

PECULIARITIES OF MECHANICAL BEHAVIOR OF FILMS OF POLYURETHANE-SILICA NANOCOMPOSITES FORMED BY THE PARALLEL SYNTHESIS METHOD

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ABSTRACT

Films of aliphatic polyurethane-silica nanocomposite containing up to 27.3 mol. % of silica were obtained by the parallel synthesis of both composite components in one common process. This method permits to obtain the nanocomposite materials with the uniform distribution of nanoparticles in the polymer matrix volume. The rise of the silica concentration in the nanocomposite film was shown to lead from one hand to the progressive fall of both the Young's modulus and yield stress and from another hand to the rise of the ultimate deformation and thermal expansion coefficient values. These effects were ascribed to the formation of the excessive free volume in the material along with the raise of silica concentration.

KEYWORDS: nanocomposite films; parallel synthesis; mechanical properties; thermal stability; free volume

INTRODUCTION

One of the most important trends of polymer material science today is concentrated at the elaboration of the optimal methods of polymer-inorganic nanocomposite materials formation and broad investigations of properties of these materials. Really, the introduction of nano-sized fillers into the polymer matrix yet in very modest concentrations let us to produce the materials with the properties which differ sensibly from these of the unfilled polymer material (Moniruzzaman et al., 2006; Tan et al., 2006).

The most commonly used method of nanocomposites formation today is the incorporation of previously synthesized nanoparticles into melts or solutions of already previously synthesized polymers at the stage of their processing to produce some final goods. It is a reasonably simple method and nanocomposite materials of different types can be produced by this way. But from another hand some other approaches can be used to solve the problem. For example the polymerization of starting monomers can be carried out in a medium, in which some quantity of previously formed nanoparticles is introduced (Lee et al., 2005), or inversely the process of nanoparticles formation via sol-gel technology can be carried out inside the polymer matrix (Donghai Sun et al., 2005). Some systematic information concerning these and other alternative ways of nanocomposites formation or the peculiarities of physical properties of the materials, produced by these methods, can hardly be found in scientific literature.

One of these alternative methods to produce the polymer-inorganic nanocomposite materials is so called simultaneous or parallel synthesis. According to this method both the matrix polymer and the nanoparticles incorporated into it are synthesized simultaneously in one common process. To carry out this procedure such combinations of starting monomers should be used that yield under the appropriate reactions two different products at the same time. One of these products is the polymer which forms the matrix of the nanocomposition. The other product of these reactions is an inorganic matter which yields in the concentration substantially less than that of the matrix polymer. And just after the acts of their formation the molecules of this second matter form under the condensation processes some particles in the volume of the polymer matrix. The sizes of these particles can differ in a broad range depending on the synthesis conditions. In certain conditions the nano-sized particles of inorganic filler can be formed by this way, and in this case the formation of the nanocomposite material will take place.

Parallel synthesis methods of nanocomposites formation are more complicated from the viewpoint of practical realization than, for example, mixing of nanoparticles and matrix polymer at the stage of polymer processing. But these methods have some valuable advantages over others methods mentioned above. The most significant of them is a possibility to obtain by a simple way the uniform distribution of nanofiller particles in the volume of the polymer matrix. This uniform nanoparticles distribution is

a very important condition of the formation of polymer-inorganic nanocomposite materials with the high level of properties. While using other methods of nanocomposites formation it is a difficult problem to insure the fulfillment of this claim. But if we use the parallel synthesis method the problem can be solved by the thorough homogenization of the starting reaction mixture which looks as a rule like a solution of all reagents, which we need, in a common solvent. In this case the reaction, which leads to the formation of the nanoparticles, proceeds in the uniform conditions and with the same speed in all regions of the reaction volume.

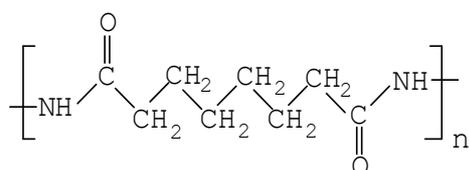
One important peculiarity of the methods under consideration should be taken into account while their practical use. Under the clear thermodynamical reasons only the particles of spherical or quazy-spherical shapes can be formed by the parallel synthesis. Meantime it is known that while we introduce the nanoparticles of such geometry into any polymer matrix we can not produce as a rule the deep variations of such valuable properties of the material as mechanical, transport, or electrical ones. To get these goals at the moderate concentrations of nanofillers the use of nanoparticles of the anisotropic geometry is preferable, namely nanolayers or nanoparticles of cylindrical geometry (nanotubes or nanofibers) (Garboczi et al., 1995; Becker et al. 2002; Xie et al., 2005; Yudin et al., 2007; Yudin et al., 2008).

