluation of relaxation processes in various types of HRP and application of such high performance materials it is very important to know their structure-property relations.

RESEARCH PROCEDURES

For analysis of structure-property relations of HRP the high-performance polymers such as two different types of polyimides (PI2, PI3) and polybenzoxazole (PBO) were considered [12]. The specimens of block-shaped material were produced by the method of compression moulding at high temperatures (370 – 520 °C) and pressures (50 – 200 MPa) with further application of machining. Processing conditions of investigated HRP and optimisation of their technology were considered in [14].

For investigations of mechanical behavior of HRP the small-scale specimens were applied with gauge dimensions $3 \times 3 \times 4.5$ mm. The investigations of relaxation processes were performed under uniaxial compression in isothermal and non-isothermal stress relaxation conditions. The levels of initial strains and stresses were varied covering regions of linear and non-linear viscoelasticity. The ranges of temperatures were varied in the limits from low of –170 °C up to the region of glass transition (softening) temperature of a polymer.

The glass transition temperatures of HRP were determined applying the temperature-scanning method with constant temperature elevation rate (β_T = 4 °C/min) [7]. For investigation of polymers structure and their morphology, the X-ray diffraction (DRON-6, CuK$_\alpha$ radiation, λ = 1.537 Å) and scanning electron microscopy (JEOL JES-5600) methods were applied.

For analysis of morphology by scanning electron microscopy (SEM) the surface of polymer was obtained due to brittle fracture of block-shaped specimens in the liquid nitrogen. The surface of polymer before it analysis by SEM was coated by thin layer of Cu (copper) in vacuum.

GLASSY-STATE TRANSITIONS

For development of high-performance thermoplastic heat-resistant polymers (HRP) the specific monomer compounds are used. Such polymers have in their backbone the aromatic rings and contain various heterocycles [3 – 5]. The corresponding heterocycles being in the backbone define such well-known HRP as polyimides, polyamide–imides, polybenzimidazoles, polybenzoxazoles, polyoxadiazoles and others.

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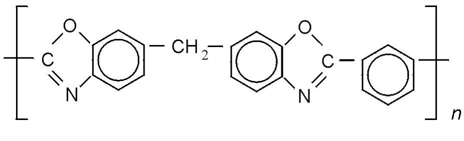
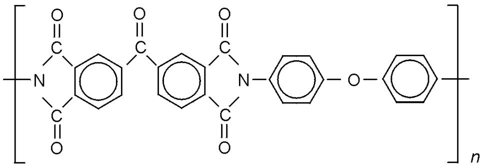
The thermoplastic HRP applied for investigations of their structure-property relations have different chemical structure of monomers, which is represented as follows:

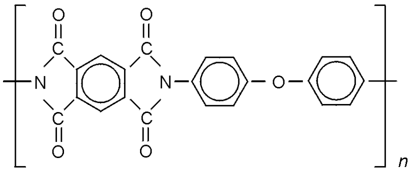
Polybenzoxazole (PBO)



Polyimide (PI2)



Polyimide (PI3)



According to the represented monomer structure the main chains of macromolecules of investigated HRP contain aromatic rings, various heterocycles and different number of hinge-type links. Aromatic rings or cyclic groups in the backbone reduce flexibility and add bulkiness. Flexibility and bulkiness of the monomer unit and the polymer chain that is built from it influence some important properties directly [3 – 7].

For thermoplastic HRP as materials developed for high-temperature service primarily the thermal characteristics as the most important are to be evaluated. The importance of glass transition temperature as a material property can be understood in terms of loss of rigidity that accompanies the transitions. Hence, the T_g as the key controlling parameter in the time temperature- dependent viscoelastic behavior of a polymer is often an important factor in the determining the usefulness of a given polymer [1, 2].

The glass transition temperature for solid polymers of various structures may be determined applying the non-isothermal stress relaxation method [7]. The curve $\sigma_m = f(T)$ is considered as response of a material being under sustained constant strain in conditions of continuously heating.

The results of test data usually are represented as stress relationships with respect to temperature and known as stress relaxation curves in non-isothermal conditions [7]. Such curves have maximum, which corresponds to the stress σ_m. The relationships $\sigma_m = f(T)$ constructed for various polymers are shown in Fig. 1.

The curves $\sigma_m = f(T)$ that confine the region of stresses and temperatures at which polymer behaves like a solid material enable to determine glass transition or softening temperatures of investigated HRP.

