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Structural Aspects of Modification of Polymers with Low-Molecular-Mass Substances

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Specific features of polymer modification based on complexation between low-molecular-mass modifying agents and polymers were discussed in terms of structural inhomogeneity of amorphous glassy polymers. Complexation between low-molecular-mass compounds (LMs) and polymer macrochains in structural regions with different packing densities was shown to be responsible for the distribution of LMs between two forms, which are characterized by different energetics of interaction with polymer matrix. The occurrence of such distribution was controlled by chemical structure of LM molecules and local packing of polymer macrochains. This distribution was responsible for a complicated character of molecular dynamics in the polymer/LM systems and mechanical behavior of such materials in whole. The cases, when macroscopic mechanical behavior of as-modified polymers was primarily controlled by the form, in which the modifying agent existed in polymer matrix, were considered. The future development of this direction of polymer modification was discussed and possibilities of its practical application for controlled improvement in mechanical response of polymer materials were outlined.

Keywords: Polymers; low-molecular-mass compounds; interaction; complexation; structure; physical and mechanical properties

INTRODUCTION

In many cases physical modification of polymer materials may be achieved by introduction of compatible low-molecular-mass additives (plasticizing agents, dyes, reinforcing agents, flame-retardants, etc.)

into polymers. Compatibility of the components is controlled by nonchemical interaction between molecules of low-molecular-mass compounds (LMs) and polymer chains. Such interaction is provided by hydrogen bonding, electrostatic, dispersion, and similar interactions, which, in general case, are responsible for complexation between the components of polymer composites. Physical and mechanical characteristics of the as-modified polymer materials are decided, within the first approximation, by energetics of interaction between polymer chains and molecules of modifying agent.

In some cases LM molecules are known to be distributed within polymer matrix between two different forms, which are characterized by different energy of interaction with polymer [1–4]. As a result, physical and mechanical behavior of such complex polymer/LM systems shows a number of peculiar features. In particular, one and the same modifying agent may have quite an opposite effect on mechanical properties of the polymer depending on the form, in which it exists in polymer matrix [3, 5].

In connection with this, the studies on distribution of LM in polymer matrix between two forms are of great interest and will allow one to gain, on one hand, a deeper insight into the mechanisms of this phenomenon and, on the other hand, to take advantages of this phenomenon for controlled modification of the polymer materials.

The aim of the present work is to summarize the published data on interaction of LMs with polymers. The principle idea of this work is not to cover all the related aspects but to attract the attention of scientists to this fascinating problem and to outline general ways of its further development.

STRUCTURAL FEATURES OF POLYMER INTERACTION WITH LOW-MOLECULAR-MASS COMPOUNDS

In some cases, introduction of low-molecular-mass compounds (LMs) into the polymer materials is accompanied by distribution of LM between two different forms, which are characterized by different energy of interaction with polymer matrix. This phenomenon was described in publications devoted to modification of PA-6 with oxyaromatic compounds (OACs) [1, 2], sorption by Br₂ by PAN fibers

from aqueous bromine solutions [3], transport of dioxydine in ternary system based on dioxydine, water and copolymer of N-vinylpyrrolidone with methyl methacrylate [4].

In all cases, characteristic features of this phenomenon are the following. LMs, which were introduced into the polymer matrix from the swelling solutions (in all cases studied, aqueous solutions were used), appear to be distributed within the polymer matrix between two different forms, which are characterized by reversible or irreversible binding with polymer matrix. Hereinafter, such forms are referred to as reversibly (RB) and irreversibly bound (IB) states. As compared with IB form, RB form may be easily removed from the polymer matrix by keeping the polymer samples in a pure solvent (water).

The common feature of all the above polymer systems is related to the fact that LMs show a high affinity to polymer matrices. Thermodynamical studies of sorption of Br_2 by PAN fibers [3] and OAC by PA-6 films [2] revealed that partition coefficients of LMs between polymer matrices and aqueous media are rather high, that is, preferential sorption of LMs from their aqueous solutions is observed. In the cases studied, the origin of high affinity between polymers and LMs is related to complexation of molecules of LMs and polymer chains. In particular, interaction between Br_2 and PAN is associated with charge-transfer complexation between Br_2 and nitrile polymer groups [3]. In the case of the PA-6/OAC systems, complexation between polymer chains and molecules of LM is provided by hydrogen bonding of phenol hydroxyls of OAC with amide polymer groups [1, 6–11].