Taking into account these circumstances it is especially interesting to study the cases in which the incorporation of spherical nanoparticles into any polymer matrices insures the substantial variations of the mechanical properties of the material under consideration yet at modest concentrations of nanofiller. Namely this situation was examined in our work. We have studied the mechanical and thermal properties of composite films of aliphatic polyurethane filled by the spherical silica nanoparticles, obtained by the parallel synthesis method by using the sol-gel technology (Ellsworth and Novak, 1993). The analysis of the mechanical and thermal behavior of these materials containing different amounts of nanoparticles permits us to clarify some interesting peculiarities of the structural organization of these systems.

EXPERIMENTAL

MATERIALS

The polyurethane containing the long (6 -CH₂-groups) aliphatic fragment in the elementary unit was used as a matrix polymer:



The parallel synthesis which yields this polyurethane and spherical SiO₂ particles of the average diameter 50 - 100 nm, embedded into the polymer volume, was described in details in (Trofimov et al., 2007). By this way the polyurethane-silica nanocomposite films were obtained with the SiO₂ concentrations from 7.7 to 27.3 mol. %. The thickness of the films under study was 30±5 microns.

CHARACTERIZATION

The mechanical tests of the films under study were carried out with the UTS 10 mechanical test system (Germany) in uniaxial tension mode using the band-like film samples of 2 mm width and 20 mm long. The extension speed was 2 mm/min. The Young's modulus *E*, yield points σ_y , tensile strengths σ_b , and ultimate strains ε_b were determined by these tests.

The longitudinal coefficients of thermal expansion (CTE) of the films were determined with the UTS 10 test system in the temperature range 50-150 °C.

The thermogravimetric analysis (TGA) was conducted using 10 mg samples contained in a platinum crucible under a heating rate of 5°/min in the self-generating atmosphere. TGA data obtained at these tests were used to calculate the indices of thermal stability of the polymer fraction of the films tested: τ_5 and τ_{10} – the temperature values at which polymer sample losses 5 and 10 % of its initial mass under the thermal destruction processes.

The densities of the nanocomposite films were measured at room temperature by using the flotation method in the mixtures of CCl₄ and toluene.

RESULTS AND DISCUSSION

The results of the mechanical tests of the nanocomposite films under study (Fig. 1, Table 1) demonstrate the strong dependence of the films' properties on the concentration of the SiO₂ nanoparticles. But the character of these dependences is really opposite to the common tendencies that can be detected while introducing the nanoparticles of different types into different polymers (Delozier et al., 2002; Xie et al., 2005; Gofman et al., 2007).

As a rule the rise of the nanoparticles concentration in the material leads to the progressive rise of both the Young's modulus and yield stress and from another hand to the progressive fall of ultimate deformation in tension. But the rise of silica concentration in the nanocomposite films studied provokes the progressive fall of both Young's modulus and yield stress and the rise of the deformation at break.

It should be pointed out that the matrix aliphatic polyurethane used in our work is in the unfilled state a very brittle system with high level of the inner mechanical stresses. As a result no practically usable materials can be processed from this polymer: the

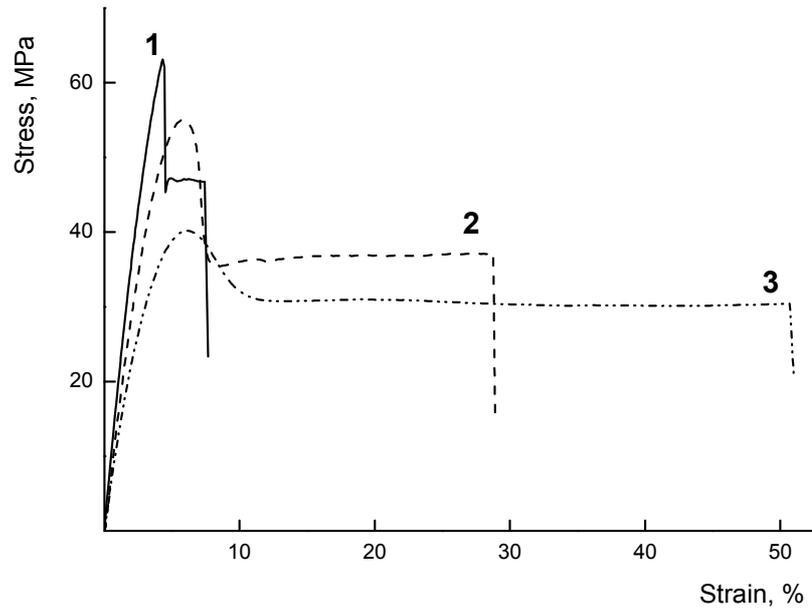


Fig. 1 Stress-strain curves of the nanocomposite films with different silica concentrations: 1 – 7.7 mol. %, 2 – 20.0 mol. %, 3 – 27.3 mol. %.

