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Modification of Films of Heat-Resistant Polyimides by Adding Hydrosilicate and Carbon Nanoparticles of Various Geometries[1]

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Abstract—The possibility of modifying the properties of poly(4,4'-oxydiphenylene)pyromellitimide films by introducing into prepolymer solutions nanoparticles of various compositions and structures [hydrosilicate nanoparticles in the form of layered structures (montmorillonite) and nanotubes; carbon nanofibers] was examined. New intercalating agents, tetranuclear aromatic diamines, were suggested for pretreatment of montmorillonite prior to introduction into heat-resistant polymers. The mechanical characteristics of the nanocomposites with hydrosilicate nanotubes can be optimized by chemical pretreatment of the nanotubes prior to introduction into the polymer matrix. Introduction of the above-named nanoparticles into the polymer matrix appreciably increases the elastic modulus of the material. The largest increase in the elastic modulus is observed with hydrosilicate nanotubes of the chrysotile structure, coated with an aromatic modifier.

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One of priority problems of the modern polymeric materials science is the development of novel highly heat-resistant film materials and improvement of the existing materials. These materials are necessary for many branches of the modern engineering such as aviation and aerospace engineering, ship building, electronics, instrument making, and some special fields of electrical engineering.

Wide opportunities to solve this problem are offered by nanotechnological approaches, namely, by modification of the existing polymeric materials by introducing various nanoparticles into the polymer matrix. Numerous studies in which this approach is applied to modification of diverse polymeric materials have been published during the past decade. Among them are studies concerning the effect of introducing nanoparticles (mainly montmorillonite and carbon nanotubes) into aromatic polyimides [1–12].

Interest in such polymeric materials is due to their unique set of properties [13]. They combine extremely high heat resistance (today aromatic polyimides are the most heat-resistant among polymeric materials commercially produced in the world), excellent dielectric properties, high mechanical characteristics, and high chemical and radiation resistance. That is why aromatic polyimides are much in demand by various branches of engineering, and development of new materials based on polymers of this class is an extremely urgent problem.

The range of nanoparticles of various compositions suitable (from the structural and morphological viewpoint) as modifiers for polyimide matrices considerably expanded recently, but the results of their introduction into polyimide matrices are poorly understood. Furthermore, the majority of papers concerning polyimide nanocomposites do not allow comparative evaluation of different types of nanoparticles as polyimide modifiers.

The goal of this study was to compare the performance of various types of nanoparticles added into a polyimide matrix. To this end, a series of nanoparti-

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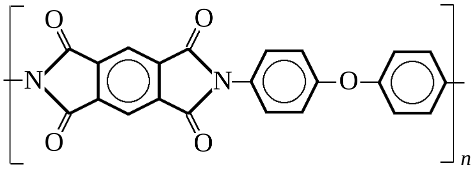
Table 1. Types of nanoparticles used in this study for modifying polyimide films

Run no.	Nanomodifier	Producer
1	Natural montmorillonite $m\{Mg_3[Si_4O_{10}][OH]_2\}p\{(Al,\ Fe^{3+})_2[Si_4O_{10}][OH]_2\}\cdot nH_2O$, transverse size of nanolayers 50–100 nm, interlayer distance ~1 nm	Cloisite, the United States, http://www.nanoclay.com
2	Synthetic hydrosilicate nanotubes of the chrysotile structure, $Mg_3Si_2O_5(OH)_4$; outside diameter ~20–25 nm, inside diameter ~4 nm, axial ratio 10–50	Developed by the Institute of Silicate Chemistry, Russian Academy of Sciences, http://isc.nw.ru
3	Carbon nanofibers; diameter ~100–150 nm, axial ratio 50–100	Showa Denko Carbon Sales, the United States– Japan, http://sdkc.com

cles differing both in the chemical composition and in the structure, morphology, and geometric characteristics were introduced into the same polyimide matrix, with the conditions of nanocomposite preparation being as similar as possible. The modification efficiency was judged from the extent of changes in the mechanical characteristics of the nanocomposite films relative to the films of the initial polyimide.

As the polymeric matrix we chose poly(4,4'-oxydiphenylene)pyromellitimide (polyimide PM):



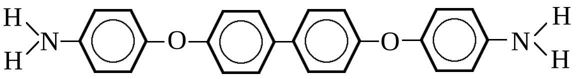
Among polyimide film materials commercially produced in the world, polyimide PM is the most popular. In the course of our study, we added into this material nanoparticles differing in the chemical composition, morphology, and geometric characteristics. The most interesting results were obtained with the following kinds of nanoparticles: nanolayers based on natural montmorillonite [14, 15], hydrosilicate nanotubes of the composition $Mg_3Si_2O_5(OH)_4$ with the chrysotile structure, prepared at the Institute of Silicate Chemistry, Russian Academy of Sciences [16, 17], and carbon nanofibers [18, 19]. The characteristics of the nanoparticles used are given in Table 1.