Kinetic and thermodynamic studies of sorption of Br_2 by PAN fibers from the bromine aqueous solutions at temperatures from 25 to 40°C allowed Lewin *et al.* [3] to advance the following mechanism of distribution of Br_2 in PAN matrix between IB and RB forms.

Interaction between PAN and LM was interpreted in terms of structural heterogeneity of amorphous component of semicrystalline polymer, that is, the coexistence of, at least, two different noncrystalline phases with different packing density and ordering. One should mention that the structural heterogeneity of the amorphous regions in semicrystalline polymers and completely amorphous polymers is an intriguing problem, which is being vigorously discussed in literature [12–18].

According to this approach, sorption of Br_2 by PAN fibers involves two stages [3]. The first stage is associated with polymer swelling in aqueous bromine solution. As a result, bromine appears to be dissolved in loosely packed regions of polymer amorphous phase and RB form is developed. At the second stage, bromine molecules diffuse to more densely packed regions, which are inaccessible to water molecules. In this case, bromine molecules disrupt a part of interchange dipole interactions of CN groups, produce relatively stable charge-transfer complexes with nitrile groups, and become immobilized, forming thus IB portion of LM.

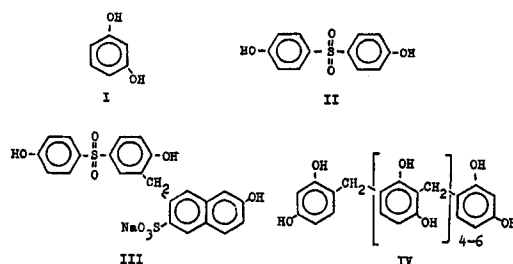
To conclude, according to Lewin [3] the development of IB from of LM in polymer matrix is accounted for by diffusion of Br_2 molecules into the densely packed domains and their subsequent immobilization via charge-transfer complexation. In this case, formation of the charge-transfer complexes in the loosely packed regions is likely to be absent.

Thermodynamic and kinetic studies of sorption of synthetic tanning agent (BNS) by PA-6 films at 100°C showed [2] that the mechanism advanced in [3] may also be invoked to explain the distribution of LM in polymer matrix between two IB and RB forms.

However, the question arises: Why does immobilization of the molecules of LMs in the polymer matrix via complexation (if this very factor is responsible for irreversible binding of LM in polymer matrix) proceed only in densely packed regions of the amorphous phase? This question seems to be of vital importance for the PA-6/OAC systems because phenol hydroxyls of OACs show very high tendency for complexation with amide groups [6, 11]. In connection with this, one can hardly explain the absence of interaction between polymer chains and OACs molecules in the loosely packed regions of amorphous phase of PA-6.

To answer the above question, a comprehensive study of mechanism of distribution of OACs molecules between RB and IB forms in the amorphous regions of PA-6 based on speculations concerning the complexation between the components involved was carried out [19]. Resorcinol (I), dioxydiphenylsulfone (II), synthetic tanning agent BNS (III), and resorcinol-formaldehyde novolac (IV) were used as OACs.

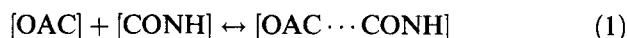
As was shown, only compounds III and IV are able to produce IB form, and compounds I and II are not. The studies on sorption of



water vapors by the PA-6/OAC samples at 20°C allowed one [2] to conclude that IB form of compound III is primarily localized in the densely packed regions of the amorphous phase of PA-6, which are unaccessible for water molecules at sorption temperatures in a whole range of relative humidities. The RB form occupies disordered regions of amorphous phase, the water penetration into which is known to control the water sorption by the polymer samples [1, 20].

In the case of compound IV, the formation of IB form takes place in the loosely packed regions of the amorphous phase of PA-6. However, there is still an open question: Do molecules of compound IV penetrate the densely packed domains of amorphous phase in PA-6 or they are localized only in the loosely packed regions?

From the standpoint of complexation, the distribution of LM between two forms may be represented as a result of occurrence of two reactions of complexation between the components of the PA-6/OAC system:



The difference between the above reactions is related to reversible character of reaction (1) and irreversible character of reaction (2). The subsequent treatment of the PA-6/OAC samples with a pure solvent (water) is associated with shifting the equilibrium state of reaction (1) to the left until complete dissociation of the complex. At the same time, the complex formed via reaction (2) shows no dissociation under the above conditions.

