Predicting the properties of polymeric materials from data of relaxation spectrometry

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The diagnostics of polymers consists in establishing the relationship between composition, structure, and their properties. Prognosis is the scientifically sound prediction of the behaviour of polymeric materials both under different service conditions and during their storage for a long period of time. Both diagnostics and prognosis can be carried out most effectively using data of relaxation spectrometry, which makes it possible to observe the appearance, in wide temperature and frequency ranges, of a sudden change in molecular mobility. Each of these regions is characterised by quite specific values of their parameters (the most probable relaxation time, the activation energy, the relaxation time distribution function, and the parameter of the width of the relaxation spectrum). Between these regions, which have the form of maxima of dielectric (or mechanical) losses, there are intermediate intervals with stable values of the corresponding physical quantities. The relaxation maxima are characterised by four parameters, one of which (the width of the maximum at its half-height) characterises the degree of structural inhomogeneity of the polymer. The magnitude of this size depends on the composition and on the structure of the polymers, i.e. makes it possible to carry out the diagnostics of the properties of the polymers. The value of the width of the intermediate intervals (“plateau” sections) makes it possible to carry out prognosis of the properties of the polymers. Investigation of the influence on the parameters of the half-width of the maxima and the width of the “plateau” of modifying factors (the introduction of plasticisers and fillers into the polymers) makes it possible, according to data of single measurements of the temperature–frequency dependences of different physical quantities, to carry out the diagnostics and prognosis of the properties of polymers.

An examination is made of the results of investigating molecular mobility in single-component and composite polymeric systems. Single-component systems differ in chemical composition and molecular and supermolecular structures. Some of them are non-crystalline (amorphous), while others are characterised by a different degree of crystallinity. Composite polymeric systems consist of high and low molecular weight components characterised by a different degree of compatibility and properties, depending on their type and ratio.

In connection with the considerable widening of the areas of application of different polymeric materials in engineering and commercial industry, a comprehensive investigation of the relationship between their chemical, molecular, and supermolecular structures and physical properties is extremely urgent. Taking into account that real polymeric materials containing different ingredients (plasticisers, fillers, etc.) are multicomponent and consequently structurally inhomogeneous systems, their investigation is particularly important. Since processes of structure formation processes and the different physical properties of such polymeric systems are influenced considerably by the relaxation processes occurring in them, the most effective means of diagnosis and prognosis is to study the nature of molecular mobility in wide temperature–time ranges under the action of different force fields [1]. Processes of molecular mobility in structurally inhomogeneous polymeric systems of different
classes determine all their physical properties.

The investigation was carried out on single-component and composite polymeric systems characterised by different forms and nature of structural inhomogeneity. A comparative study was made of processes of molecular mobility both in model and in industrial specimens. Aromatic polysulphones with a linear structure of chains, fluorine-containing polymers with small side chains, and polyorganosiloxanes with branches of different sizes were investigated as single-component polymeric systems. The composite materials studied were blends of polymers, the components of which differed considerably in chain flexibility and had different proneness to crystallisation. Their structural inhomogeneity was determined substantially by the presence of interfaces of polymer components incompatible at the molecular level.

To study the structure and properties of the indicated polymeric systems, use was made of a combination of different (main and secondary) physical methods making it possible to obtain mutually complementary information. Here, the use of methods of relaxation spectrometry in mechanical, electrical, and magnetic fields proved to be most effective. Interpretation of the results obtained in this case was carried out on the basis of state-of-the-art models of single-component and composite polymeric systems. Single-component polymeric materials were examined as complex systems consisting of several weakly interacting subsystems. With the probing of such systems by different external force fields, the responses of subsystems comprising a combination of relaxers (kinetic units) appear. For composite polymeric systems, of most importance is the presence of boundary layers separating the molecularly incompatible components with significantly differing physical characteristics and a different number of linear defects in the form of microcracks.

The physical quantities characterising the properties of the polymers investigated were calculated on the basis of experimental data using formulae obtained on the basis of state-of-the-art theories. On the basis of measurements carried out under conditions of the action of different force fields on the polymers investigated, it was established that the physical quantities characterising them in wide temperature-frequency ranges have substantial differences. For scientifically sound interpretation of the experimental data obtained, we used methods for calculating the activation energy and degree of structural inhomogeneity of the polymer systems investigated, using dual correlation diagrams and relaxation Debye spectrograms respectively.