As noted above, in the course of preparing samples of nanocomposites with different modifiers, particular attention was given to ensuring as similar conditions and modes of the process as possible. However, it was apparently impossible to make the preparation conditions fully identical with different nanoparticles. The differences concerned pretreatment of nanoparticles prior to their introduction into the polymer matrix.

This procedure is particularly important in the case of composites with nanoparticles based on hydrosilicates of platelike morphology, prepared from natural montmorillonite. It is known [14] that particles of this hydrosilicate are stacks of parallel hydrosilicate nanolayers with a fixed interlayer spacing, 1.14 nm; the adjacent layers are linked by van der Waals and hydrogen bonds. To successfully use montmorillonite as a nanoadditive for polymeric nanocomposites, it is necessary to draw these nanolayers apart and to diminish interaction between them, so as to ensure the exfoliation of the nanoparticles into separate nanoplates and their subsequent uniform distribution in the bulk of the polymer. This is commonly done by intercalation of montmorillonite with a series of organic agents, most frequently with quaternary aliphatic amine derivatives, sometimes with silanes. The intercalant molecules are inserted into the interlayer space of montmorillonite, interacting with the ions on the montmorillonite surface. The intercalation procedure is well mastered; moreover, a series of montmorillonite brands impregnated with various agents and ready to introduce into polymers are commercially available.

However, our analysis of the intercalation systems described in the literature shows that, as a rule, they are hardly applicable to introduction of montmorillonite into heat-resistant polyimides. The major drawback of these intercalation systems is their poor heat resistance: Their active degradation starts, as a rule, in the range 200–250°C (Fig. 1). Thus, decomposition of intercalating agents with vigorous gas evolution starts already in the course of preparation of composite films based on polyimides, namely, in the course of themal cyclization of the prepolymer.

Therefore, it was necessary to choose new substances for the modification of montmorillonite, providing its intercalation and exhibiting elevated heat resistance. As such agents we chose tetranuclear aromatic diamines of the following structures.



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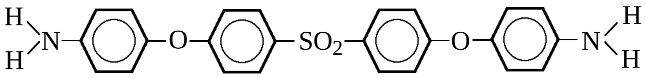

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These diamines, indeed, ensure efficient intercalation of montmorillonite, and their heat resistance is higher than that of the existing intercalants (Fig. 1). Finally, the presence of these lengthy organic molecules on the surface of montmorillonite nanolayers makes the nanoparticles hydrophobic, which should be favorable for the interaction of the nanoparticles with the polymer matrix. This interaction should be efficient to obtain a nanocomposite with high characteristics. The point is that these diamines are used as monomers in the synthesis of some polyimides; therefore, in the course of cyclization of the polyamido acid nanocomposite they can form chemical bonds with the polymer chain.

Initially we believed that chemical pretreatment of hydrosilicate nanotubes is considerably less important for ensuring optimal conditions of introduction of nanoparticles into the polymer. Although these nanoparticles show some tendency to aggregation because of their high surface energy [17], stable nanodispersions of these nanoparticles in aprotic solvents can be prepared without any chemical pretreatment. Initially the nanotubes were introduced into the polymer matrix in the unmodified state. However, the results showed that, to ensure the optimal interaction of the nanotubes with the matrix, the pretreatment is advisable. Therfore, we tested several organic agents for the pretreatment of these nanoparticles: hydroquinoline, aniline, butylamine, naphthalene, pyridine, phenol, and aminopropyltrimethoxysilane. The best results, from the viewpoint of the mechanical characteristics of the film obtained, were attained on treatment of the nanotubes with pyridine. Finally, in some experiments we introduced into the polymer carbon nanofibers without their pretreatment.

Figure 2 shows a family of tensile stress–strain diagrams obtained in mechanical tests of polyimide nanocomposites with various concentrations of montmorillonite (intercalation with diamine **I**). The families of diagrams corresponding to the composites with hydrosilicate nanotubes and carbon nanofibers are qualitatively similar to that shown in Fig. 2 and differ only in the scale of changes in the deformation and strength properties depending on the nanoparticle concentration.