According to these results investigated HRP are characterized by very high glass transition (softening) temperatures, which are different for the definite polymer and being of 250 °C (PBO), 380 °C (PI2) and 500 °C (PI3).

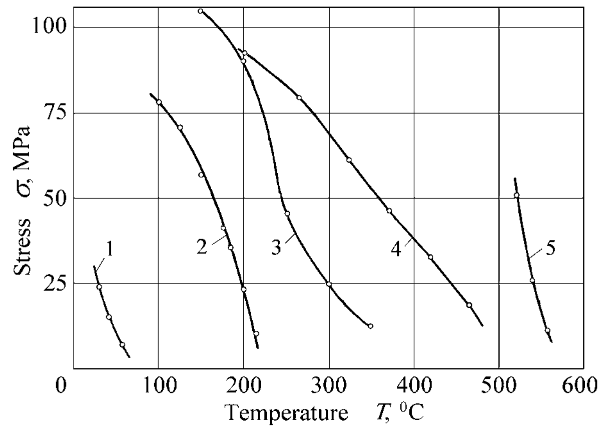


Fig. 1. The relationships of $\sigma_m = f(T)$ for various polymers: 1 – polymethylmethacrylate (PMMA), 2 – polybenzoxazole (PBO), 3 – polyimide (PI2), 4 – polyimide (PI3), 5 – potassium-silicate glass. Curves 2 – 4 are obtained in this investigation, the rest of them are adopted from [3]

Essential difference in the values of glass transition temperatures, and of course in the properties of various types of HRP primarily is dictated by the monomer structure, which in its turn is influenced by basic chemical composition. The T_g increases with the stiffness of the backbone of the polymer chain. The higher energy barrier of main chain the larger rotational movement necessary for long-range than for short-range segmental motion associated with T_g.

Thus, by introducing in polyimide PI2 main chain additionally to hinge-type link –O– such link as –CO– it is possible to change it flexibility and create plastic material compared to the brittle polyimide PI3. But increase of flexibility of macromolecules of such polymer is related to decrease of glass transition temperature (Fig. 1, curve 3).

Increase of rigidity of polymer macromolecules leads to an essential change of it glass transition temperature. Such relationship is evident considering polyimide PI3 monomer structure (Fig. 1, curve 4). Not so high glass transition temperature for PBO is dictated by the monomer structure of such heat-resistant polymer (Fig. 1, curve 2). Various hinge-type links change essentially the flexibility of macromolecules as well as heat resistance of material but thermal stability of polymers usually remains equivalent [4, 5].

The curves $\sigma_m = f(T)$ also let to compare various types of polymers with respect to the levels of they load-bearing capability. The load-bearing capability in non-isothermal conditions means the ability of a polymer to resist failure and softening within the entire range of temperatures, stresses, and strains possible for that polymer. These questions were considered in detail in [12].

According to the results obtained the increase of rigidity of polymer macromolecules leads also to an essential increase of stress level possible for different polyimides at the same temperature regions (Fig. 1, curves 3, 4). Chemical composition and structure of PBO macromolecules do not enable to get high levels of stresses and temperatures compared to polyimides (Fig. 1, curves 2 and 3, 4).

The glass transition temperature for amorphous polymers reflects the transition of a material from the rubbery state to the glassy one. The inter-conversion of these two states by cooling or heating is known as main or second-order transition [4, 5]. A drop of several decades in the modulus of elasticity from a common value at T_g is usually observed above the transition temperature.

Below the glass transition temperature the amorphous polymers show secondary transitions, which also have influence on viscoelastic properties of a material. The effects of secondary transitions are smaller and are often less obvious. Such transitions can be detected by studies of dynamic mechanical spectrometry, by nuclear magnetic resonance, or by electric loss measurements over a range of temperature [3, 15].

RELAXATION SS-TRANSITIONS

On a basis of investigations under isothermal stress relaxation conditions the relaxations ss-transitions (solid-solid transitions) in HRP were disclosed [9 – 11]. Such transitions in the glassy-state of a polymer may be detected applying relationships $\lambda_r = f(T)$, where λ_r is the parameter of stress relaxation. Summary of results of investigated polymers is shown in Fig. 2.