Examination of published evidence on complexation of PET [21] and poly(ethylene oxide) (PEO) [22] with resorcinol in melt, poly

(N,N-dimethylacrylamide) with phenol-formaldehyde resins in the solutions [23] and the general speculations concerning the mechanism of complexation between polymer and oligomer chains [24] allowed one to specify two interdependent conditions for the development of stable intermolecular complexes:

1. Realization of joint dense packing of the molecules of the reacting compounds [21, 22]. In other words, reacting components should be complementary: geometric structure of the interacting species should not prevent the development of intermolecular bonds [24];
2. The complexation reaction should involve a certain sequence of active complexing groups, the number of which is equal to or exceeds critical one [23, 25]. This condition implies cooperativity of a set of intermolecular bonds in the complexes with polymer chains. Just cooperativity of interaction is primarily responsible for relatively high stability of the reaction products as compared with that of the complexes between the low-molecular-mass analogs.

Let us first discuss what to different authors mean when speaking about a "stable complex".

For example in [24], "stable complex" is treated from the kinetic standpoint. In the case of complexation reactions between polymer chains and oligomers, an increased stability of the formed complex was accounted for by an increase in the constant of equilibrium, i.e., by shifting the equilibrium towards the complex formation. The above reactions were shown to possess reversible character. In particular, the reaction of complexation between polymer and oligomer chains is reversible under varying the concentration of oligomer in the solution: a decrease in concentration of the oligomer is accompanied by shifting the equilibrium towards accumulation of the initial reagents until complete dissociation of the complex.

On the other hand, in the case of the complexation between poly(N,N-dimethylacrylamide) and phenol-formaldehyde resins [23] in organic solvents, the stable complex was referred to as the reaction product, which precipitated under the reaction conditions. Let us emphasize that the formed complex showed no dissociation under washing with a pure solvent. This evidence suggested irreversible character of the complexation reaction.

The similar situation was observed in the case of the complexation between aliphatic PA with OACs in the solutions of formic acid [6, 26] and alcohol [26]. In this case, compound III and sulfonated phenol-formaldehyde oligomer were used as OACs. Interaction of the above compounds with polymers (in particular, with PA-6) is accompanied by precipitation of the complex, which shows dissociation neither in a pure solvent nor in a boiling water.

A certain inconsistency in treating the term of "stable complex" does not conflict with the above conditions for complexation, which were advanced to explain the mechanism of specific interaction of OACs with polymer chains in the amorphous regions of PA-6. However, to prevent any terminological misunderstanding, in this work "stable complex" is the complex, which shows no dissociation under treating in a pure solvent, i.e., which is formed via reaction (2).

The occurrence of reaction (2) in amorphous regions of PA-6 is allowed when the number of active complexing groups in OAC molecules is high enough, and such groups are able to react with polymer amide groups so that the number of reacting groups should be equal to or higher than critical one. The latter requirement is especially important for the complexation reactions in solid bodies, since as compared with solutions and melts, the macromolecular mobility in the solid phase is substantially inhibited (in our case, in amorphous regions of PA-6 swollen in aqueous solutions of OAC).

Inhibited mobility of polymer chains prevents the possibility for phenol hydroxyls of OACs and polymer amide groups to approach each other within the distance necessary for the development of hydrogen bonds. Furthermore, in the amorphous regions of PA-6, as compared with solution or melt, the mutual arrangement of macromolecules and, hence, the chain fragments with amide groups is fixed. Mutual arrangement of polymer amide groups is primarily controlled by polymer packing density in amorphous regions of PA-6. The heterogeneity in packing density in PA-6 was discussed in [18].

From this standpoint, the occurrence of reaction (2), i.e., the development of IB form, in the amorphous phase of PA-6 takes place only in the local structural regions which serves as a specific "trap" for OAC molecules. Just within such a trap, the above conditions for the development of stable complex are fulfilled and irreversible binding of OAC with polymer matrix is promoted. Let us discuss the

experimental evidence obtained for complexation of PA-6 with OACs from this standpoint.

