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M. S. Arzhakov^a; E. V. Nechaeva^a; I. I. Khairullin^a; A. V. Volkov^a; A. L. Volynskii^a; N. F. Bakeev^a

^a Polymer Department, Faculty of Chemistry, Moscow State University, Moscow, Russia

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Physical and Mechanical Behavior of Polyamide-6 Containing Oxyaromatic Compounds

M. S. ARZHAKOV*, E. V. NECHAEVA, I. I. KHAIRULLIN,
A. V. VOLKOV, A. L. VOLYNSKII and N. F. BAKEEV

*Polymer Department, Faculty of Chemistry, Moscow State University,
Vorob'evy Gory, Moscow, 119899 Russia*

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The distribution of oxyaromatic compound in PA-6 amorphous regions between two structural forms, which are characterized by different energy of interaction with polymer matrix, was studied. Physical and mechanical properties (glass transition temperature, water sorption, elastic modulus) of PA-6 containing oxyaromatic compound were shown to be controlled not only by the net content of oxyaromatic compound in polymer, but by its distribution between these structural forms. This distribution appears to govern the mechanical properties of the polymer in the region of its relaxation transition from glassy to rubbery state, whatever this state was achieved by increasing the concentration of plasticizer (water) or by increasing the temperature. The experimental evidence obtained was discussed with the account for structural heterogeneity of the amorphous regions of semicrystalline PA-6.

Keywords: Polyamide-6; oxyaromatic compound; modification; mechanical properties

INTRODUCTION

Improvement of physical and mechanical properties of polymer materials may be achieved by their physical modification via introduction of compatible low-molecular-mass compounds (LMs) into polymers. Generally, for these polymer/LM systems, compatibility of the components is controlled by complexation between

*Corresponding author.

polymer macrochains and molecules of LM via hydrogen bonding, electrostatic, dispersion, and similar interactions. Physical and mechanical behavior of as-modified polymer materials is decided by energetics of interaction between components of polymer composite.

In some cases, LMs, which were introduced into the polymer from the swelling solutions, appear to be distributed within polymer matrix between two different forms, reversibly (RB) and irreversibly bound (IB) with polymer [1–4]. As compared with IB form, RB form may be easily removed from polymer by keeping polymer/LM samples in a pure solvent. In other words, the above forms of LM are characterized by the different energy of interaction with polymer. As a result, physical and mechanical behavior of these polymer materials are expected to be primarily controlled by the distribution of modifying agent between RB and IB forms.

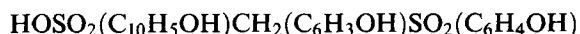
Mechanism of the distribution observed was discussed [1, 2, 5, 6] in terms of structural inhomogeneity of amorphous polymers or amorphous phase in semicrystalline polymers - existence of, at least, two different noncrystalline regions with different packing densities and ordering. Note, that the structural inhomogeneity of the amorphous phase in semicrystalline polymers and completely amorphous polymers is an intriguing problem, which is being vigorously discussed in literature [7–15]. According to mechanism proposed, development of IB form of LM in polymer is associated with the formation of a stable complex between LM molecules and polymer macrochains in densely packed structural regions of polymer. Complexation of LM molecules with polymer macrochains in loosely packed structural regions is accompanied by development of RB form of LM with lowered energy of interaction as compared with IB form. As a result, RB form of LM is able to be removed from polymer matrix. This approach allows controlled occupation of different structural regions of polymer with LM molecules, i.e., separate modification of the above structural regions.

In this paper, for model systems based on PA-6 modified with oxyaromatic compound (OAC), the effect of distribution of modifying agent between loosely and densely packed structural regions within amorphous phase of polymer on physical and mechanical behavior of as-modified polymer material was studied. OACs are known [3, 16–18] to be well compatible with aliphatic polyamides because of

complexation between phenol hydroxyls of OAC with amide polymer groups via hydrogen bonding. This complexation was shown to be responsible for increase in the energy of intermolecular interaction in polyamides, and, as a result, for increasing mechanical characteristics of polymer [19, 20]. Distribution of OACs within amorphous phase of aliphatic polyamides was noted in [4–6]. Moreover, the ratio between IB and RB forms of OAC in PA-6 was shown to be controlled by changing concentration and time regimes of the treatment of PA-6 samples in swelling OAC solutions.

EXPERIMENTAL

We studied commercial isotropic films of PA-6 with a thickness of 0.1 mm. Before testing, the samples were treated in boiling water for 3 h. After that, they were dried over P_2O_5 until constant mass was attained. As a modifying agent, we used an oxyaromatic compound prepared by condensation of sulfonated β -naphthol and dioxydiphenylsulfone with formaldehyde, with the following structural formula:



To introduce OAC to PA-6, polymer films were treated with OAC aqueous solutions with concentrations of 0.007, 0.036, 0.072, and 0.14 mol/l for 5, 15, 30, 60, and 180 min. at 373 K. Then, the PA-6/OAC samples were allowed to dry over P_2O_5 until constant mass was attained. Concentration of OAC sorbed by the polymer samples was estimated gravimetrically.