An investigation of aromatic polysulphones showed that, in a wide temperature range, both local and segmental processes occur. The former are connected with the mobility of individual atomic groups, while the latter are governed by thermal motion of the kinetic units (or relaxers) of much greater size, which it is customary to call segments. Change in the local mobility in the polysulphone was observed close to +145°C, while processes connected with the motion of segments appeared in a fairly wide temperature range (from +190°C to 260°C). Here, on the basis of calculation of the temperature dependence of the longitudinal speed of sound \( v_{long} \), it was established that change in the segmental mobility in polysulphone occurs in two stages (the occurrence of a twofold change in the slopes of the rectilinear segments of the dependence \( v_{long} = f(T) \)). This indicates the presence in the polysulphone of structural inhomogeneity and gives grounds for separating their segments into free and combined (the latter lie on the boundaries of amorphous and crystalline regions, and therefore their relaxation processes are characterised by a larger activation energy). It must be pointed out that the relaxation properties of polysulphones of different types (industrial PSN-A and model PSN-D and PSN-S) have marked differences, which becomes particularly clear when their Debye spectrograms are compared. Here, according to data of dielectric relaxation spectrometry, the greatest degree of structural inhomogeneity is characteristic of model polysulphone PSN-S.

The heat-resistant fluorine-containing polymers PVF, PVDF, PCTFE, and PTFE investigated by us, differing in types of system, elementary cell periods, and density, are characterised by considerable differences in glass transition temperature, melting point, and temperature of thermal breakdown, and also different electrical properties. The greatest values of the temperature of thermal breakdown (428°C) and electric strength (27 MV/m) are characteristic of polytetrafluoroethylene which has a triclinic system and a density of 2.25 g/cm³. At the same time, it has the lowest (compared with the other fluorine-containing polymers) dielectric losses and permittivity (at a temperature of 20°C and a frequency of 1 kHz) \( \varepsilon = 10^{-4} \) and \( \delta = 2.2 \). For all fluorine-containing polymers, broad maxima of dipole-group and dipole-segmental dielectric losses appear, which indicates structural inhomogeneity both in the amorphous and in the crystalline parts [2]. It can be changed by heat treatment schedules for the quenching and annealing of specimens. Data obtained as a result of investigations of the dielectric properties of fluorine-containing polymers at various temperatures and frequencies indicate the presence of a distribution (spectrum) of relaxation times (in all cases, the value of \( \Delta \varepsilon(w/w_{max}) \) was considerably greater than the magnitude of 1.2 logarithmic decades that follows from Debye theory with a single relaxation time). For an analysis of the nature of the relaxation spectra of fluorine-containing polymers, arc diagrams were plotted in \( \varepsilon'–\varepsilon'' \) coordinates. Here it turned out that the dependences \( \varepsilon'' = f(\varepsilon') \) of fluorine-containing polymers differ from symmetrical Cole arc diagrams. This indicates the presence of two types of relaxation spectrum relating to segmental mobility in the amorphous and crystalline parts of specimens. From the obtained asymmetrical diagrams in \( \varepsilon'–\varepsilon'' \)
coordinates, values of the dielectric permittivities \( \varepsilon' = \varepsilon_0 \) (with \( w \to 0 \)) and \( \varepsilon'' = \varepsilon_\infty \) (with \( w \to \infty \)) were determined by extrapolation. It turned out that, with increase in the structural inhomogeneity of specimens after their quenching, the values of \( \varepsilon_0 \) and \( \varepsilon_\infty \) differ more substantially, whereas, after annealing, their difference \( \Delta \varepsilon = \varepsilon_0 - \varepsilon_\infty \) (characterising the effective dipole moment of the kinetic units oriented in a variable electric field) decreases. Consequently, by the annealing of fluorine-containing polymers, it is possible consistently to lower the degree of structural inhomogeneity, which promotes stability of their physical properties.

Investigation of polyorganosiloxane polymeric systems by the pulsed NMR method and the dielectric spectrometry method showed that, in a wide temperature range, both local and segmental processes appear in them, as indicated by the minima on the dependences \( T_1 \), \( T_2 = t \) (1/t), where \( T_1 \) is the spin-lattice relaxation time in a rotating coordinate system.

The former are connected with the limited rotational motion of \( \text{CH}_3 \) and \( \text{C}_6\text{H}_5 \) groups, and also with the mobility of side aliphatic radicals and individual fragments of the main chains. The latter are governed by rotational abrupt diffusion and random reorientations of atomic groups, depending considerably on the length and volume of the side branches. The true values of activation energy calculated from the dependences of the frequency of correlation on inverse temperature are in quite satisfactory agreement with the magnitudes obtained from experimental data for various processes. There is also sufficiently good agreement between the theoretical and experimental values of the times of spin-lattice relaxation \( T_1 \), that correspond to the temperatures of appearance of minima for various types of segmental mobility of single-component polymers and composites.

To establish the laws governing the influence on the change in the degree of structural inhomogeneity \( \Delta \) of the investigated single-component polymer systems and composites of various factors characterised by modifying parameters \( P_m \). Debye spectrograms of two types \( \text{tg} \delta/\text{tg} \delta = -\log \nu/\log \nu'' \) and \( \varepsilon''/\varepsilon' = -T/T_m \) were calculated and plotted, and from these the dependences \( \Delta = f(P_m) \) for PSN-S, PTFE, and polysiloxanes containing branches of different length and volume were calculated. An analysis of the results obtained indicates that, with increase in the frequency of action of the external field on polysulphone PSN-S \( (P_m = \nu) \) and with increase in the number of atoms \( n \) in branched polyorganosiloxanes \( (P_m = n) \), the degree of their structural inhomogeneity increases. At the same time, increase in temperature \( (P_m = t) \) for a PVDF specimen leads to a consistent decrease in the degree of its structural inhomogeneity, which indicates equalisation of the conditions of mobility of the segments.

