Creep/Stress Relaxation of Novel Hybrid Organic-Inorganic Polymer Systems Synthesized by Joint Polymerization of Organic and Inorganic Oligomers

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Summary: The scientific and industrial field of hybrid organic-inorganic polymer systems (HOIS) is widened in recent years due to possibility of combination of various organic and inorganic building blocks and obtaining hybrid materials with novel characteristics. The aim of the present paper is to develop the knowledge of the relationships between mechanical properties and structure of the synthesized HOIS. Novel hybrid organic-inorganic polymer systems have been synthesized by joint polymerization of organic and inorganic components due to reactions between their reactive groups, namely free NCO-groups in the organic component and OH-groups in the inorganic component. Creep and stress relaxation measurements of HOIS with different chemical composition of the organic component have been fulfilled. Good correlations between changes of mechanical parameters, structure of hybrid organic-inorganic networks, which are formed during synthesis of HOIS, and the theoretical model have been established.

Keywords: hybrid organic-inorganic polymers; joint polymerization; mechanical properties; networks; structure

Introduction

Hybrid organic-inorganic polymer systems (HOIS) are a new class of polymers, the study of large-scale structure and properties of those were started relatively recently. The reason of the interest to these systems is the possibility of variation of their chemical structure at synthesis which includes organic and inorganic blocks, that, in turn, enables to change the properties of HOIS in a wide range and to obtain materials with necessary characteristics.

Today the most widespread way of HOIS obtaining is sol-gel method, which is effective for the synthesis of hybrid organic-inorganic systems with specified properties. Thus, the possibility of designing of the multifunctional organic-inorganic systems using the sol-gel technology by changing the chemical composition and structure of inorganic phase was considered.[1,2] However, this method is multistage and rather complicated. The original method of HOIS synthesis by joint polymerization of liquid reactive organic and inorganic oligomers having reactive functional groups has been proposed.[3,4] The structure of such HOIS was realized in a form of an organic polymer matrix with inorganic phase inclusions, the inclusion of these are from nanometer dimensions, namely the order 7–10 nm,[5] to several micrometers.[6] Such a structure provides specific physical-mechanical properties of HOIS.

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The purpose of this work was to establish the dependences of mechanical properties - creep (deformation of the material in time under the constant load) and stress relaxation (the recovery of sample deformation after unloading) on chemical composition of the HOIS, in which the organic component was based on mixture of isocyanate-containing oligoetherurethane and low-molecular polyisocyanate, while the inorganic component was the metal silicate. The results were described by a theoretical approach based on Burger's four-element mechanical model.[7]

Materials and Methods

HOIS were synthesized in the reactive mixture of organic component, which had free reactive NCO-groups and the inorganic component with reactive OH-groups. The organic component consists of oligoetherurethane (UO) - macrodiisocyanate with Mw = 4500 and 3,6% of NCO-groups and low-molecular polyisocyanate with Mw = 250 and 32% of free NCO-groups (PIC). The ratio UO/ PIC was varied from 0/100 to 100/0%; the total number of NCO-groups in the organic component was calculated from additive contributions of components. The inorganic component was metal silicate (MS), the water solution of that exists in the form of oligomer.[8] The ratio of organic/inorganic components was equal to 70/30 for all HOIS. Detailed reactions of HOIS polymerization are described in.[5,9] The reactive mixture of organic and inorganic components was carefully mixed until the completely homogenization state, placed in teflon form with appropriate configuration (in the form of disks), in which the HOIS curing was proceeded at room temperature (22 ± 1 °C) during 24 hours.

Creep and stress relaxation investigations were fulfilled using TA Instruments TMA Q400 EX equipment and methods, which are similar to the methods described in,[10,11] in the penetration mode with constant load that provided the indenter pressure on the sample equal to 0,057 MPa. HOIS samples with 12 mm in diameter and a thickness of 1,5 mm were loaded using the flat-end indenter with 3 mm in diameter. Loading time (creep time) was taken 5 minutes; the measuring of deformation was provided with frequency of 1 s^{-1}. Further the force was unloaded and the stress relaxation was determined during next 5 minutes with the same frequency of measurements of the deformation recovery.

Theoretical Model

The simplest model, which describes the stress relaxation is Maxwell's two-element model,[12] but its usage for mechanical deformation in polymer and composite systems interpretation leads to significant discrepancies with experimental results. In this paper for description of the experimental creep and stress relaxation curves the Burger's four-element viscoelastic model[7] has been used. This model is a combination of elastic elements (springs) with the Hookean deformation and dampers, which are deformed according to Newton's law [12–15] (Figure 1, a). Theoretical creep and stress relaxation curves of Burger's model are shown in Figure 1, b.