The development of only RB form for compounds I and II suggests that the chemical structure of the molecules of the above compounds (molecular sizes and number of the complexing groups) prevents the fulfillment of the necessary condition for the formation of stable intermolecular complex via reaction (2). In this case, interaction of phenol hydroxyls with polymer amide groups is described by reaction (1) and reversible character of binding of LM with polymer is realized.

When passing to OAC III, increase in molecular sizes and number of complexing hydroxyl groups result in appearance of IB form of LM. This implies that the number of active complexing groups is sufficient to produce stable complex with PA-6. However, the formation of IB form of OAC III takes place only within the densely packed regions of the polymer amorphous phase. This experimental evidence allows one to conclude that macromolecular arrangement only in the densely packed regions provides the conditions of cooperative interaction of all complexing groups of OAC with amide groups of PA-6, occurrence of reaction (2), and irreversible binding of OAC molecules with polymer matrix. In other words, the chemical structure of compound III molecules is so that the "traps" for them exist only in the densely packed regions of amorphous phase of PA-6. In the case of more loosely packed regions, the mutual arrangement of molecules in such regions prevents simultaneous interaction of amide groups with phenol hydroxyls of compound III in quantity necessary for the occurrence of reaction (2). As a result, the interaction between the components of the PA-6/OAC system is described by reaction (1) and the formation of only RB form is observed.

With further increasing the molecular sizes and the number of the active complexing groups, i.e., compound IV, one can observe the development of IB form also (or only) in the loosely packed regions of the amorphous phase of PA-6. This evidence suggests that, as compared with molecules of compound III, the molecules with such molecular structure are able to find the "traps" in the regions with lowered packing density.

The above speculations allow us to generalize the mechanism of distribution of LMs between IR and RB forms as advanced in [3].

Sorption by polymer of LMs from the aqueous solutions involves two stages. The first stage is associated with diffusion of molecules of LMs into the swollen regions of the polymer amorphous phase, which are characterized by lowered packing density. The second stage is related to diffusion of molecules of LMs from loosely to densely packed regions. The sorption is accompanied by binding of molecules of LMs by polymer chains both in loosely and densely packed regions of the polymer amorphous phase via complexation between the components.

In general case, complexation between the molecules of LMs and polymer chains in polymer amorphous phase can be described by reactions (1) and (2). The formation of IB form of LMs is described by reaction (2). The occurrence of this reaction is provided by fulfillment of the above conditions of development of stable intermolecular complex. The possibility of fulfillment of these conditions in the polymer amorphous phase is decided by the chemical structure of molecules of LMs (molecular size and functionality) and packing density of polymer chains. In connection with this, IB form of LMs may be realized either in loosely or in densely packed regions of polymer amorphous phase or does not form at all.

However, the mechanism of diffusion of molecules of LMs into the densely packed regions and their withdrawal from such regions is still unclear. The penetration of molecules of LMs into the densely packed regions proceeds from their aqueous solutions, which are able to swell polymer matrix. On the other hand, desorption of molecules of LMs from the densely packed regions implies transition of molecules of LMs from polymer matrix into the pure solvent – water. The question arises: Does water swell the above regions or, in other words, whether such regions are accessible to water molecules?

The data reported in [3] clearly demonstrated that the densely packed regions of amorphous phase of PAN are unaccessible for water molecules under sorption and desorption of Br₂ from aqueous solutions. The formation of IB form of dioxydine in copolymer of N-vinylpyrrolidone with methyl methacrylate was also treated [4] within the standpoint of the existence of structural zones in the amorphous regions of moderately hydrophilic polymers, which are unaccessible for water molecules. However, in the case of the PA-6/OAC systems such conclusions do not seem quite obvious.

As was shown in [2, 19], the densely packed regions of the amorphous phase of PA-6 are inaccessible for water molecules under water sorption from the vapor phase at 20°C in a whole range of relative humidities. On the other hand, water sorption of PA-6 was shown to increase by approximately 30% as the temperature increases from 25 to 1000°C [27]. Hence, the assumption that densely packed regions of PA-6 are accessible to water molecules under sorption of OACs from aqueous solutions at 1000°C and desorption on treatment the PA-6/OAC samples in boiling water seems to be quite reasonable.

In connection with this, let us discuss the importance of an exact knowledge whether the densely packed regions are accessible for water molecules with respect to the mechanism of distribution of LMs in the polymer between IB and RB forms. Furthermore, the solution of this problem seems to be rather interesting from the viewpoint that according to [27] the accessibility of amorphous regions of semicrystalline polymers (in particular, PA-6) for water molecules is not constant but depends on sorption temperature.

