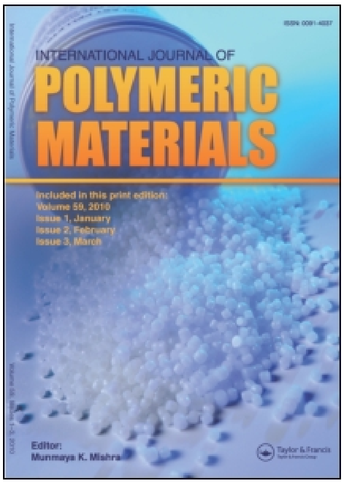

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An Approach to Improvement in the Mechanical Properties of Nylon-6 in a Humid Atmosphere

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Mechanical properties of Ny-6 isotropic films modified with oxyaromatic compounds were studied. The introduction of oxyaromatic compounds into Ny-6 is accompanied by an increase in the elastic modulus and strength of the polymer. The resistance of mechanical parameters to the action of moisture is controlled by an intermolecular interaction in the Ny-6/oxyaromatic compound systems and can be enhanced by going from low-molecular-mass oxyaromatic compounds to high-molecular-mass ones. The results observed were discussed in terms of a complexation between the components of the Ny-6/oxyaromatic system taking place in amorphous regions of the polymer.

KEY WORDS Nylon-6, mechanical properties, humidity

INTRODUCTION

The high sensitivity of the physical/mechanical properties of aliphatic polyamides (nylons) (primarily, glass transition temperature and elastic modulus) to moisture is widely discussed in the literature.[1–3] Water sorption by nylons is known to be due to the interaction of water molecules with the CONH amide groups *via* hydrogen bonding. Without going into details of this phenomenon, this interaction is known to be responsible for lowering the energy of intermolecular interactions as a result of scission of intermolecular amide-amide hydrogen bonds by water molecules and their subsequent replacement by the newly formed water-amide hydrogen bonds.[2,4,5] As a consequence of this, a dramatic decrease in the glass transition temperature is observed which is accompanied by concomitant lowering of the elastic modulus related to the transition of the polymer's amorphous regions from a glassy to a rubbery state.

From this standpoint, the problem of improvement in physical/mechanical properties of nylons in humid atmospheres is directly related to the enhancement of the intermolecular interaction in the amorphous regions of the polymer, resulting in high stability for intermolecular bonds with respect to the action of water.

Oxyaromatic compounds (OACs) (tanning agents) are known[6,7] to be promising modifying agents for nylons, improving their physical/mechanical properties. The common functional groups of OACs are phenolic hydroxyls which are able to form stable hydrogen bonds with polymer amide groups, providing polymer systems which have a high energy for intermolecular interaction.

In this paper, we advance an approach to improvement in the physical/mechanical properties of Ny-6 films in humid atmospheres by their modification with OACs. This approach is based on the possibility of controlling intermolecular interactions induced by hydrogen bonding between the components.

EXPERIMENTAL

In this study, commercial isotropic films of Ny-6 (trade mark PK-4) with mean molecular mass of 30,000 and thickness of 0.1 mm were used.

To modify Ny-6, synthetic tanning agent BNS, phenol-formaldehyde (PF), and resorcinol-formaldehyde (RF) resins were used as OACs.

BNS is a product of the condensation between sulfonated β-naphthol and 4,4′-dihydroxydiphenyl sulfone with formaldehyde. Its formula follows:

$$HOSO_2(C_{10}H_5OH)CH_2(C_6H_3OH)SO_2(C_6H_4OH)$$

To introduce BNS into the amorphous regions of Ny-6, polymer samples were immersed in aqueous BNS solutions at 100°C for 3 h. The concentration of the BNS solutions varied from 5 to 100 g/L.

Phenol-formaldehyde oligomers (precursors for the polycondensation to produce PF) were synthesized in basic aqueous solutions of phenol and formaldehyde at 80°C. Oligomers were introduced into Ny-6 films from their solutions in i-PrOH at 80°C for 3 h. The concentration of alcohol solutions of phenol-formaldehyde oligomers varied from 5 to 100 g/L. To produce a three-dimensional network of PF within the amorphous regions of the polymer. The Ny-6 samples with phenol-formaldehyde oligomers were annealed at 150°C for 1 h.