The kinetic sorption curves (Fig. 1) show that equilibrium sorption of OAC by PA-6 samples is achieved within 3 h. With increasing the time of treatment of 6 h, no further sorption of OAC by PA-6 films was observed.

To obtain quantitative estimations on distribution of OAC introduced to PA-6 films between RB and IB forms, the PA-6/OAC samples were treated in boiling water for 1, 2, 3, 6, and 12 h. We showed that RB form of OAC can be removed from the polymer within 6 h. With increasing the time of treatment to 12 h, no marked desorption of OAC from PA-6 was observed. In this connection, the

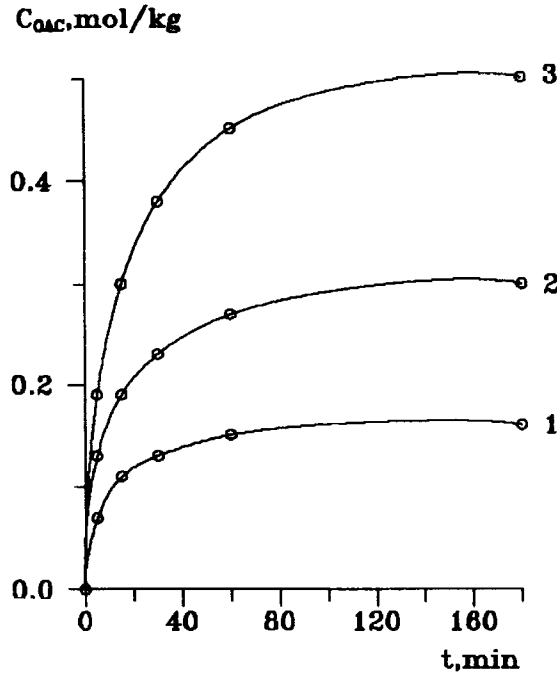


FIGURE 1 Kinetic curves of OAC sorption by PA-6 films from aqueous OAC solutions with concentrations 0.036 (1), 0.072 (2), and 0.14 mol/l (3).

IB form of OAC can be defined as the fraction of OAC, which cannot be removed from the PA-6/OAC samples upon their treatment in boiling water for 6 h. The fractional content of IB form of OAC was estimated as $C_{IR} = [IR]/([IR] + [RB])$.

Figure 2 shows the kinetic curves of accumulation of IB form of OAC in amorphous regions of PA-6. For all aqueous OAC solutions, with increasing the time of treatment of PA-6 films to 3 h, fractional content of IB form of OAC approaches the same value (0.32 ± 0.02). This value is likely to be related to equilibrium distribution of OAC between IB and RB forms, since it remains the same even for the PA-6 samples treated with aqueous OAC solutions for 6 h.

Hence, the variations in the net content of OAC in PA-6 as well as in the fractional content of IB form of OAC in polymer samples can be carried out using the following procedures:

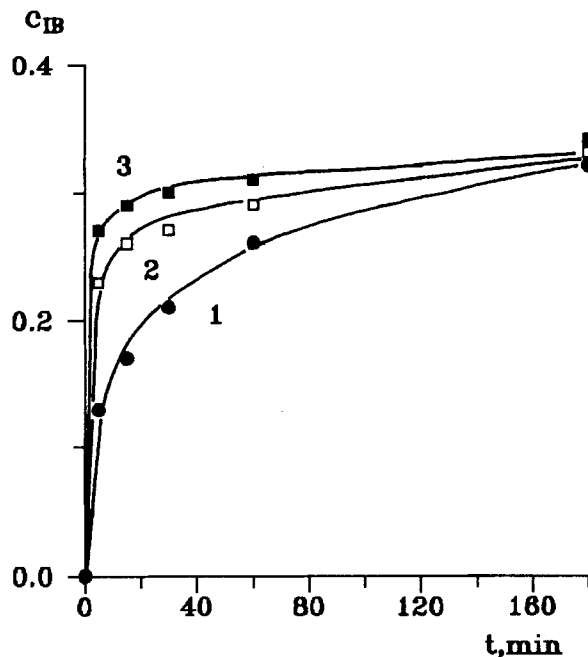


FIGURE 2 Fractional content C_{IB} of IB form of OAC in PA-6 films versus time of treatment of PA-6 with aqueous OAC solutions with concentrations 0.036 (1), 0.072 (2), and 0.14 mol/l (3).

1. Treatment of PA-6 films with aqueous OAC solutions of different concentrations for 3 h allows one to vary the net content of OAC at fixed fractional content of its IB form -0.32 ± 0.02 (Samples I).
2. Treatment of PA-6 films with aqueous OAC solutions of fixed concentration for various periods of time allows one to vary fractional content of IB form of OAC in the range not exceeding 0.32 (Samples II).
3. Removal of RB form of OAC from PA-6/OAC samples allows one to increase fractional content of IB form of OAC in polymer to 1.0 (Samples III).

The dynamic properties of PA-6/OAC dry samples were studied with Rheometrics solid analyzer RSA-II (USA) over temperature range from 290 to 450 K; deformation frequency was 5 Hz; strain was less than 0.5%; heating rate was 2 K/min. Glass transition tempera-

tures of PA-6/OAC samples were estimated from temperature dependences of loss tangent.