The results of investigating composite polymeric systems consisting of amorphous and crystalline components show that the structural features of these composites, according to data of X-ray diffractograms, indicate a difference in their structural inhomogeneity. When only amorphous components are present in the composite, irrespective of their ratio, there are no reflexes on the diffractograms and in the range of angles \( 2\theta = 5–40^\circ \) there is only a blurred halo of different intensity. When one of the components of the composite is amorphous while the other is crystalline, single reflexes appear on the diffractogram (for polyethylene in the range of angles \( 2\theta = 21–23^\circ \)). However, if both components of the composite are partially crystalline, then double reflexes appear clearly on the diffractogram. Thus, for a PE + PP composite in a ratio of 1:1, reflexes relating to PE appear at 21–23°, and reflexes relating to polypropylene (PP) appear at 35–39°.

The study of molecular mobility in polymer composites consisting of two non-crystallising components differing in effective chain flexibility (PS + SKS-30 and PMMA + PBMA) showed that, in a wide temperature range, regions of relaxation appear that are clearly separated from each other, associated with change in the segmental mobility of the components. Between these regions there is a fairly wide temperature range in which the dynamic mechanical characteristics (the elastic modulus \( E_g \) and the factor of mechanical losses \( \text{tg} \delta \)) change without changing the temperature position of the regions of relaxation. It must be pointed out that, for composites of this kind, local mobility in the capture temperature range proves to be practically insignificant [3].

In the case of a composite consisting of amorphous and crystallising polymers, two or three regions of relaxation can appear, depending on the type and ratio of the components. Thus, a blend of amorphous elastomer SKB and crystalline PE with a ratio of 10 and 90 wt.% respectively is characterised by the presence of three maxima of internal friction. The appearance of an intermediate maximum indicates that, owing to diffusion of the flexible macromolecules of SKB into the amorphous part of PE, there is a change in the effective chain rigidity of the composite. A similar picture occurs for a blend of amorphous elastomer SKMS-30 and crystalline PP. It is customary to call composites of this kind “quasicompatible”.

Composites with both crystalline components are characterised by an even more complex picture of occurrence of relaxation processes. For a PP + PE blend, the two components of which have both amorphous and crystalline phases, molecular mobility with increase in temperature is initially realised in disordered amorphous regions of these polymers, and then at their boundaries with crystalline regions, while at higher temperatures it is also realised in ordered structures. The dynamic elastic modulus \( E_g \) of this blend occupies an intermediate position compared with \( E_g \) of each component, while the level of its mechanical losses \( \text{tg} \delta \) is higher than for PP but lower than for PE. This may be explained on the basis of concepts of the presence in the given composite of two
interpenetrating frameworks consisting of ordered structures of PP and PE. In the case of a PE + SKI-3 composite, maxima appear at 212 K (SKI-3) and 252 K (PE) that are governed by change in the segmental mobility of the components, while at 303 K there is an intermediate maximum connected with motion of segments at the boundaries of the ordered and disordered regions. Finally, at 402 K a relaxation transition occurs, governed by chain mobility in the crystalline phase of the composite. The practical importance of such composites consists in their being materials combining good deformation and strength properties, as the crystalline polymers contained in them act as reinforcing agents promoting the strengthening of the elastomers [4].

In the study of polymer composites containing crystalline components, it is important to assess the degree of their compatibility. Whereas methods of IR and UV spectroscopy do not make it possible to distinguish between mechanical mixtures and copolymers, methods of relaxation spectrometry make it possible to obtain for them substantially differing pictures with different ratios of the components both in mixtures and in copolymers. For PE + PP composites at temperatures ranging from −100°C to +40°C, two regions of relaxation clearly appear, relating to change in the segmental mobility of components. Here, the shape and height of the given maxima are determined by the proportion of the mixed components and depend on the degree of their mutual solubility. At the same time, for an ethylene–propylene copolymer, only one maximum of mechanical losses appears, the height and shape of which depends on the content of corresponding monomers (propylene and ethylene). The temperature position of this region of relaxation of the given copolymer is also determined by its composition, while the maximum magnitude of mechanical losses $\tan \delta$ with a change in the propylene content of up to 50% is proportional to its concentration. Differences in the nature of intra- and intermolecular interaction in copolymers and corresponding blends of polymers also determine the different laws governing the macroscopic manifestation of processes of molecular mobility with change in the concentration of the corresponding components.

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