To modify Ny-6 with RF, polymer samples were kept in aqueous resorcinol solutions (concentration ranged from 5 to 200 g/L) at 100°C for 3 h. To condense the resorcinol with formation of three-dimensional RF networks in the amorphous regions of the polymer, Ny-6/resorcinol samples were treated at 150°C for 75 min with gaseous formaldehyde, produced by the thermal decomposition of paraformaldehyde.

The OACs content of the Ny-6 was determined gravimetrically. Mechanical properties of Ny-6 samples were studied using an "Instron-1100" tensile machine at a strain rate of 100%/min (20°C). Elastic modulus was measured at strains not higher than 3%.

Before the mechanical tests, polymer samples were conditioned in different humidities at 20°C for at least 24 h.

RESULTS AND DISCUSSION

Figure 1 shows the plot of elastic modulus of Ny-6/BNS films versus BNS content at different humidities. It is seen that the elastic modulus increases with BNS content

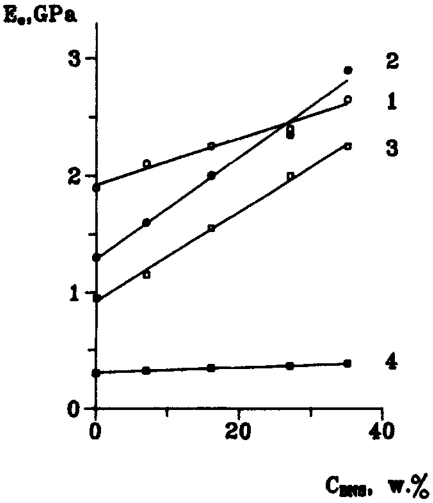

FIGURE 1 Elastic modulus of Ny-6/BNS films versus BNS content at 0(1), 47(2), 66(3), and 100(4) % RH.

at relative humidities (RH) of 0, 47, and 66% (Figure 1, curves 1–3). The increase in elastic modulus can be attributed to an increase in the energy of intermolecular interaction in Ny-6 on introduction of BNS into the polymer, due to formation of a complex between the components of Ny-6/BNS system. This complex is stabilized by the hydrogen bonds between the OAC molecules and the polymer amide groups.[8,9] The development of these hydrogen bonds proceeds via the introduction of phenolic hydroxyls of OAC through the N—H***O═C hydrogen bonds of nylon. It is worth noting that the strength of the newly formed O—H***O═C hydrogen bond exceeds the strength of the N—H***O═C bond in the initial polymer.[10]

So, intermolecular interactions in Ny-6/BNS systems are controlled not only by N—H***O═C hydrogen bonds, as observed in the virgin polymer, but also by intermolecular hydrogen bridges involving more energetic O—H***O═C hydrogen bonds. Increases in BNS content in the Ny-6 films implies an increase in the concentration of the more energetic intermolecular hydrogen bridges with the participation of BNS molecules in the amorphous regions of the polymer and, hence, an increase in the energy of the intermolecular interaction. This is reflected by the increase in the elastic modulus with increasing BNS content in dry Ny-6 (Figure 1, curve 1).

Humdification of Ny-6 is accompanied by a lowering of the energy of the intermolecular interactions due to the interaction of N—H***O═C intermolecular hydrogen bonds with water molecules. As a result, a marked decrease in the elastic modulus of the initial Ny-6 on an increase in RH is observed. The same situation is realized for Ny-6/BNS films (Figure 1). An increase in RH is attended by a decrease in the elastic modulus of Ny-6/BNS samples at a fixed BNS content. The only exception is related to the behavior of the elastic properties of Ny-6 with a BNS content above 20 weight% at 47% RH (Figure 1, curve 2). The higher values for the elastic modulus of wet samples, in comparison with those of dry ones, are explained by the antiplasticizing action of water on the polymer under the conditions studied.

Nevertheless, at 47 and 66% RH there is a noticeable increase in the elastic modulus of Ny-6 for an increase in BNS content (Figure 1, curves 2 and 3). It allows us to conclude that, under these circumstances, water molecules cannot break down the O—H***O═C hydrogen bonds between BNS molecules and the amide groups. In this case, an increase in the BNS content in Ny-6 is accompanied by an increase in the concentration of high-energy intermolecular hydrogen bridges involving O—H***O═C bonds and, hence, it should result in an increase in the elastic modulus to a value similar to that of the dry Ny-6/BNS samples.