To study water sorption, the PA-6/OAC samples were conditioned over saturated aqueous solutions of inorganic salts at a given humidity at 293 K until constant mass. Water sorption was measured gravimetrically.

Mechanical tests were carried out with an Instron-1100 tensile machine (Great Britain) at a strain rate of 100 % min. at 293 K. The initial elastic modulus was measured at strains below 3%. Prior to mechanical tests, the samples were conditioned over saturated aqueous solutions of inorganic salts at a given humidity until equilibrium.

Uniaxial drawing of isotropic PA-6 films was carried out in water at 293 K to strain of 160%. After that, the stressed samples were dried in vacuum. Dry stressed PA-6 samples were treated in aqueous OAC solutions with concentrations of 0.007, 0.036, and 0.072 mol/l for 3 h at 373 K. Removal of RB form of OAC was carried out by treatment of stressed oriented PA-6/OAC samples in boiling water for 6 h. Then, oriented PA-6/OAC samples were dried in vacuum and unloaded. Temperature-induced shrinkage of oriented PA-6/OAC samples was studied in the temperature range from 293 K to 483 K. Residual deformation at a given temperature was estimated as $\varepsilon_{\text{res}} = (l_T - l_0) / (l_{\text{def}} - l_0)$, where l_0 - initial length of PA-6 sample, l_{def} - the length of the oriented sample, l_T - the length of the sample at a given temperature.

RESULTS AND DISCUSSION

Figure 3 shows the temperature dependences of storage moduli E' for Samples I. As is visible, the temperature dependences of E' have an inversion point, T_I . That is, at temperatures below T_I , increasing the content of OAC in PA-6/OAC samples lead to an increase in E' , whereas at temperatures above T_I with increasing the content of OAC in polymer E' decreases.

Such behavior may be attributed to the antiplasticizing (reinforcing) action of OAC on the mechanical properties of PA-6 at temperatures below T_I and to the plasticizing (weakening) action at temperatures above T_I . Note, that, for Samples I, T_I is independent of the content of

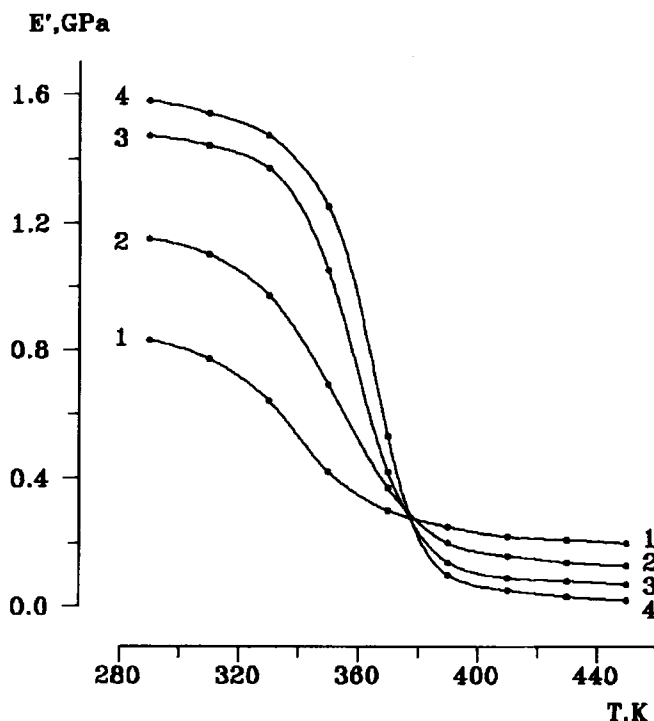


FIGURE 3 Temperature dependences of storage moduli E' of initial PA-6 (1) and PA-6 treated with aqueous OAC solutions with concentrations 0.007 (2), 0.072 (3), and 0.14 mol/l (4) for 3 h (Samples I).

OAC in PA-6. A plausible explanation of this phenomenon will be given below.

When RB form of OAC is removed from PA-6/OAC samples by their treatment in boiling water (transition from Samples I to Samples III), T_I is shifted towards higher temperatures (Fig. 4). It is of particular interest to analyze the behavior of the elastic properties of PA-6/OAC samples in the temperature range from 373–383 to 413–423 K.

In this temperature range, the values of storage moduli E' for Sample I (Fig. 4, curve 2), which contains both IB and RB forms of OAC, are lower than those for the initial polymer (curve 1). In the case of Sample III (curve 3), which contains only IB form of OAC, the values of E' are still higher than those for the initial polymer. This