Generally, in the frame of this model, the deformation in time under the constant load can be divided into three successive stages: the instantaneous deformation, primary (short) creep and static creep.[14,16–19] According to, [12,14,20–22] in the Burger's model the full deformation of the system during short creep ε_c is the sum of three types of deformation: instantaneous deformation:

$$\varepsilon_{ci} = \frac{\sigma}{E_1} \tag{1}$$

elastic deformation:

$$\varepsilon_{ce} = \frac{\sigma}{E_2}\left[1 - \exp\left(\frac{E_2 t}{\eta_2}\right)\right] \tag{2}$$

and plastic (residual) deformation (which is Newtonian flow):

$$\varepsilon_{cr} = \frac{\sigma t}{\eta_3} \tag{3}$$

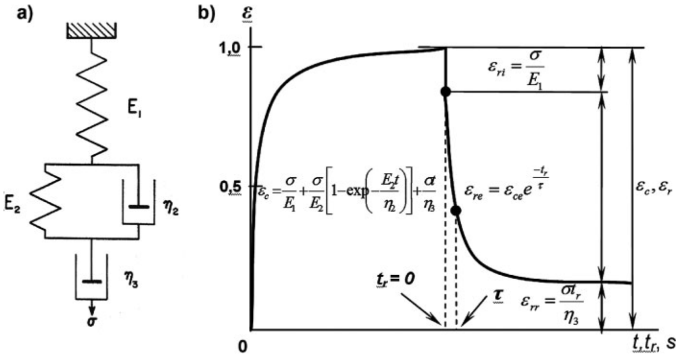

Figure 1.
Burger's four-element theoretical model (a); theoretical creep and stress relaxation curves of Burger's model (b).

It can be described by the following Equation (4):

$$\begin{aligned}\varepsilon_c &= \varepsilon_{ci}+\varepsilon_{ce}+\varepsilon_{cr}\\ &= \frac{\sigma}{E_1}+\frac{\sigma}{E_2}\left[1-\exp\left(-\frac{E_2t}{\eta_2}\right)\right]+\frac{\sigma t}{\eta_3}\end{aligned} \tag{4}$$

where E_1 and E_2 are the elasticity modulus of elastic elements, η_2 and η_3 are the viscosity of liquid in dampers, σ is load force and t is creep time.

At the load moment $t=0$ the initial deformation of the system is only equal to the instantaneous deformation ε_{ci} of the spring E_1. Further strain ε_{ce} is due to the creep of the system, i.e., spring E_2 deformation and damper η_2 displacement, as well as damper η_3 displacement, which is responsible for residual deformation ε_{cr}.

After unloading at $t_r=0$ (see Figure 1, b) the strain recovery (which is a result of stress relaxation) can be described by the Equation (5) similar to the Equation (4):

$$\begin{aligned}\varepsilon_r &= \varepsilon_{ri}+\varepsilon_{re}+\varepsilon_{rr}\\ &= \frac{\sigma}{E_1}+\varepsilon_{ce}\left[\exp\left(-\frac{t_r}{\tau}\right)\right]+\frac{\sigma t_r}{\eta_3}\end{aligned} \tag{5}$$

In this equation the value of $\tau=\eta_2/E_2$ can be defined as the stress relaxation time. At the unloading moment $t_r=0$ the strain $\varepsilon_{ri}=\sigma/E_1$ is momentary recovered and does not take a part in the system relaxation. The recovery of the deformation occurs also except damper η_3 displacement, the residual deformation $\varepsilon_{rr}=\sigma t_r/\eta_3$ remains. Thus, the stress relaxation corresponds to elastic deformation ε_{re} only that is described by Equation (6):

$$\varepsilon_{re}=\frac{\sigma}{E_2}\left[1-\exp\left(\frac{E_2t}{\eta_2}\right)\right]\exp\left(-\frac{t_r}{\tau}\right) \tag{6}$$

where t_r – is running time for the process of the deformation recovery; the value of t corresponds to the value of $t_r=0$ at unloading. The stress relaxation time τ can be determined from the experimental recovery curve in the normalized form:

$$\frac{\varepsilon_{re}}{\varepsilon_r-\varepsilon_{ri}-\varepsilon_{rr}}=e^{-\frac{t_r}{\tau}} \tag{7}$$

The ratio $e^{-\frac{t_r}{\tau}}=e^{-1}=0.368$ corresponds to the time $t_r=\tau$, i.e. to the stress relaxation time value, when normalized value of ε_{re} riches to 0.368 (Figure 1, b and Figure 2).

Results and Discussion

Figure 2 represents the creep under the constant stress equals to 0,057 MPa, and the recovery of deformation as a result of stress relaxation after unloading versus time for the samples with 3,6%, 13,5% and 26,1% content of NCO-groups.