The family of curves shown in Fig. 2 clearly demonstrates the main trends in variation of the mechanical characteristics of films with increasing amount of

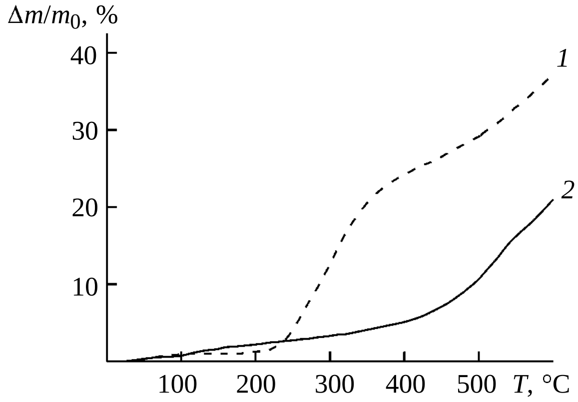

Fig. 1. DTA curves of montmorillonite samples intercalated with various agents: (*1*) commercial material 15A (Cloisite, the United States): montmorillonite intercalated with a quaternary aliphatic amine derivative; and (*2*) montmorillonite intercalated with tetranuclear aromatic diamine **I**.

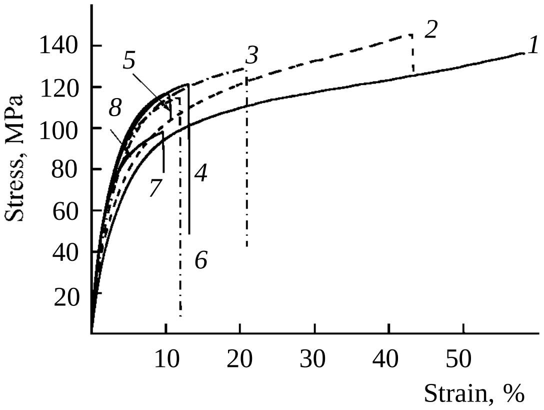

Fig. 2. Tensile strain–stress diagrams of nanocomposites of polyimide PM with nanoplates based on montmorillonite. Nanoparticle concentration, vol %: (*1*) 0, (*2*) 0.67, (*3*) 2.04, (*4*) 3.36, (*5*) 4.7, (*6*) 6.04, (*7*) 8.05, and (*8*) 10.07.

Table 2. Mechanical characteristics of films of nanocomposites of polyimide PM with various nanoparticles introduced in various concentrations

Hydrosilicate nanotubes			Hydrosilicate nanotubes treated with pyridine			Montmorillonite intercalated with diamine **I**			Carbon nanofibers		
C, vol %	*E*, GPa	ε_b, %	*C*, vol %	*E*, GPa	ε_b, %	*C*, vol %	*E*, GPa	ε_b, %	*C*, vol %	*E*, GPa	ε_b, %
0	2.95	67	0	2.91	65	0	2.90	49	0	2.99	56
0.59	3.03	57	0.59	3.07	58	0.67	3.10	46	0.705	3.10	38
1.18	3.10	38	1.18	3.28	54	1.34	3.26	42	1.41	3.25	34
1.77	3.23	27	1.77	3.36	44	2.01	3.42	22	2.115	3.41	25
2.95	3.43	19	2.95	3.78	30	3.36	3.65	13	3.525	3.69	22
4.13	3.72	17	4.13	3.97	23	4.7	3.94	10	4.935	3.98	21
5.9	4.01	14	5.9	4.29	19	6.04	4.18	11	7.05	4.28	12
7.07	4.16	11	7.07	4.38	16	8.05	4.23	10	10.575	4.31	11
8.84	4.25	12	8.84	4.41	14	10.07	3.96	7			
10.61	4.16	8	10.61	4.35	12						

nanoparticles introduced: The material becomes more rigid (the elastic modulus and tensile stress in the initial portion of the stress–strain curve increase), but the breaking elongation regularly decreases. The dynamics of these changes for the nanocomposites studied are given in Table 2.

Introduction of all the three kinds of nanoparticles leads to a considerable increase in the elastic modulus. This clear trend is observed at relatively low (units of vol %) concentrations of the nanoparticles introduced. With an increase in their concentration (in the range ~7–8 vol %), the growth of the modulus decelerates, and with further introduction of nanoparticles it ceases to grow and, in the case of montmorillonite-based nanoplates, even decreases. This phenomenon was described previously [2, 5] and is attributable to aggregation of nanoparticles, starting at their increased concentration. This process leads to structural segregation of the material, gives rise to internal stresses, and increases the porosity.