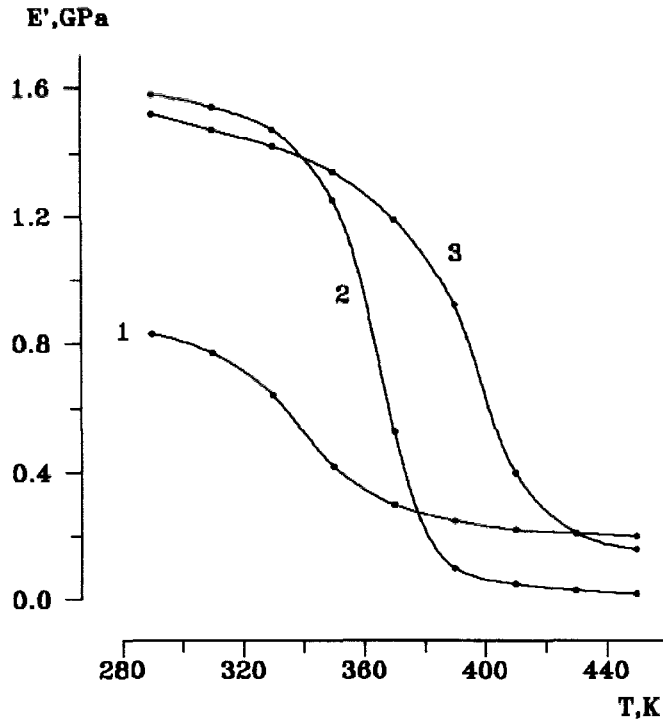


FIGURE 4 Temperature dependences of storage moduli E' of initial PA-6 (1), PA-6 treated with aqueous OAC solution with concentration 0.14 mol/l for 3 h (Sample I) (2), and, then, with boiling water for 6 h (Sample III) (3).

means, that in the samples studied, the same modifying agent may have opposite effect on the elastic properties of the polymer, depending on its form in the polymer matrix. Let us discuss the behavior of elastic properties of PA-6/OAC samples in terms of the molecular mobility of OAC in PA-6.

With increasing temperature, the mobility of OAC molecules in PA-6 increases. Increasing mobility of OAC molecules is responsible for decreasing the energy of intermolecular interaction between polymer macromolecules. As a result, antiplasticizing action of OAC on PA-6 is replaced by plasticizing action. For the PA-6/OAC samples, this mechanism may be invoked to explain the existence of the inversion point T_I in the temperature dependences of storage moduli.

The peculiarities of the mechanical behavior of the PA-6/OAC samples are related to their complicated molecular organization, i.e., to the existence of two different forms (IB and RB) of OAC in polymer matrix. In a certain temperature range, mobility of RB form of OAC is likely to be higher than that of IB form. This difference in mobility of IB and RB forms can be explained by the fact, that IB form of OAC is localized within the densely packed structural regions of amorphous phase of PA-6, which are characterized by a high level of intermolecular interaction. The RB form of OAC occupies loosely packed structural regions of amorphous phase with lower energetics of intermolecular interaction. As a result, molecular mobility of RB form appears at lower temperatures as compared with IB form. From this standpoint, in the temperature range from 373–383 to 413–423 K, the molecular mobility of RB form of OAC is rather high, and this form of OAC appears to plasticize the polymer, thus decreasing the elastic modulus. On contrary, molecular mobility of IB form of OAC is still frozen. As a result, this form of OAC exhibit an antiplasticizing action on PA-6. In other words, the elastic properties of PA-6/OAC samples are controlled by the interplay between the plasticizing action of RB form and the antiplasticizing action of IB form. The resulting effect appears to be decided by the ratio between IB and RB forms in the polymer matrix or fractional content of IB form in PA-6.

From this standpoint, the existence of the same T_g for all Samples I studied (Fig. 3) is well correlated to the fact, that all these samples are characterized by the same fractional content of IB form of OAC in polymer -0.32 ± 0.02 (Fig. 2). It is of particular interest to study the effect of accumulation of IB form in PA-6 on dynamic mechanical properties of polymer. As was mentioned above, for Samples II, increasing treatment time of PA-6 films in aqueous OAC solutions results in increasing fractional content of IB form of OAC in polymer (Fig. 2). As follows from (Fig. 5), with increasing fractional content of IB form in PA-6 T_g shifts towards higher temperatures.

Hence, this experimental evidence unequivocally demonstrates the influence of the molecular distribution of OAC between RB and IB forms within polymer matrix on the mechanical properties of PA-6/OAC samples. This behavior is likely to be associated with the difference in temperature-induced molecular mobility of IB and RB forms of OAC because of their localization within different structural