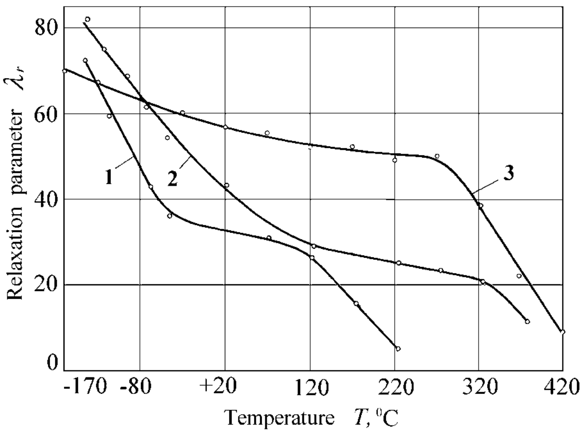


Fig. 2. Relationships of relaxation parameter λ_r with respect to temperature for various HRP: 1 – polybenzoxazole (PBO), 2 – polyimide (PI2), 3 – polyimide (PI3)

The relaxation parameter λ_r expresses the inverse value of rate of relaxation process going on in a polymer being under load. The larger values of relaxation parameter λ_r correspond to the slower rates of relaxation processes and vice versa. This parameter reflects the relaxation processes in the region of linear as well as non-linear viscoelasticity [11]. The relaxation ss-transitions in HRP are considered as intrinsic material-dependence phenomenon and reflect increase or decrease relaxation processes with respect to temperature at the definite it regions.

In general, the relaxation ss-transitions for HRP determined on a basis of relaxation data may be in the region of high (Fig. 2, curves 2, 3) as well as low temperatures (curve 1). Considering a wide range of glassy-state temperatures from glass transition temperature up to –170 °C only two ss-transitions for HRP were detected. The values of relaxation transition temperatures for investigated HRP are represented in Table 1.

This points to the fact that ss-relaxation transitions occur long before to the glass transition temperature (Table 1) and they are the result of acceleration of relaxation processes in a solid state. The definite transition temperatures T_{ss} correspond to the certain relaxation ss-transition and divide the temperature range of glassy-state into some sub-states with different rates of relaxation process.

Table 1. Characteristic temperatures of HRP

Polymer	Characteristic temperatures *T*, °C		
	T_g^*	T_{ss1}	T_{ss2}
PBO	250	–70	120
PI2	380	110	300
PI3	500	40	300

According to the results represented in Fig. 2 the shape of relationships and location of relaxation ss-transitions for various polymers are different. The values of relaxation parameter λ_r that are related to the rates of relaxation process vary in very wide limits.

The intensity of relaxation processes in the region of low temperatures for all considered HRP is essentially lower than that being in the region of high temperatures (Fig.2, curves 1-3). For considered HRP of different macromolecular structures the relationship $\lambda_r = f(T)$ is expressed by a curve having characteristic shape with the definite regions of relaxation ss-transition temperatures.

The regions of relaxation ss-transition temperatures depend on macromolecular structures of HRP. The relationships $\lambda_r = f(T)$ of polymers with larger rigidity of macromolecular chain are shifted to the side of higher temperatures (Fig. 2, curves 2, 3). But according to the results obtained the λ_r may occur in the different regions of glassy-state.

Intensity of relaxation processes of different HRP in the same temperature interval depends on monomer chemical structure and composition as well as on rigidity of macromolecular chain. Thus, the polyimide PI3 with larger rigidity of macromolecular chain is characterizing by less intensive relaxation processes even in the region of rather high temperatures (Fig. 2, curve 3 is shifted to the side of higher values of λ_r).

The relaxation ss-transition temperatures for the same HRP investigated under different loading conditions (tension, compression, stress relaxation, creep) were obtained in the same temperature regions [11]. But intensity of relaxation processes for the same polymers due to various loading conditions was different.

In stress relaxation and creep conditions the intensity of relaxation processes differs non-essentially and usually is of same order. Essential increase of intensity of relaxation processes is noticed under tension conditions [11]. Thus, comparison and analysis of intensity of relaxation processes on a basis of relaxation parameter λ_r have sense only in the case of the same loading conditions.