In terms of complexation, the stability of the O—H***O═C hydrogen bonds toward the action of water is related to the stability of a complex between BNS and Ny-6 formed in the amorphous regions of the polymer in a humid atmosphere. As we could see, at 47 and 66% RH, the complex between the components of Ny-6/BNS systems appears to be stable, providing good resistance of the elastic properties against moisture.

At 100% RH (Figure 1, curve 4), there are no noticeable changes in the elastic modulus of Ny-6 relative to BNS content. This is evidence that, at this humidity, interaction of water molecules with the O—H***O═C hydrogen bonds leads to their scission and, hence, to dissociation of the complex. All intermolecular hydrogen bridges involving BNS molecules are destroyed and, consequently, increases in the BNS content have no influence on the elastic modulus.

Improvement in the elastic properties of Ny-6/OAC systems is associated with the formation of a complex between the components in the amorphous regions of the polymer. The stability of the enhanced elastic properties in a humid atmosphere is determined by the stability of the complex against the action of water molecules. To summarize, improvement in the elastic properties is directly related to an increase in the stability of the complex between the components of Ny-6/OAC systems.

The enhancement of the complex stability may be achieved by going from low-molecular-mass OACs (LM OACs) to high-molecular-mass ones (HM OACs). In the latter case, the cooperative character of the interaction between the components is realized, and one may expect an increase in the stability of the complex against the action of moisture, as compared to Ny-6/LM OAC systems.

Figure 2 presents the elastic modulus of Ny-6/PF films (curves 1–4) and Ny-6/RF films (curves 5 and 6) versus HM OACs content at different humidities. The comparison of the elastic properties of Ny-6/HM OACs systems (Figure 2) with those of Ny-6/LM OAC ones (Figure 1) indicates that, in both cases, an increase in OAC content is accompanied by an increase in the elastic modulus at 0, 47, and 66% RH. However, at 100% RH, these two types of systems show quite a different behavior for the elastic modulus. A sharp increase in the elastic modulus on increasing both PF and RF content (Figure 2, curves 4 and 6) is observed, in contrast to that of Ny-6/BNS samples (Figure 1, curve 4). Moreover, all the plots of the elastic modulus against PF content in Ny-6 at 0, 47, 66, and 100% RH (Figure 2, curves 1–4) can be extrapolated to the value of the elastic modulus in the vicinity

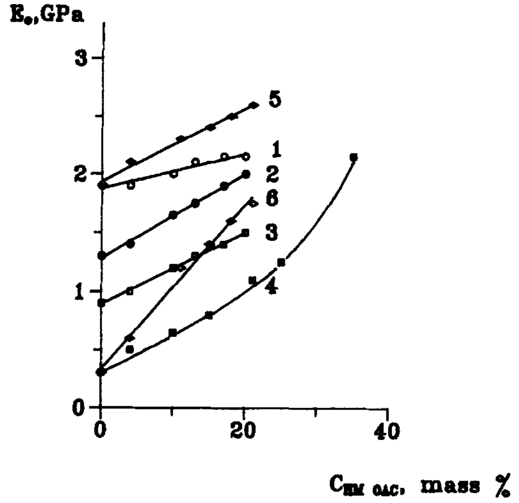

FIGURE 2 Elastic modulus of Ny-6/PF (1–4) and Ny-6/RF (5 and 6) films versus HM OAC content at 0(1 and 5), 47(2), 66(3), and 100(4 and 6) % RH.

of 2.2–2.4 GPa. In other words, the system of Ny-6/PF with PF content about 30–35 weight% appears to be quite stable to the action of moisture.

As we see, an increase in the elastic modulus of both Ny-6/PF and Ny-6/RF systems at 100% RH can be attributed to the stability of a complex between the components of these systems to the action of water molecules. In the case of Ny-6/HM OACs systems, enhancement in stability of the complex in a humid atmosphere, in comparison with Ny-6/LM OAC systems, is explained by increasing the cooperative interaction between the components by formation of a three-dimensional PF (or RF) network in the amorphous regions of the polymer.

It is worth mentioning that the introduction of OACs into Ny-6 is accompanied by a reduction in water sorption. This can be considered as a contributory factor to the enhancement of elastic properties in a humid atmosphere. However, at 100% of RH, both Ny-6/LM OAC and Ny-6/HM OACs systems show very similar values for the reduction of water sorption, which does not exceed a 2-fold decrease. So, the difference in the behavior of the elastic modulus of Ny-6/LM OAC and Ny-6/HM OACs systems at 100% RH cannot be explained on this basis. The improvement in elastic properties of Ny-6/OAC systems in a humid atmosphere is dictated by the increasing energy of the intermolecular interactions and by the stability of the intermolecular bridges involving OAC molecules against the action of moisture.