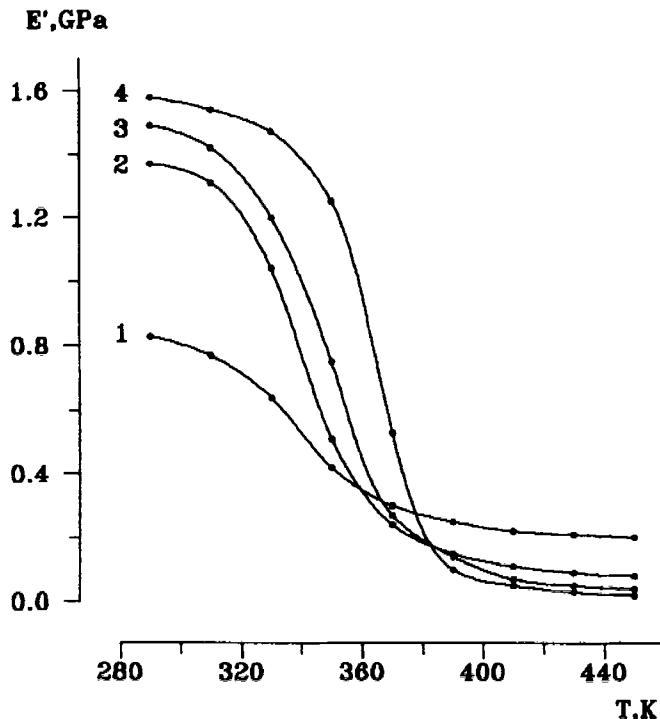


FIGURE 5 Temperature dependences of storage moduli E' of initial PA-6 (1) and PA-6 treated with aqueous OAC solution with concentration 0.14 mol/l for 5 (2), 30 (3), and 180 min. (4) (Samples II).

regions in polymer amorphous phase. For detailed discussion of this phenomenon, let us consider generalized data concerning the physical and mechanical behavior (T_g , T_f , and E') of PA-6/OAC samples.

For Samples I, II, and III, Figure 6 shows the plots of T_g and T_f versus OAC content in PA-6. This allows one to follow the behavior of these parameters of PA-6/OAC samples which are characterized by the different fractional content of IB form of OAC at fixed net content of OAC in polymer. As might be seen, the above parameters are not controlled by the net content of OAC in polymer, but by fractional content of IB form of OAC in PA-6. For Samples I which are characterized by the same fractional content of IB form, the dependence of T_g on OAC content is very weak in the range of

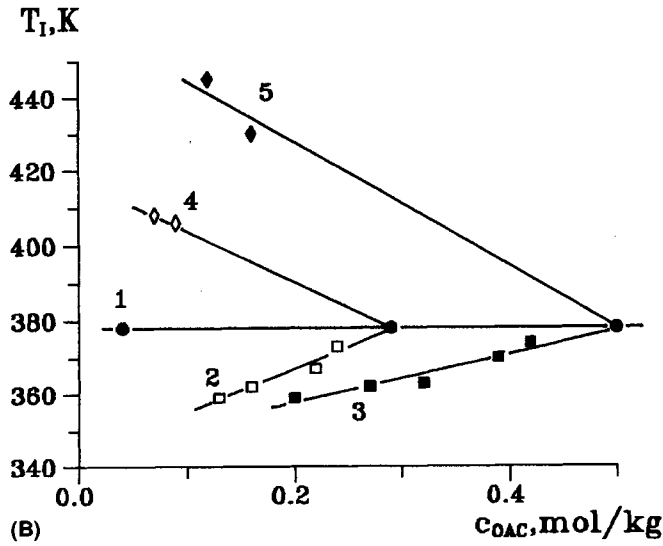
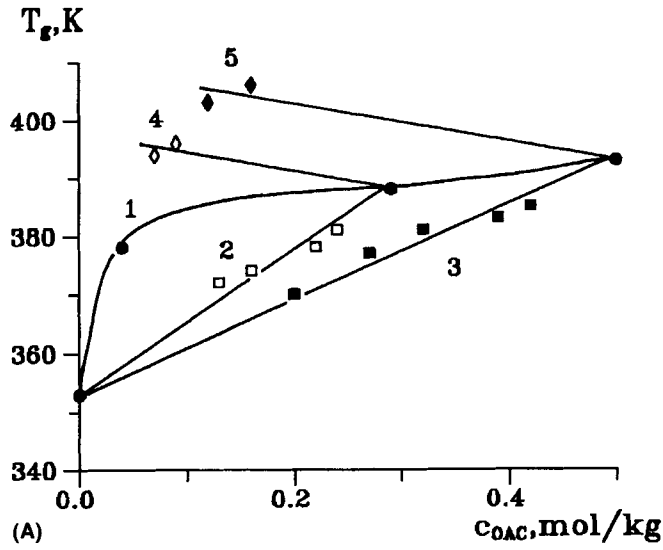


FIGURE 6 Glass transition temperature T_g (A) and inversion point of elastic modulus T_i (B) versus OAC content in PA-6. Samples I (1), Samples II (2 and 3), and Samples III (4 and 5).

OAC content from 0.04 to 0.5 mol/kg (Fig. 6A, curve 1). For these samples, T_I appears to be independent on OAC content (Fig. 6B, curve 1). For Samples II, with increasing periods of treatment time with aqueous OAC solutions fractional content of IB form of OAC increases, and, as a result, both T_g and T_I increases (Fig. 6, curves 2 and 3). For Samples III, removal of RB from PA-6/OAC samples results in a dramatic growth in both T_g and T_I (Fig. 6, curves 4 and 5).