The calculated curve of deformation under the load and the stress relaxation of HOIS with 3,6% of NCO-groups is overhead on the experimental points and demonstrates excellent correspondence to them. A good correlation between experiment and calculation was also found for all

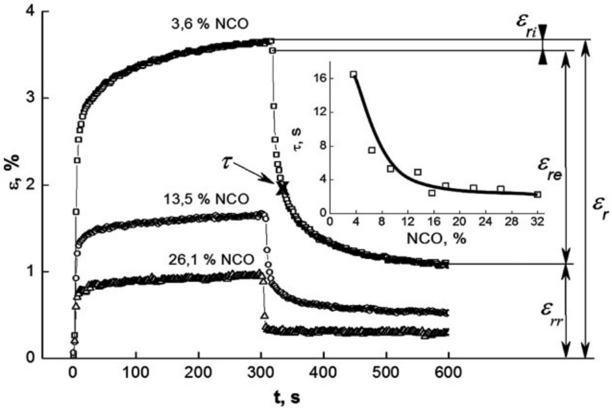

Figure 2.
Dependencies of creep and stress relaxation on time for the samples with different content of NCO-groups. Solid line – calculated function, points – experimental values. In the insert: stress relaxation time τ versus content of NCO-groups.

HOIS. The values of complex deformation ε_r and its components (instantaneous deformation ε_{ri}, elastic deformation ε_{re} and residual deformation ε_{rr}) are also marked in the figure. Apparently, HOIS have rather high residual deformation ε_{rr}, while instantaneous deformation ε_{ri}, calculated as $\varepsilon_{ri} = \varepsilon_r - \varepsilon_{re} - \varepsilon_{rr}$, gives a low contribution in the total deformation comparing to ε_{re} and ε_{rr}.

Similar behavior of creep and stress relaxation time was shown in.[16,18] In[16] authors studied the influence of preloading in the nonlinear viscoelastic–viscoplastic response of carbon–epoxy composites. Experimental results showed that the nonlinear parameters had no dependence on the preloading conditions however viscoplastic strain was developed due to preloading and affects the overall time dependent response of the material. In[18] the experimental study of creep resistance of PI/SiO_2 hybrid thin films with silica-fillers weight varying in the range of 0–8% were presented. It has been shown that the suitable silica contents can effectively improve the creep resistance and fatigue life of PI/SiO_2 composite films. However, as the silica doping level increased to 8 wt.%, the fatigue life of materials is significantly decreased although the creep resistance keeps a further improvement. In our case it is obviously that the values of complex deformation (ε_c and ε_r) and their components depend on number of NCO-groups in organic component and, respectively, on structural organization of the synthesized HOIS.

The Figure 2 also represents the value of stress relaxation time τ and its behaviour with change of chemical structure of the organic part. The dependence of stress relaxation time τ on content of NCO-groups is presented in the insertion of figure. It follows that the stress relaxation time decreases rapidly with increasing the number of NCO-groups and reaches almost constant value in the interval 15–32%.

Previously the structural model of this HOIS type was proposed,[23] which describes the presence of two hybrid organic-inorganic networks with different crosslink density and molecular mobility. The first network is elastic with higher molecular weight of the segment between the network sites and high molecular mobility, which is formed by the reaction of the first part of the organic component - oligoetherurethane UO (with a number of NCO-end-groups 3,6% and molecular weight equal to 4500) and inorganic component – metal silicate (MS). The second network is rigid and appears as the result of interactions between the second part of the organic component -

polyisocyanate PIC (with 32% of NCO-groups and molecular weight equal to 250) with MS. This network has a shorter molecular segments and, consequently, low molecular mobility. The variation of the content of free NCO-groups in the composition of the organic component gives the opportunity to obtain hybrid systems with different ratio of rigid and elastic hybrid networks, which determines the total mechanical properties of HOIS.

This general model can be illustrated in more details. Figure 3 shows the evolution of the structure by variation of the ratio of constituents UO/PIC in the HOIS organic phase, which explains the change of mechanical characteristics. In a system with a ratio UO/PIC = 100/0, which, respectively, contains 3,6% of NCO-groups, only the elastic hybrid organic-inorganic network UO/MS exists (Figure 3, a). This network is characterized by the high value of strain ε_c and long stress relaxation time τ (Figure 2).

The injection of low-molecular PIC into organic part of HOIS increases the number of reactive NCO-groups and leads to appearance the second rigid hybrid organic-inorganic network in the reaction of PIC and MS, which is formed as domains in the prevailing elastic hybrid network volume (Figure 3, b). These inclusions restrict the elasticity of the UO/MS network and lead to the reduction in deformation and relaxation time. Further increasing of the content of NCO-groups up to 15–17% (owing to insertion of the PIC component) develops more extensive rigid hybrid network and leads to the formation of two interpenetrating hybrid networks in the volume of HOIS (Figure 3, c). Within this NCO content interval the deformative and relaxation properties of HOIS are significantly reduced.