STRUCTURE-PROPERTY RELATIONS

At present time the main attention of structure-property investigations of HRP is devoted to influence of

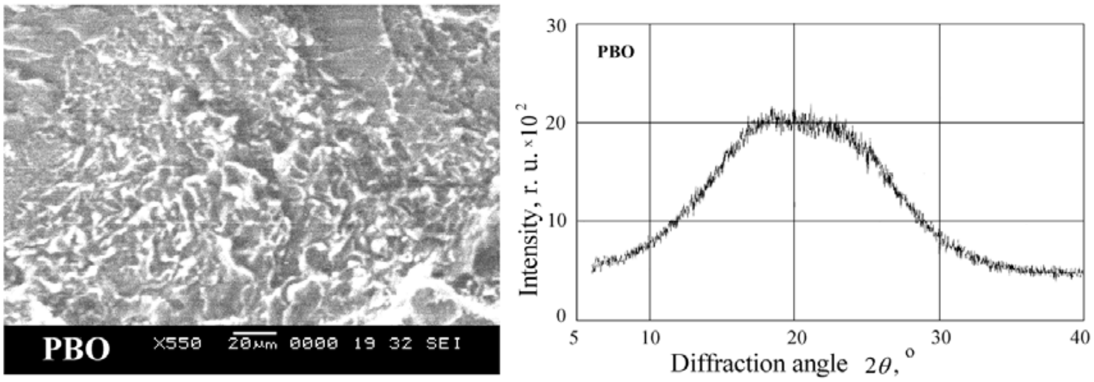


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Fig. 3. The SEM microphotograph (×550) of polybenzoxazole (a) and X-ray diffraction pattern (b)

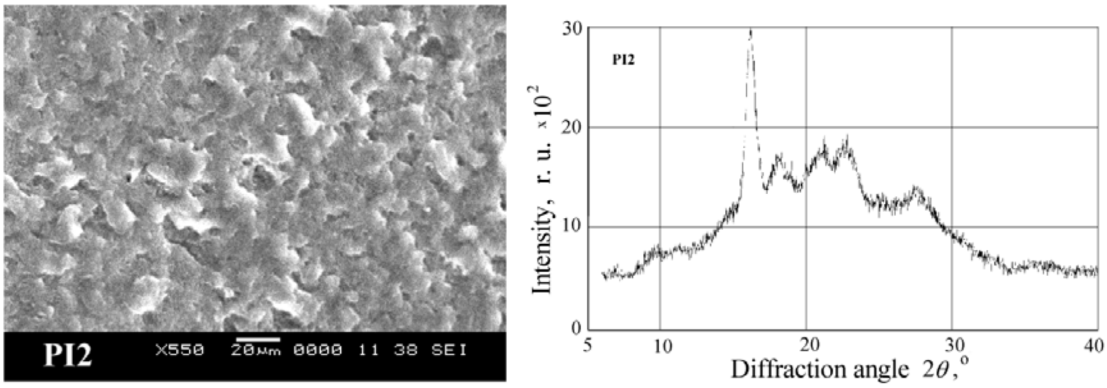

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Fig. 4. The SEM microphotograph (×550) of polyimide PI2 (a) and X-ray diffraction pattern (b)

chemical structure. By changing chemical structure and composition of monomers the properties of HRP can be regulated in a rather wide range [3, 5].

Investigated thermoplastic HRP are composed almost completely of linear chains. But aromatic structure of HRP and rather large rigidity of chains lead to very complicated conditions of supermolecular structure formation process.

The SEM microphotograph of polymer PBO and it X-ray diffraction pattern are represented in Fig. 3, a and b.

According to the X-ray diffraction results PBO produces diffuse halo, which is characteristic for polymers with amorphous structure (Fig. 3, b). The supermolecular formations of PBO are constituted by structure elements of various shapes and have complicated arrangement, which is seen on the SEM microphotograph (Fig. 3, a).

The SEM microphotograph of PI2 and corresponding X-ray diffraction pattern are represented in Fig. 4, a and b.

The hinge-type groups in the main chain of polyimide PI2 are involved and flexibility of macromolecules to some extent is increased. According to the X-ray diffraction results polymer PI2 has tendency to crystallization, which passes in such type of polymers in a rather complicated manner [3, 13].

The X-ray diffraction pattern of PI2 illustrates an existence of limited amount of short-range order in the considered polymer. The supermolecular formations of PI2 are constituted by globular-type structure elements of various shapes and have definite arrangement, which is seen on the SEM microphotograph (Fig. 4, a).

The SEM microphotograph of PI3 surface and X-ray diffraction pattern are represented in Fig.5, a and b.

The X-ray diffraction pattern of polyimide PI3 also illustrates an existence of limited amount of short-range order in such polymer. Similar arrangement of supermolecular formations based on globular-type elements is also seen on the SEM microphotograph of polyimide PI3 (Fig. 5, a).