For Samples I, II, and III, Figure 7 shows the dependence of E' on content of OAC in PA-6 at 363 K. At this temperature, a marked difference between the influence of IB and RB forms of OAC on the elastic properties of PA-6 is observed. When passing from Samples I to Samples III (transition from curves 1 to curves 4 and 5, Fig. 7), increasing fractional content of IB form of OAC in PA-6/OAC samples is responsible for the fact, that, at the same net OAC content in PA-6, for Samples III, the values of storage moduli exceed those for Samples I. For Samples II, with increasing fractional content of IB form storage moduli increase (Fig. 7, curves 2 and 3). As we mentioned above, this phenomenon may be attributed to the interplay

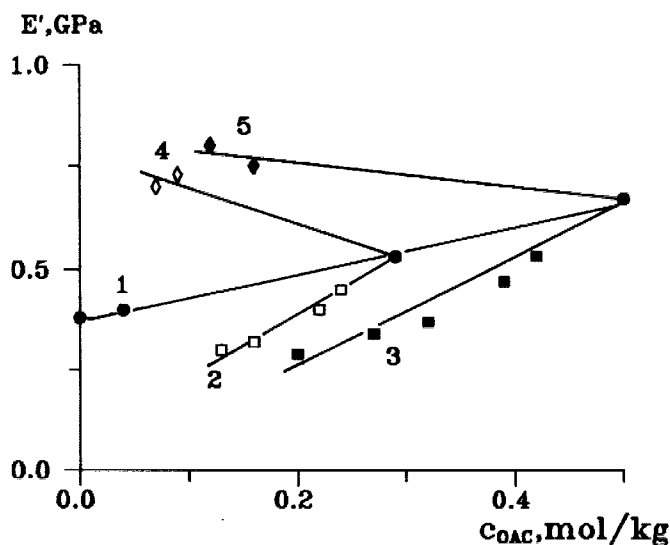


FIGURE 7 Storage moduli E' versus OAC content in PA-6 at 363 K. Samples I (1), Samples II (2 and 3), and Samples III (4 and 5).

between plasticizing action of RB form of OAC on mechanical properties of PA-6 and antiplasticizing action of IB form.

Note, that at 293 K, for Samples I, II, and III, concentration dependences of E' fit one curve. In other words, there is no difference in influence of both IB and RB forms of OAC on elastic properties of PA-6, and elastic moduli are controlled only by the net content of OAC in polymer. This experimental evidence can be explained by the fact, that, at this temperature, molecular mobility of both IB and RB forms is inhibited. As a result, both these forms have an antiplasticizing action on polymer. Similar behavior is observed at 413 K when all samples are in rubbery state. In this temperature region, molecular mobility of both OAC forms is enhanced, and their plasticizing action of PA-6 is well pronounced.

Hence, a marked difference between the influence of IB and RB forms of OAC on mechanical properties of PA-6/OAC samples is observed in the temperature region associated with the transition from glassy to rubbery state.

To investigate the effect of distribution of OAC between IB and RB forms on physical and mechanical behavior of oriented PA-6 samples, temperature-induced shrinkage of oriented polymer samples was studied (Fig. 8). 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.

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

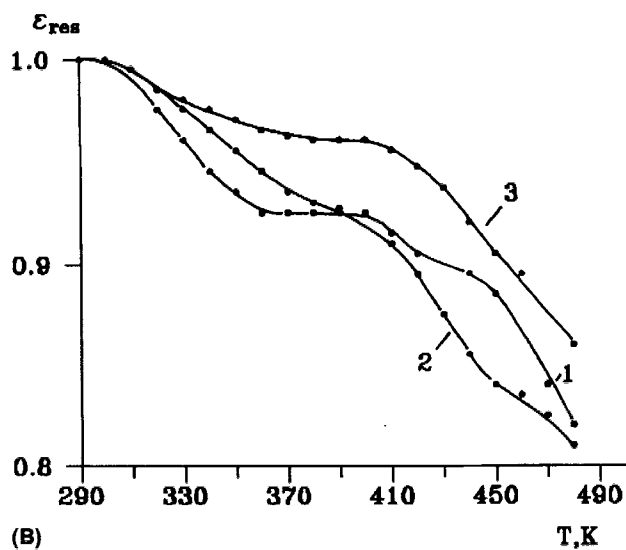
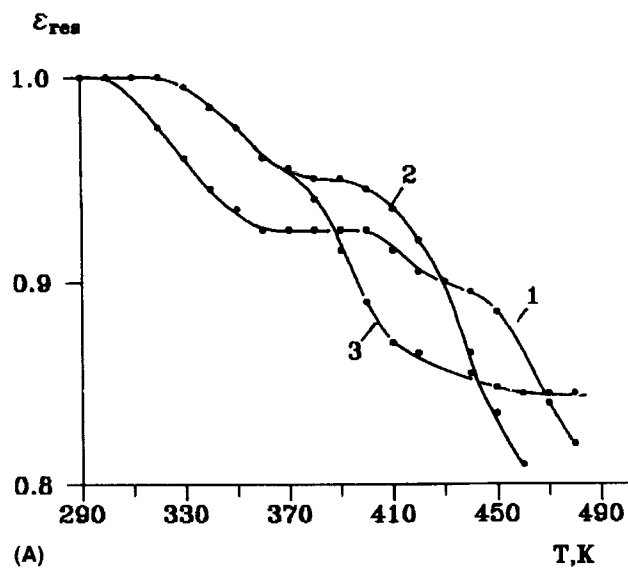


FIGURE 8 Temperature dependences of relative residual deformation ϵ_{res} of initial oriented PA-6 (1), oriented PA-6 treated with aqueous OAC solutions with concentrations 0.07 (A) and 0.007 mol/l (B) for 3 h (2), and, then, with boiling water for 6 h (3).