To gain a deeper insight into the mechanism of distribution of LMs in polymer matrix between two forms, let us consider both cases: densely packed amorphous regions are accessible for water molecules under sorption and desorption (i), and densely packed amorphous regions are inaccessible for water molecules under sorption and desorption (ii).

Let us first assume that the densely packed regions of the polymer amorphous phase are accessible for water molecules under sorption and desorption of LMs. The point is that this version agrees well with the above mechanism of distribution of LMs between IB and RB forms. Aqueous solutions of LMs swell the densely packed regions of polymer matrix and the molecules of LMs are able to penetrate these regions. The treatment of the polymer/LM systems in a pure solvent (water) is also associated with swelling of the above regions in water, however, taking into account the above reasoning, in some cases, no dissociation of the polymer/LM complex takes place.

According to the assumption that densely packed regions are inaccessible for water molecules, the amorphous polymer phase under sorption and desorption of LMs may be visualized as heavily swollen loosely packed regions and "dry" densely packed regions. In this case, diffusion of molecules of LMs into the densely packed regions is

carried out through a sharp boundary between swollen and “dry” polymer. Actually, we deal with distribution of LMs between loosely packed water-swollen regions and “dry” densely packed domains. In the case of the PAN/Br₂ and PA-6/OAC systems, this explanation seems to be quite plausible due to a high affinity between polymer and LMs [3, 19].

On further treatment the polymer/LM samples in water, desorption of LMs from the densely packed regions proceeds as distribution of LMs between loosely packed water-swollen regions and densely packed dry regions containing this LM. The LM may be completely extracted by solvent from the densely packed regions only in the case when molecules of this agent show sufficient mobility within such structural units. Such situation is likely to be realized for the PA-6/OAC systems only for the compounds I and II, which are able to produce only RB form. The molecules of compound III appear to be immobilized only in the densely packed regions, and no complete extraction of this agent is allowed.

Hence, there is no conflict between the above speculations and the mechanism of distribution of LMs in the polymer matrix between RB and IB forms. In other words, this mechanism provides a plausible explanation of the formation of IB form of LM in polymer matrix independently of the fact whether densely packed regions are accessible for water molecules or not.

So, the development of IB form of LMs in polymer matrix is associated with peculiar features of complexation between molecules of LMs and polymer chains as a result of structural heterogeneity of the amorphous polymer state. In connection with this, the systems, which show the formation of IB forms only in the densely packed regions of the polymer amorphous phase are of more interest, that is, PAN/Br₂ [3] and PA-6/(OAC III) [2, 5, 19] systems. The point is that in this case we can realize a unique possibility of separate modification of different structural levels in polymer amorphous phase. Actually, sorption of LMs from their aqueous solutions by polymers is associated with penetration of molecules of LMs into loosely and densely packed regions of polymer amorphous phase. In other words, both structural levels appear to be modified. The removal of RB fraction of LMs from the loosely packed regions allows one to obtain the polymer samples, in which only one structural level with dense packing of polymer chains is modified.

To understand the peculiar features and possibilities of such separate modification of structural levels of the polymer amorphous phase, let us carry out a comparative analysis of experimental evidence obtained for the polymer systems based on PA-6 and OAC III.

STRUCTURAL FEATURES OF MECHANICAL AND PHYSICAL BEHAVIOR OF POLYMER/(LOW-MOLECULAR-MASS COMPOUND) SYSTEM

The systems based on PA-6 and OAC III are of great interest from the viewpoint of realization of separate modification of different structural levels in the polymer amorphous phase [2, 19]. The treatment of PA-6 films in aqueous solutions of OAC III is associated with modification of both structural levels (Samples I). The removal of RB form from the loosely packed regions implies that only one structural level, that is, densely packed regions, appears to be modified (Samples II).

The temperature dependences of storage modulus E' of dry samples of initial PA-6 samples and Samples I and II (Fig. 1) allows one to outline the following general features of physical and mechanical behavior of such systems [5].

First, the temperature dependences are characterized by the existence of the inversion point of elastic properties of the materials, T_I . At temperatures below T_I , OAC III shows reinforcing action on the polymer elastic properties, whereas at temperatures above T_I this action is weakening.

