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INFLUENCE OF AGING ON FATIGUE AND CREEP PROPERTIES OF POLYURETHANE

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Abstract. Polymers and polymer-based materials are intensive implemented in many areas of engineering practice. These applications frequently have a very high performance demand, which makes their long-term characteristics of paramount importance. These materials were subject to degradation due to environmental factors, including light, temperature, stress, and others. Because of aging process, the physical and mechanical properties of these materials are significantly changed. This paper is devoted to the experimental investigations of this problem. The research program includes experiments on alternating of fatigue, creep, long-term climatic and deformation aging of polyurethane specimens. Results have shown the effect of considerable hardening and embrittlement during the aging process.
Keywords: polymer materials, polyurethane, degradation, climatic aging, deformation aging, fatigue, creep, effective time parameter

1. Introduction

Polymers and polymer-based materials are intensive implemented in almost all areas of engineering practice: industry, construction, aircraft, rocket science, shipbuilding and medicine. These applications frequently have a very high performance demand, which makes their long-term characteristics of paramount importance. At the same time, they were subject to degradation due to environmental factors, including light, temperature, stress, and others. During the aging, the degradation of polymer materials leads to significantly changes in the physical and mechanical properties [1-2]. As the result of degradation, the material becomes less deformable and brittle. The influence of aging on the mechanical properties of the different polyurethane sorts at various environmental factors are investigated in works [3-11].

In the paper [3], the effects of weathering on the mechanical properties of the precipitated and compact polyurethane films are investigated. The natural weathering of polyurethane films carried out in earth, seawater and exposure to sunlight was compared with untreated samples. Stress-strain, elongation, modulus and ultimate tensile strength decreased with increasing of the weathering time. The effect of seawater exposure on these polyurethanes was performed. It was found, that the treatments in seawater improved the mechanical properties of the elastomers.

Physical and mechanical properties of thermoplastic polyurethane were investigated in [4] after immersion in water at a temperature of 70°C up to 6 months. The mechanical properties in bulk material, obtained from tensile test, were affected by aging. Elastic modulus and stress at 200% of strain of the studied polyurethane were decreased after sufficient exposure to moisture. The mechanical properties of the material surface were investigated in abrasive wear test. A decrease in wear resistance of the aged polyurethanes was discerned. The reversibility of mechanical and physical properties after moisture exposure was also assessed. The polymer degradation was found as irreversible phenomenon.

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The effects of environmental aging on the mechanical performance of elastomeric polyurethane were investigated in [5] using two accelerated aging techniques: ultraviolet and hygrothermal. Samples were subjected to ultraviolet and hygrothermal exposure for a period of 5 months. The stress and strain to failure, tearing energy, and storage modulus were evaluated at different intervals for both aging techniques. It was found that the ultraviolet exposure caused severe degradation of the polyurethane in comparison with the hygrothermal exposure. A reduction of more than 98% in the tearing energy was observed for the ultraviolet exposed samples after 5 months compared with only a 35% reduction in the tearing energy for the hygrothermal-exposed samples. A similar trend was observed for tear strength and storage modulus.

Paper [6] presents results of experimental study of polyurethane samples of two hardnesses (40 and 90 Shore A), which have been subjected to immersion in artificial sea water for periods up to two years at temperatures from 50 to 100°C. In parallel samples have been immersed at sea in the Brest Estuary for up to five years. Mechanical properties have been measured on tensile specimens after ageing. An estimation based on a linear Arrhenius extrapolation indicates that the timescale for 50% property loss at sea temperatures is in excess of 100 years. The results from sea ageing confirm that these materials retain 100% of their initial tensile properties after five years of immersion.

The estimation of degradability of different polyurethanes in the Baltic Sea water and liquid medium containing sea water with sodium azide (NaN_3) was the subject of study in [7]. The incubation of polymer samples took place in both environments for a period up to 12 months. The characteristic parameters of seawater and their influence on degradation of polyurethanes are discussed. The changes of weight, tensile strength and morphology of polyurethane samples were tested after particular period of incubation in both environments. It is demonstrated, that the degree of degradation of polyurethanes in seawater is dependent on the degree of crosslinking.