As a result, for PA-6/OAC oriented samples, temperature-induced shrinkage is higher as compared with initial PA-6.

For oriented PA-6 samples treated with aqueous OAC solution with concentration of 0.07 mol/l, at temperatures above 450 K, removal of RB form of OAC is accompanied with suppression in shrinkage as compared with initial PA-6 and PA-6 containing both IB and RB forms of OAC (Fig. 8A). At lower temperatures, for oriented PA-6 sample containing only IB form of OAC (curve 3), temperature-induced shrinkage is higher than that for PA-6 sample containing both IB and RB forms of OAC (curve 2). Note, that for oriented PA-6 samples treated with aqueous OAC solution with concentration of 0.007 mol/l, removal of RB form of OAC results in suppression in shrinkage within the whole temperature range not above melting point (Fig. 8B). Hence, for oriented PA-6 films modified with OAC, their temperature-induced shrinkage is controlled by distribution of OAC between RB and IB forms. As for isotropic PA-6/OAC samples, the influence of distribution of OAC on physical and mechanical behavior of oriented PA-6/OAC samples is decided by difference in temperature-induced molecular mobility of the above forms of OAC within polymer matrix, and, as a result, by opposite action of these forms on polymer properties in certain temperature intervals.

To gain a deeper insight into the influence of distribution of OAC between IB and RB forms on physical and mechanical behavior of PA-6/OAC samples, let us discuss the data on water sorption by the samples of the initial PA-6 and PA-6 containing OAC.

For Samples I and III, Figure 9 shows isotherms of water sorption at 293 K by the amorphous regions of the samples studied. As can be seen, the values of water content of PA-6 and Sample III containing only IB form of OAC (curves 1 and 2, respectively) quantitatively coincide. However, for sample I with the same net content of OAC (curve 3), a marked decrease in water content is observed. In other words, the sorptional properties of PA-6/OAC samples are controlled by the fractional content of IB form of OAC in the polymer. This experimental evidence suggests that IB form of OAC is distributed in the densely packed domains of the amorphous phase of the semicrystalline polymer, which are inaccessible for water molecules in a whole range of relative humidities. The RB form of OAC occupies disordered regions of the PA-6 amorphous phase, which are

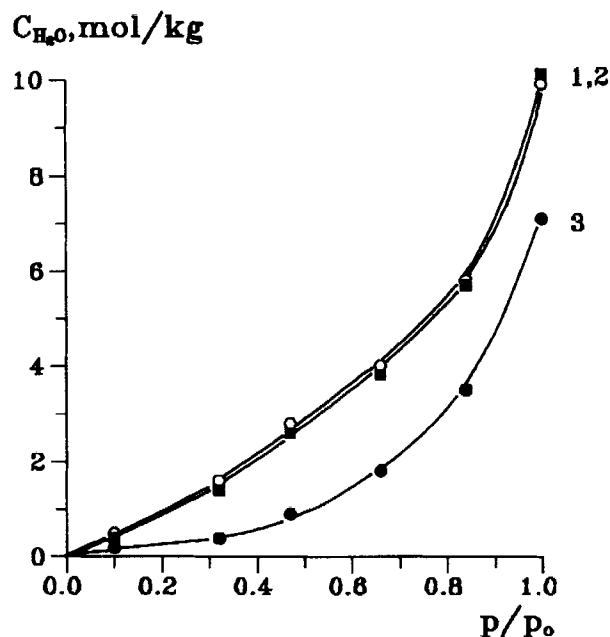


FIGURE 9 Isotherms of water sorption (293 K) by amorphous regions of initial PA-6 (1) and PA-6/OAC samples with OAC content 0.14 mol/kg (2, 3). 2 - Sample III, 3 - Sample I.

responsible for water sorption of PA-6. The introduction of OAC molecules into the above disordered regions is accompanied by physical cross-linking of macromolecules via formation of strong hydrogen bonds between phenolic hydroxyls of OAC and amide groups of PA-6. This gives rise to a drop in sorption capacity of such material as compared with the initial polymer.

The studies of elastic properties of the PA-6/OAC samples in a humid atmosphere also support a complicated pattern of influence of OAC on the mechanical properties of the polymer. Figure 10 shows the dependences of elastic modulus E_0 of PA-6/OAC samples versus OAC content at $p/p_0 = 0.47$ and 0.66 . Curves 1 and 2 correspond to the Samples I for which with increasing net content of OAC fractional content of IB form remains constant -0.32 ± 0.02 . Curves 3, 4, and 5 are associated with Samples II. These samples show an increase in fractional content of IB form of OAC with increasing the net content