Table 1 Mechanical and thermal properties of polyurethane-silica nanocomposite films.

Sample No	SiO ₂ concentration, mol.% - mass.%	Film properties					
		E, GPa	σ _y , MPa	ε _{br} , %	CTE, deg ⁻¹ × 10 ³	τ ₅ , τ ₁₀ , °C	ΔV _{free} , %
1	0	2.03±0.09	-	0.5±0.1	-	257, 277	0
2	7.7 – 2.7	1.82±0.10	63±5	7±1	3.4	255, 275	0.6
3	11.1 – 3.9	1.68±0.08	57±3	15±3	3.7	255, 273	1.5
4	20.0 – 7.1	1.63±0.04	55±2	38±2	4.6	254, 272	4.0
5	25.0 – 8.8	1.59±0.03	54±2	43±3	5.0	247, 267	4.7
6	27.3 – 9.7	1.28±0.08	39±2	48±4	5.3	246, 265	5.1

intensive cracking takes place already at the stage of material formation. But the films of polyurethane-silica nanocomposites, produced by the parallel synthesis method, demonstrate the plastic character of the deformational behavior (Fig. 1): the stress maximum – the yield point is clearly seen at the stress-strain curves followed by necking process.

As a result the nanocomposite formation permits in this situation to obtain the elastic non-brittle films based on the brittle polyurethane matrix. These materials can be used in practice for different applications.

We should point out that the effects described above (the progressive rise of the ultimate deformation and fall of the stiffness) can be traced up to the maximal silica concentration (~ 27 mol. % or ~ 10 mass. %). It means that in these compositions does not take place the tendency to the realization of nanoparticles agglomeration processes at the rise of their concentration. While using other methods of the nanocomposite formation these undesirable processes lead often to the gradual disappearance of the positive effects of nanofilling while the rise of nanoparticles concentration up to ~ 9-12 % (Gu et

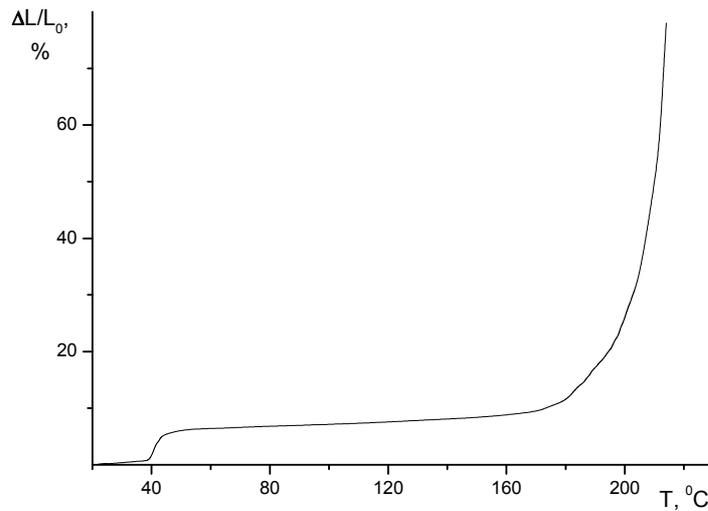


Fig. 2 A typical thermo-mechanical curve of the polyurethane-silica nanocomposite film.

al., 2001; Chang et al., 2002; Liu et al., 2002; Gofman et al., 2007).

The thermo-mechanical tests do not show any differences in temperatures of relaxational transitions in films with different concentrations of silica. All compositions demonstrate two transitions (Fig. 2) – the low temperature one in the temperature region 35-40 °C (the low intensity of the rise of chain mobility) and the intense transition in the region 195-215 °C with the pronounced rise of the segmental chain mobility, apparently the glass transition. Taking into account the same values of transition temperatures of all compositions studied we can conclude that the glass transition temperature of the unfilled polyurethane used in our work as a polymer matrix is situated in the same temperature region (the direct determination of the thermo-mechanical behavior of this unfilled polyurethane film is impossible because of its brittleness).

The values of the temperatures of thermally stimulated transitions were used to choose the diapason of temperatures in which we determined the CTE of the composite films: 50-150 °C. In this temperature region no thermally stimulated transitions take place in these materials. The progressive raise of CTE value was detected along with the rise of silica concentration (Table 1).

The TGA data demonstrate the gradual depression of both τ_5 and τ_{10} values of the polyurethane component of nanocomposite films along with the rise of silica concentration (Table 1).

Analyzing all results described above we can suggest that along with the raise of silica nanoparticles concentration the realization of less dense structure of the material takes place as compared to that of the unfilled polyurethane. This loosening of the material

means in other words the fall of the density of intermolecular interactions in the polymer matrix.