With reaching the content of NCO-groups more than 17% the hybrid highly cross-linked rigid network PIC/MS becomes dominant with elastic lowly cross-linked network UO/MS inclusions, i.e. a phase inversion takes place. That leads to the reinforcing effect, so recovery deformation and the relaxation time values become constant because the contribution of elastic network UO/MS inclusions in deformative characteristics is negligible, so mechanical

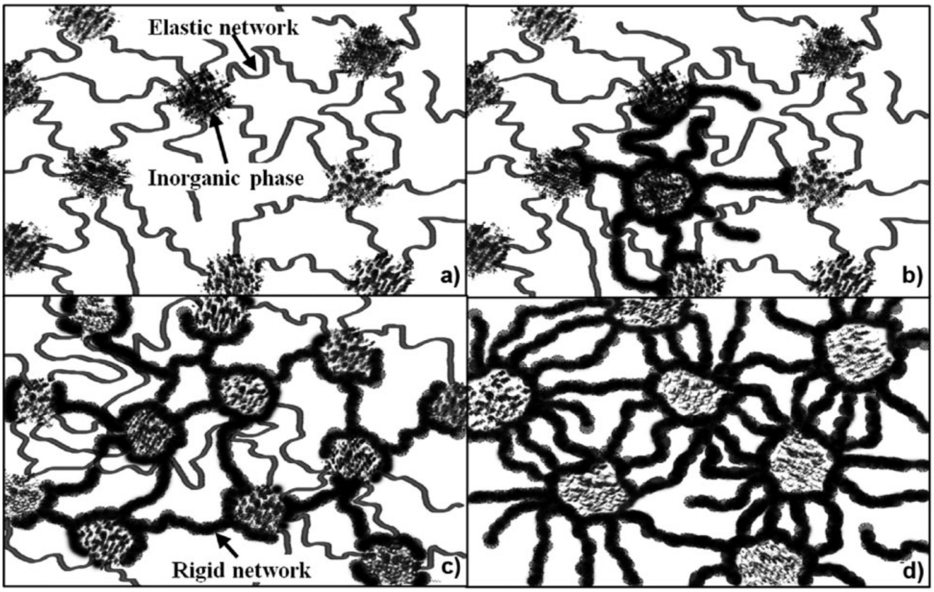

Figure 3.
HOIS structural model: the evolution of the structure by variation of the UO/PIC ratio in organic phase. Number of NCO-groups increases from 3,6% (a) through 9–10% (b), 15–17% (c) to 32% (d).

parameters of HOIS are mainly determined by the influence of the highly cross-linked rigid network PIC/MS. When the ratio UO/PIC = 0/100, that corresponds to 32% of NCO-group content in the organic component, only a rigid network is formed in the reaction of PIC and MS (Figure 3, d).

Stress/recovery dependencies (Figure 2) reflect this structure evolution with the changing of the NCO-groups concentration in the organic phase of HOIS. It is clear that the total deformation ε_c, ε_r decreases with increasing of NCO-groups, i.e. with increasing the contribution of rigid network. The values of elastic ε_{re} and residual ε_{rr} deformations reduce respectively while the ratio $\varepsilon_{rr}/\varepsilon_{re}$ was changed inessentially. Obtained results demonstrate different influence of two types of hybrid organic-inorganic networks on the deformative properties of HOIS. The rise of inclusions of the rigid network in HOIS with a dominant elastic network leads to a sharp decrease of the stress relaxation time, meanwhile, when the rigid network becomes dominant; the influence of the elastic network inclusions on the stress relaxation time is minor.

Conclusion

Thus for HOIS, in which the chemical structure of organic phase was changed, namely the ratio UO/PIC (isocyanate-containing oligoetherurethane UO and low-molecular poliisocyanate PIC) was varied, the number of NCO-groups was consequently changed. The structural model, which describes the formation of HOIS structure, depending on the NCO-group content, either in the form of elastic organic-inorganic network UO-MS with rigid network inclusions or as a rigid organic-inorganic network PIC-MS with elastic network inclusions explains the obtained results adequately. The phase inversion occurs in the average content of NCO-groups due to existence of two interpenetrating networks. Deformative properties of HOIS reflect these structural changes. In HOIS with the prevailing elastic network the values of relaxation parameters decrease rapidly with increasing the content of NCO-groups and, accordingly, growing of rigid network inclusions. When the rigid network becomes prevailing the elastic inclusion gives an insignificant contribution into the deformative properties of HOIS that leads to the constant values of relaxation time τ.

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