Second, the removal of RB form from PA-6 (transition curve 2 to curve 3) is accompanied by shifting T_I towards higher temperatures.

The above behavior was described in [5] in terms of polymer antiplasticization-plasticization with LMs [28, 29]. Molecular mobility of LMs (for example, OAC III) in polymer increases with temperature. An increased molecular mobility of LMs is associated with a decrease in energy of intermolecular interaction between polymer chains, and this provides the conditions for the transition from reinforcing (antiplasticizing) action to weakening (plasticizing) action of OAC III on PA-6. The macroscopic manifestation of this behavior is associated with the appearance of inversion point T_I in the corres-

ponding temperature dependence of elastic properties of polymer systems.

Examination of the behavior of elastic properties of the PA-6/(OAC III) systems in a temperature range from 100–110 to 140–150°C is of particular interest. In the case of Samples I containing OAC III in both IB and RB forms, the corresponding elastic modulus E' is lower than that of initial polymer sample (curve 2) in this temperature range. For samples II containing only IB form of LMs, the values of E' appear to be higher than those of PA-6 samples.

From the viewpoint of molecular dynamics, this experimental evidence suggest that in the above temperature range the molecular mobility of RB form is well-pronounced. Consequently, the RB molecules are able to plasticize the polymer, and a concomitant decrease in elastic modulus is observed. In contrary, molecular mobility of IB form is still frozen-in and its action on polymer matrix is antiplasticizing (reinforcing). In other words, the mobility of RB

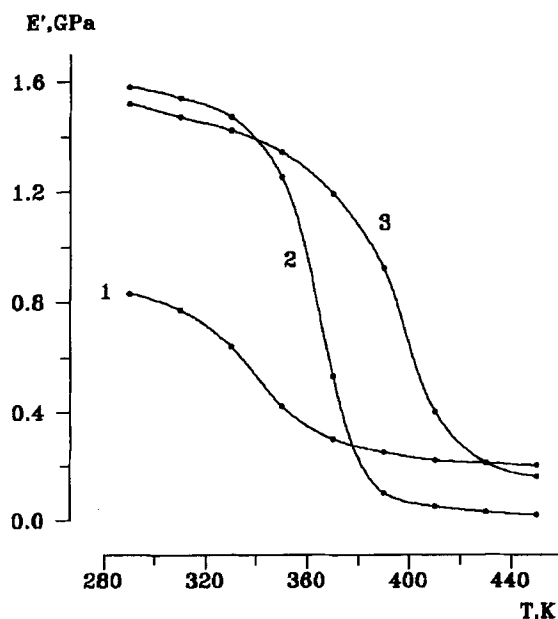


FIGURE 1 Temperature dependences of storage moduli E' of PA-6 (1) and PA-6/(OAC III) samples. OAC content: 0.5 mol/kg (Sample I) (2), and 0.16 mol/kg (Sample II) (3).

fraction of OAC III appears at temperatures by 40–50°C lower as compared with IB form.

According to our theoretical speculations, the difference between the molecular mobilities of RB and IB forms in a certain temperature range may be rationalized by the fact that IB form is localized in the densely packed domains of the amorphous phase, which are characterized by relatively high level of intermolecular interaction. In connection with this, manifestation of molecular mobility of IB form of OAC is allowed only at elevated temperatures. As the RB fraction of OAC occupy only loosely packed regions of the amorphous phase, which are characterized by lower energetics of intermolecular interaction, then the molecules of this RB fraction acquire mobility at much lower temperatures.

The above evidence allowed us to draw the following conclusions concerning the specific character of elastic behavior of the PA-6/(OAC III) samples. In the aforementioned temperature interval, the situations is realized when one and the same modifying agent is able to have quite different (even opposite) effect on the elastic properties of the material, depending on the form of its existence within the polymer matrix. In other words, in a given temperature range, elastic properties of the PA-6/(OAC III) samples containing OAC in both RB and IB forms are controlled by interplay between plasticizing action of RB form and antiplasticizing action of IB form. The net result depends on the ratio between IB and RB forms of OAC in polymer matrix [5]. This ratio may be changed either by varying the concentration-time regimes of introduction of OAC into the polymer matrix or by desorption of RB fraction of LM from PA-6 [2].