The dimensions of globular-type structure elements vary in the range of 7 – 10 µm. The structure elements may be considered as roughly spherical particles of relatively large size. Without more detailed investigations it is not possible to say definitely the nature of creation of such oblong structural formations based on globular-type structure elements.

The arrangement of structure formations for polyimides PI2 and PI3 (Fig. 4 and 5) is more expressed compared to polybenzoxazole structure arrangements (Fig. 3). The amorphous halo overlapped with the most intensive peaks of X-ray diffraction patterns of polyimides PI2 and PI3 indicates that the disordered phase coexists with the certain ordered phase.

The smallest structural elements of all investigated HRP seen on the microphotographs obtained applying SEM method (× 300 000) are distributed rather uniformly and have globular-type elements with the similar their size. As an example such structural arrangement for polyimide PI3 is represented in Fig. 6.

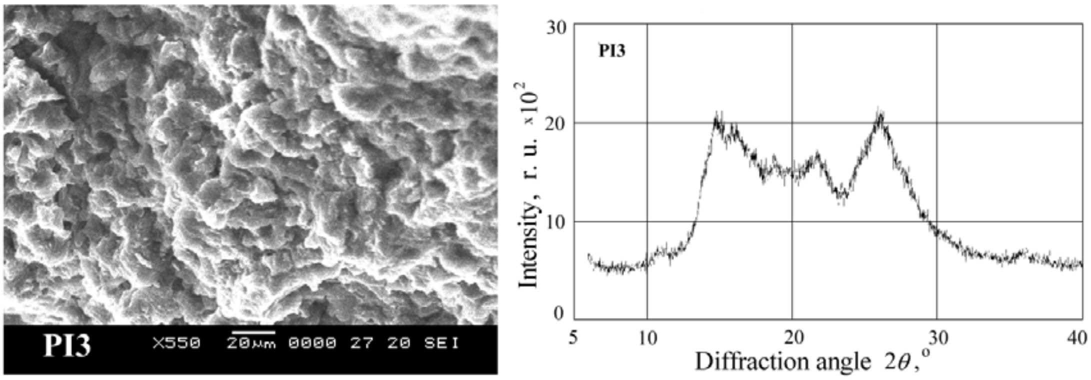

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Fig. 5. The SEM microphotograph (× 550) of polyimide PI3 (a) and X-ray diffraction pattern (b)

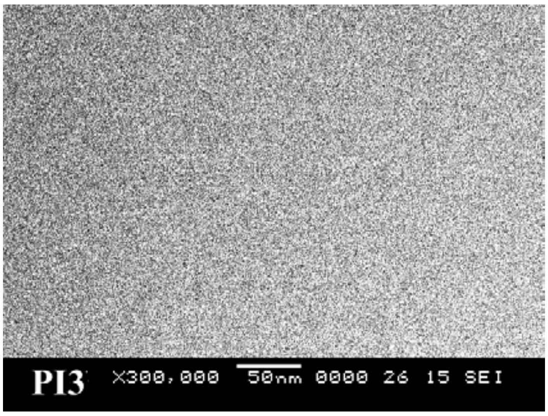

Fig. 6. The SEM microphotograph of PI3 (× 300 000)

Evaluation of influence of structure on mechanical properties of HRP is a rather complex question. Aromatic structures of monomers, various types of interactions involved in the definite units within the macromolecule and between the macromolecules lead to very complicated conditions of supermolecular structure formation process [3, 13, 16, 17]. Thus, considered circumstances let to disclose only main relationships between relaxation behavior and structures of such heat-resistant polymers.

CONCLUSIONS

Applying the data of stress relaxation and different methods of structure investigation (X-ray diffraction and scanning electron microscopy) the structure-property relations on example of heat-resistant polymers polybenzoxazole (PBO) and polyimides (PI2 and PI3) were investigated.

Hinge-type groups –O– and –CO– being in the aromatic monomer structure of investigated heat-resistant polymers lead to an increase of flexibility of main macromolecular chains and as result the relaxation processes become more expressed.

The X-ray diffraction patterns of polybenzoxazole produce diffuse halo, which is characteristic for amorphous polymers. In the structure of polyimides PI2 and PI3 according to the X-ray diffraction patterns a limited amount of short-range order exists and the disordered phase coexists with the certain ordered phase.

The supermolecular formations of investigated polyimides PI2 and PI3 are constituted by globular-type structure elements the dimensions of which vary in the range of 7 – 10 µm. The smallest structural formations of investigated polybenzoxazole and polyimides have uniformly arranged globular-type elements with the similar their size.

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