Plots of the strength of Ny-6 films *vs* BNS and PF content at different humidities are shown in Figures 3 and 4, respectively. As is obvious from these figures, the concentration dependence of the strength of Ny-6/OAC systems shows a general resemblance to those of the elastic modulus (Figures 1 and 2). The strength of these systems, as well as the elastic modulus, tends to increase on an increase in OAC content and to decrease on an increase in humidity. One can conclude that both elastic modulus and strength of Ny-6/OAC systems are controlled by the energy of the intermolecular interaction which increases on increases in OACs

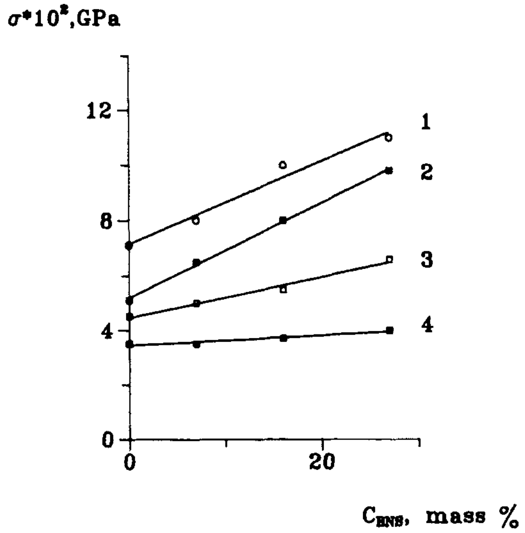

FIGURE 3 Strength of Ny-6/BNS films versus BNS content at 0(1), 47(2), 66(3), and 100(4) % RH.

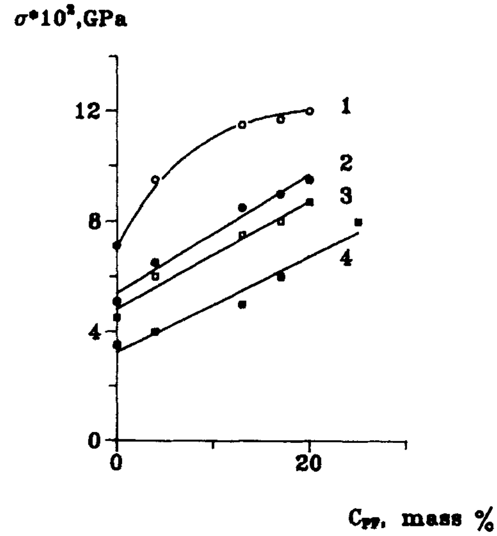

FIGURE 4 Strength of Ny-6/PF films versus PF content at 0(1), 47(2), 66(3), and 100(4) % RH.

content and decreases on increases in water content in Ny-6. This conclusion is in good agreement with the results discussed in References 11 and 12. There was also shown a correlation between both the elastic modulus and the strength and the cohesive energy density which is known to be a measure of the energy of intermolecular interactions in polymer.

It should be pointed out that the stability of the strength as well as the elastic modulus of Ny-6/OAC systems against the action of moisture is controlled by the stability of the complex between the components, and eventually, by the water resistance of the intermolecular bridges with the participation of OAC molecules. Comparison of LM OAC (Figure 3) and HM OACs (Figure 4) suggests that the latter appears to increase the stability of the strength properties of Ny-6/OAC films in a humid atmosphere (curve 4) as a result of the cooperative interaction between the components of the complex formed in a Ny-6/HM OAC system.

CONCLUSION

The introduction of oxyaromatic compounds (OACs) into the amorphous regions of Ny-6 gives rise to complex formation between the components by means of hydrogen bonding of the phenolic hydroxyls of the OACs with the polymer amide groups. This leads to a marked increase in the energy of intermolecular interaction and, as a result, to an enhancement of the mechanical properties of the polymer.

The resistance of the mechanical properties of Ny-6/OAC systems against the action of moisture is controlled by the stability of these complexes between the components and, finally, by the stability of the intermolecular hydrogen bridges involving OACs, against the action of water molecules.

The stability of the complexes to the action of moisture can be enhanced by increasing the cooperative interaction between the components of the Ny-6/OAC systems when going from low-molecular-mass OACs to high-molecular-mass OACs.

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