Taking into account the above speculations, one may easily explain the changes in glass transition temperatures T_g of PA-6 samples on sorption and desorption of OAC III (Tab. I) [5]. Introduction of OAC into the polymer matrix is accompanied by increase in glass transition temperature T_g of the polymer (Samples I, Tab. I). This is main difference between the systems studied and traditional plasticized polymer materials [28, 29]. The removal of RB form of OAC III from the test samples, which is known to exert plasticizing action on the polymer at temperatures above 1000°C, i.e., transition from Samples I to Samples II, is accompanied by a growth in T_g of PA-6 samples (Tab. I).

TABLE I Glass transition temperatures of dry PA-6/(OAC III) samples

Sample	Content of OAC III in PA-6, mol/kg	T_g , K
Initial PA-6	0	353
Sample I	0.29	388
Sample II	0.09	396
Sample I	0.50	393
Sample II	0.16	406

Note, that, for oriented PA-6 samples containing OAC III, temperature-induced shrinkage is also controlled by distribution of OAC III between IB and RB forms (Fig. 2). For oriented initial PA-6 films (curves 1), at temperatures below melting point T_m (≈ 500 K), temperature-induced shrinkage, which is characterized by decreasing residual deformation ϵ_{res} , is likely to be controlled by the relaxation of deformation within amorphous regions of polymer. With increasing temperature close to T_m residual deformation dramatically falls down because of crystallites melting.

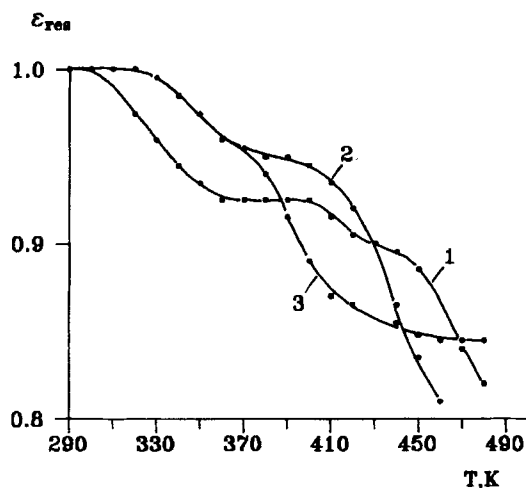


FIGURE 2 Temperature dependences of relative residual deformation ϵ_{res} of oriented PA-6 film (1), oriented PA-6 treated with aqueous OAC solutions with concentrations 0.07 (A) and 0.007 mol/l (B) (2), and, then, with boiling water for 6 h (3).

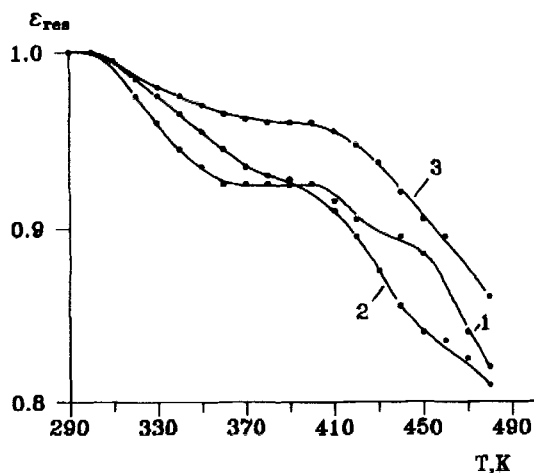


FIGURE 2 (Continued).

At lower temperatures, introduction of OAC III into oriented PA-6 films is responsible for suppression of shrinkage of oriented PA-6 samples containing OAC III (curves 2). As temperature increases the shrinkage of oriented PA-6/(OAC III) samples becomes higher as compared with initial polymer. In other words, for initial oriented PA-6 and oriented PA-6 modified with OAC III, the inversion in shrinkage is observed. As for inversion in elastic properties of isotropic PA-6 films and PA-6/(OAC III) samples, the inversion in shrinkage of oriented polymer samples may be explained by molecular mobility of OAC III in polymer matrix. With increasing temperature molecular mobility of OAC III in PA-6 increases, and decreasing energy of intermolecular interaction between polymer macrochains takes place. As a result, for PA-6/(OAC III) oriented samples, temperature-induced shrinkage is higher as compared with initial PA-6.