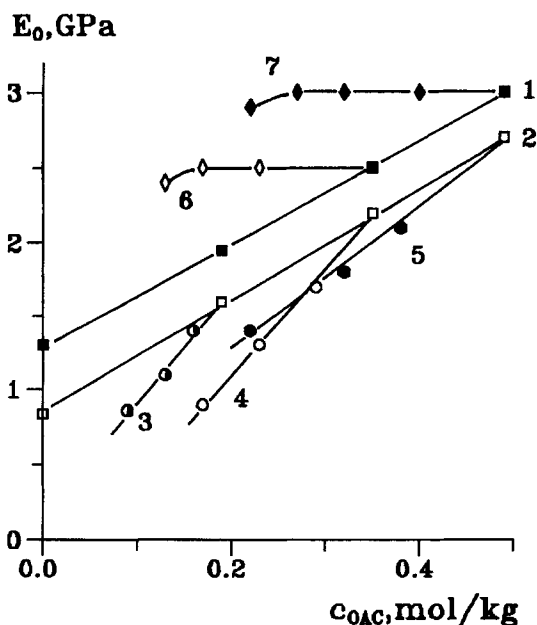


FIGURE 10 Elastic moduli of PA-6/OAC samples versus OAC content at p/p_0 0.47 (1, 6, 7) and 0.66 (2–5). Samples I (1, 2), Samples II (3–5), Samples III (6, 7).

of OAC in polymer. Curves 6 and 7 demonstrate the variations in elastic properties of the PA-6/OAC samples upon desorption of RB form of OAC (transition from Samples I to Samples III). In this case, with decreasing net content of OAC in polymer fractional content of IB form of OAC increases.

As might be seen, elastic modulus of the PA-6/OAC samples at given values of p/p_0 is determined not only by the net content of OAC in the polymer, but also by distribution of OAC between IB and RB forms. An increase in net content of OAC in the polymer amorphous regions is accompanied by increase in elastic modulus of the PA-6/OAC samples (Fig. 6, curves 1–5). However, the growth in E_0 is more pronounced, when an increase in the net OAC content is associated with increase in the fractional content of IB form (curves 3–5). Note that, in a wide range of OAC concentrations, the removal of RB form of OAC from the PA-6/OAC samples (curves 6 and 7) has no influence on elastic modulus of the polymer.

Let us emphasize, that the PA-6/OAC samples containing both IB and RB forms of OAC (Samples I and II) show a dramatic drop in water content as compared with initial PA-6 within the whole range of relative humidities. In this case, a decreased water sorption is controlled by the net content of OAC in the polymer. In other words, water sorption of the Samples I and II with the same net content of OAC (curves 1–5) is the same, despite a certain difference in the ratio between IB and RB forms of OAC. Desorption of RB form of OAC from PA-6 is accompanied by a sharp increase in water sorption. Note that water sorption of the Samples III containing only IB form of OAC is similar to that of initial PA-6 (Fig. 9, curves 1 and 2). Nevertheless, despite a high content of plasticizer (water) in the polymer, the elastic modulus of the samples is much higher than the corresponding values for initial PA-6 and Samples I and II containing both IB and RB forms of OAC.

The data presented in Figure 10 allows the following general conclusion. For the PA-6/OAC samples with the same net content of OAC, the higher modulus is observed for the samples with higher fractional content of IB form of OAC. Distribution of OAC in the polymer matrix between IB and RB forms controls not only the absolute values of E_0 of the PA-6/OAC samples, but also sensitivity of these characteristics to the plasticizing action of water. Increase in the fractional content of IB form of OAC is accompanied by a concomitant growth in E_0 , even though water sorption of the samples remains unchanged (curves 2–5) or drastically increases (curves 1, 6 and 7). The influence of IB form of OAC accumulated in the densely packed domains of the amorphous phase on elastic properties of the polymer proves the important role of these structural regions for the development of physico-mechanical properties of semicrystalline polymers.

Let us emphasize, that the above phenomena were observed only in the intermediate range of relative humidities, i.e., at 0.47 and 0.66. At $p/p_0 = 0$ or 1, the PA-6/OAC samples are in glassy or rubbery state, respectively. In this case, the elastic properties of the samples do not recognize distribution of OAC between IB and RB forms. They depend only on the net content of OAC in the PA-6/OAC samples. In other words, the decisive role of the ratio between IB and RB forms of OAC is well pronounced only in the range of relative humidities associated with transition from glassy to rubbery state.

CONCLUSION

Introduction of OAC in amorphous regions of PA-6 is associated with the distribution of OAC between two different forms reversibly and irreversibly bound with polymer matrix. The ratio between the above forms of OAC in polymer can be controlled either by varying the regimes of treatment of PA-6 samples in aqueous OAC solutions or by subsequent treatment of PA-6/OAC samples in water. Generally speaking, this ratio is responsible for the physical and mechanical behavior of PA-6 samples modified with OAC: glass transition temperature, temperature range of reinforcing action of OAC on PA-6 mechanical properties, water sorption, and elastic properties. Note, that elastic properties of PA-6 containing OAC are controlled by distribution of OAC between the above forms only in the case when polymer undergoes transition of its amorphous phase from glassy to rubbery state, regardless of whether this is realized: by increasing the concentration of plasticizer (water) or by increasing the temperature. This behavior is likely to be associated with the localization of reversibly and irreversibly bound forms of OAC with different structural sublevels in polymer amorphous phase.

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