The growth of the elastic modulus was the most significant on introduction of hydrosilicate nanotubes pretreated with pyridine. For this composite, with 8 vol % nanotubes, the elastic modulus was 1.52 times that of the unfilled polyimide film. Somewhat less pronounced increase in the elastic modulus was observed with nanocomposites of polyimide PM with platelike nanoparticles based on montmorillonite: by a factor of 1.46 with 8 vol % montmorillonite. It should be noted that such ratio of the results obtained with hydrosilicate nanotubes and montmorillonite-based nanoplates is well consistent with the theoretical concepts [20] according to which quasi-unidimensional nanoparticles (nanotubes, nanofibers) exert a stronger modifying effect on the elastic modulus of a nanocomposite, compared to nanoplates with the same axial ratio.

Somewhat weaker effect on the Young's modulus of films is exerted by introduction into the polyimide matrix of carbon nanofibers and untreated hydrosilicate tubes.

It should be noted that the data obtained clearly demonstrate the importance of ensuring the optimal interaction of nanoparticles with the polymer matrix to obtain composites with the best characteristics. Whereas with untreated hydrosilicate nanotubes the elastic modulus increased by a factor of 1.42 (at maximum) relative to a film of unfilled polyimide PM, pretreatment of the same nanotubes (with the same axial ratio) with pyridine ensured an increase in the elastic modulus by a factor of 1.52. The same conclusion follows from the comparison of the results obtained with untreated hydrosilicate nanotubes and carbon nanofibers. For these two kinds of nanoparticles, the mean axial ratio differs by a factor of 2–3. However, Table 2 shows that introduction of these nanoparticles into the polymer matrix leads to essentially similar results. This effect reflects differences in the quality of interaction of nanoparticles with the surrounding polymer, which level off the difference in the axial ratios.

A pronounced decrease in the breaking elongation (ε_b) was observed with all the examined nanocomposites on introducing 3.5–4 vol % of nanoparticles. With further increase in their concentration, the decrease in ε_b considerably decelerates. The highest ε_b values were obtained with nanocomposites of polyimide PM with hydrosilicate nanotubes pretreated with pyridine.

A decrease in the deformability of films on introduction of nanoparticles into the polymer is an important trend, because it determines the limiting concentration of a nanofiller above which the material becomes unusable.

If we assume 15% as the lower permissible limit of ε_b (such strains allow reliable use of polyimide films, because real permissible strains do not exceed 5–7%; above this level, the strains become irreversible, which is clearly seen in Fig. 2), then the limiting concentration of hydrosilicate tubes in the composite will be 6–7 vol % (Table 2). Actually, optimization of the homogenization of a prepolymer solution with nanoparticles may make this limiting concentration even higher, 8–9 vol %; still higher concentrations of nanoparticles are not appropriate in any case, as they do not lead to a further pronounced increase in the film rigidity.

Thus, introduction of nanoparticles into a polyimide matrix leads to a considerable increase in the rigidity of the nanocomposite material and, at the same time, to a decrease in the breaking elongation. The most pronounced modification of the mechanical characteristics of polyimide films is provided by introduction of hydrosilicate nanotubes pretreated with pyridine. By so doing, the highest elastic modulus is attained, with the fairly large breaking elongation preserved. Somewhat lower results were obtained with platelike montmorillonite-based nanoparticles.

Introduction of carbon nanofibers into the polyimide matrix is still less efficient. However, when assessing the potential of these nanoparticles as a polyimide modifier, we should realize that in this study nanofibers were introduced into the polymer without any pretreatment. Preliminary activation and modification of the surface of these nanoparticles may considerably improve their performance. On the other hand, nanocomposites with carbon nanofibers principally differ from those with hydrosilicate nanoparticles in that they show increased electrical conductivity. Therefore, composites of polyimides with carbon nanofibers may be promising as heat-resistant polymeric conducting materials.

EXPERIMENTAL

Films of polyimides and polyimide nanocomposites were prepared by a standard two-step procedure [13]. Nanoparticles were dispersed in *N*-methyl-2-pyrrolidone using an ultrasonic disperser and then were added to a solution of a prepolymer (polyamido acid). In our study we used a ~18% solution of poly(4,4'-oxydiphenylene)pyromellitamido acid in dimethylformamide (Estrokom, Moscow, Russia). After thorough homogenization by prolonged mechanical mixing, films were cast from the nanocomposite solutions onto glass supports. The cast films were dried at 80°C to remove the solvent and then were heated on the support to 360°C for the thermal cyclization.

Mechanical characteristics of the films were determined under the conditions of uniaxial extension with a UTS 10 unversal installation for mechanical tests (Germany). We determined the elastic modulus E, plasticity limit σ_p, tensile strength σ_t, and breaking elongation ε_b.

Thermal gravimetric analysis (TGA) of montmorillonite samples impregnated with various agents was performed with a laboratory thermal balance at a heating rate of 5 deg min^{-1} in the self-generated atmosphere.

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