For oriented PA-6 samples treated with aqueous OAC III solution with concentration of 0.07 mol/l, at temperatures above 450 K, removal of RB form of OAC III is accompanied with suppression in shrinkage as compared with initial PA-6 and PA-6 containing both IB and RB forms of OAC III (Fig. 2A). At lower temperatures, for oriented PA-6 sample containing only IB form of OAC III (curve 3), temperature-induced shrinkage is higher than that for PA-6 sample containing both IB and RB forms of OAC III (curve 2). Note, that for

oriented PA-6 samples treated with aqueous OAC III solution with concentration of 0.007 mol/l, removal of RB form of OAC III results in suppression in shrinkage within the whole temperature range not above melting point (Fig. 2B).

So, examination of physical and mechanical behavior of the PA-6/(OAC III) samples together with speculations concerning the structural heterogeneity of the polymer amorphous phase may serve as a convincing demonstration of possibilities of controlled modification of the bulk properties of polymer materials via controlled modification of different structural levels of amorphous phase of semicrystalline polymer. This conclusion is also supported by comparing the properties of Samples I and II in humid atmosphere (Tab. II).

In the case of aliphatic polyamides, sorption of water vapors is known to be accompanied by decrease in elastic modulus of the polymer samples [30, 31]. As compared with initial PA-6, the PA-6/(OAC III) samples containing both IB and RB forms of OAC III (Sample I, Tab. II) are characterized by a sharp decrease in water sorption and increase in elastic modulus [2]. Desorption of RB fraction of OAC III from PA-6 (transition from Samples I to Samples II, Tab. II) is accompanied by an abrupt increase in water sorption, which is comparable to that of initial polymer. However, no decrease in elastic modulus is observed. In other words, distribution of OAC III between IB and RB forms is associated with peculiar "division of labor": RB fraction of modifying agent occupies loosely packed structural levels of polymer amorphous phase and is responsible for water sorption of the polymer material, whereas macroscopic elastic properties of the materials in humid atmosphere are controlled by IB fraction localized in the densely packed regions. Furthermore, such complex modification results in reduced susceptibility of the resultant

TABLE II Elastic properties of the PA-6/(OAC III) samples in humid atmosphere

Sample	Content of OAC III in PA-6, mol/kg	p/p_0 , %	Water content, mol/kg	Elastic Modulus, GPa
Initial PA-6	0	0	0	1.9
	0	47	2.8	1.3
Sample I	0.50	47	0.95	2.5
Sample II	0.16	47	2.4	2.5

materials to the plasticizing action of water as evidenced by constancy of elastic modulus even at two-fold increase in water sorption when passing from sample I to sample II (Tab. II).

The above evidence on the effect of IB fraction of OAC III localized in the densely packed domains of amorphous phase on macroscopic elastic properties of the polymer samples allows one to draw an important conclusion concerning a marked role of such domains in development of mechanical properties of semicrystalline polymers.

CONCLUSION

Experimental evidence discussed in this work unequivocally shows that in some cases a complicated character of interaction of LMs with polymers is realized. The LMs introduced into the polymer matrix are shown to be distributed between two different forms: reversible (RB) and irreversibly bound (IB) forms. All systems, which show similar behavior, are characterized by high affinity between LMs and polymers, which is controlled by complexation between molecules of LM and polymer chains.

The mechanism of distribution of LMs between IB and RB forms is based on speculations concerning structural homogeneity of amorphous component in semicrystalline or completely amorphous polymers: the existence of noncrystalline regions (structural levels) with different packing density and order. The development of IB form of LMs is a result of complexation reaction between molecules of LM and polymer chains and formation of very stable complex. The possibility of occurrence of such complexation reactions is dictated by chemical structure of LM and local packing density of polymer chains. In connection with this, IB form may be localized within different structural levels or even does not form at all.

In turn, the complicated character of interaction between LMs and polymer chain is responsible for a complicated molecular dynamics of polymer/LM systems and, hence, for specific features of mechanical behavior of the material.

The approaches discussed in this work may be interpreted as underlying principles for new scientific direction, according to which interaction between LMs and polymers is primarily treated from the

viewpoint of existence of different levels of structural inhomogeneity in polymers. This direction involves some general problems related to sorption and diffusion of LMs in polymer bodies with a complicated structural organization.

On the other hand, controlled occupation of different levels of structural inhomogeneity with molecules of LM suggests many possibilities of controlled modification and improvement in mechanical properties of polymer materials.

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