To check the validity of this suggestion the density values were measured of all films under study. The results demonstrate the progressive rise of the film density along with the rise of silica concentration (Fig. 3). Then we have compared the experimental values (ρ_{exper}) to the calculated ones (ρ_{calc}) obtained using the additive scheme of the composite material:

$$\rho_{\text{calc}} = \rho_{\text{filler}} \cdot C_{\text{filler}} + \rho_0 \cdot (1 - C_{\text{filler}})$$

where ρ_{filler} is the density of nanofiller, ρ_0 is the density of matrix polymer, and C_{filler} is the mass concentration of nanoparticles in the composite material.

The density of amorphous silica (2.2 g/cm³) was taken as a conservative estimate of ρ_{filler} value.

As far as we can see comparing two values of density obtained for each composition (Fig. 3) the experimental values are less than calculated ones and the difference between ρ_{calc} and ρ_{exper} raises along with the rise of silica concentration in the nanocomposite film. This fact suggests the formation of the excessive free volume in the composite material and the raise of the amount of this volume while we raise the nanoparticles concentration. The values of this excessive free volume:

$$\Delta V_{\text{free}} = (1 - \rho_{\text{exper}} / \rho_{\text{calc}}) \cdot 100 \%$$

are listed in Table 1.

These data demonstrate the marked rise of the free volume in the films studied along with the rise of silica concentration. The characteristics of this excessive free volume – the sizes of the pores and

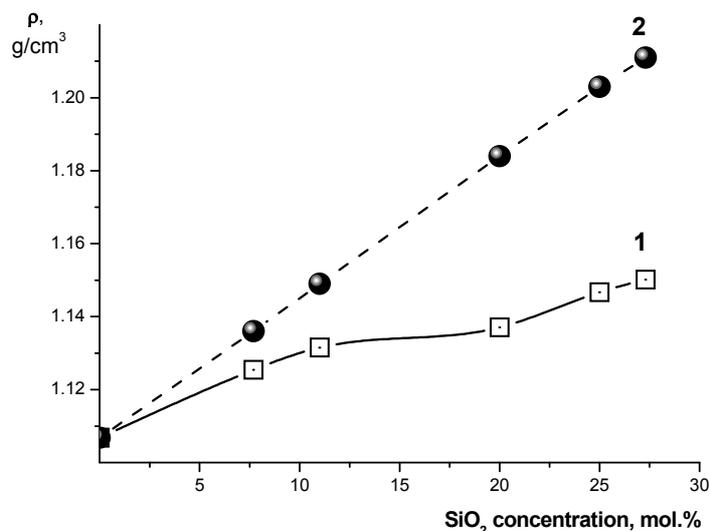


Fig. 3 The experimental (1) and calculated (2) values of the density of the nanocomposite films versus silica concentration.

their distribution in the film volume can not yet be described in details at this stage of our work. To clarify the situation a set of precise electron microscopic investigations should be carried out. But the results that we have already obtained permit us to exclude the possibility of the macro-pores formation because in this case at the expense of the heterogenization of the material structure it is difficult to insure the high level of the ultimate deformation of the material studied and the rise of this deformation along with the rise of silica nanoparticles.

The alternative explanation of the mechanical effects registered can be put forward if we suppose that the starting (unfilled) polyurethane films have partially ordered structure and the nanocomposite formation leads to the gradual amorphization of the material. To check this hypothesis the so called Vander-Vaals density of the polymer matrix ρ_{theor} was calculated in accordance with the scheme described in (Askadskii, 2003; 2005) and then the molecular packing coefficients k was derived for the polyurethane used in the work:

$$k = \frac{\rho_{\text{exper}}}{\rho_{\text{theor}}},$$

It is known that polymers of different classes demonstrate the analogous linear relations between k values and the degrees of crystallinity (Askadskii, 2003; 2005). The fully amorphous structure of polymer material is characterized by the $k = 0.683$, while the fully crystalline one – by the $k = 0.750$. The

k value of the unfilled polyurethane film was found to be 0.684. This fact means that the starting polymer film has the fully amorphous structure.

Taking into account the mechanical effects described above we can suppose that this excessive free volume distributed in the polymer matrix acts in our composite systems as a structural plasticizer which depresses the material's stiffness and insures the plastic type of the deformational behavior of these films.

One possible additional effect should be mentioned which can affect the non-brittle deformational behavior of the nanocomposite films. It is the well known effect of the racks formation stoppage at the expense of their interactions with holes distributed in any materials subjected to the action of the mechanical load (Cherepanov, 1998).

From another hand the presence of the system of pores distributed in polymer matrix insures the effective rise of the diffusion speed of volatile products of the polymer thermal destruction across the polymer volume towards the surface. As a result some depression of the indices of thermal stability was registered along with the rise of silica concentration.

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