The samples from thermoplastic polyurethanes were made using 3D printing and then subjected to the aging process in synthetic mine water at intervals of 2, 7 and 30 days [8]. The values of stress at the yield strength, stress at break, elongation at the yield strength and elongation at break did not change significantly regardless of the aging time. Shore A hardness tests also showed no changes in the hardness of the aged samples with respect to the native samples. The Fourier transform infrared spectroscopy tests of native and aged samples additionally confirmed that during the aging process the polyurethane chain was not degraded.

Article [9] is devoted to investigation of accelerated and outdoor aging up to 10 years of the acrylic polyurethane coatings with and without UV-stabilizers. Coatings containing photo-absorbers exhibited an excellent weathering durability, up to 72 cycles upon accelerated aging and 10 years in natural outdoor exposure, while the unstabilized coatings appeared serious cracks, damages and chalking after 48 cycles of accelerated aging and after 5 years in outdoor weathering exposure. The degradation of coatings was also investigated by monitoring atomic force microscopy, weight loss and gloss loss, cracking, blistering and flacking of the coating.

In the work [10], the degradation behavior of some polyurethane membranes exposed to artificial weathering environment for different exposure time was studied. The specimens were investigated before and after exposure to accelerated ageing during 0, 100, 300 and 600 h. It is observed that the mechanical properties of the polyurethane membranes change as function of ageing time. A slight decrease of the mechanical properties namely, tensile strength and elongation at break was remarked. Fatigue tests on non-aged and aged polyurethane membranes were performed for a total of 5 cycles at both maximum and minimum retention time of 2 s, and an elongation of 100% and 2%, respectively. In the cyclic fatigue test, the same behavior is observed as in the tensile strength measurements, namely the

analyzed samples needs different stress to break the macromolecular chains. The investigations of material surface properties were also conducted. The appearance of some particles and clusters due to the erosion of the surface, but no noticeable cracks were observed after the 600 h of accelerated ageing. Experimental results show that the decomposition of polyurethane membranes is a complex process and is the results of a multitude of physical and chemical phenomena, which involves the combination of several steps such as chain scission, re-arrangement of them and crosslinking.

Experiments on the alternation of deep compression of rectangular polyurethane specimens and long-term climatic and deformation aging [11] were carried out. According to the obtained experimental results in the process of long aging of about nineteen years, the hardening of material is no monotonic. The maximum value of hardening (according to stress value) is more than 30 times compared to the specimens without aging. With increasing of aging time, the material become softening. These effects need further research.

In this paper the research program includes experiments on alternation of fatigue, creep, long-term climatic and deformation aging of polyurethane specimens. A round reinforced polyurethane drive belt Continental Contitech with the diameter of 4 mm was used. Experiments were carried out on specimens with the working length of 2.5-3.1 mm. Fatigue experiments were conducted on a desktop servo-hydraulic fatigue test machine Si-Plan SH-B and creep experiments on Shimadzu AGX-50 plus tearing machine.

2. The influence of climatic and deformation aging on fatigue strength of polyurethane specimens

Cyclic experiments of polyurethane specimens with repeated tension with the variation of the deformation $\varepsilon = 1.5$ and loading frequency of 10 Hz was conducted. Thus, the average number of cycles N to fracture, which was about 120 000 cycles, was determined.

The following experimental programs to study the influence of climatic and deformation aging on fatigue strength were used.

Program 1. Specimens were initially placed in water at room temperature, then were frozen at temperature - 18°C and exposure in ice during 4, 11, 19 and 23 days. Then specimens were tested to N/1.2 cycles under noted loading parameters; were aged in the laboratory during 1 year and then tested to fracture.

Program 2. Specimens were initially placed in boiling water for 1 hour and exposure in water at room temperature during 11 and 18 days. Then specimens were tested to N/1.2 cycles under noted loading parameters; were aged in the laboratory during 1 year and then tested to fracture.

The results of the influence of climatic and deformation aging on the cyclic strength of polyurethane specimens according programs 1-2 are presented in Table 1.

Table 1. The influence of climatic and deformation aging on the cyclic strength of polyurethane specimens at $\varepsilon = 1.5$ and a frequency of 10 Hz according to different programs

	Without aging	Aging					
		Program 1				Program 2	
		exposure in ice during				exposure in water during	
		4 days	11 days	19 days	23 days	11 days	18 days
Average number of cycles to fracture N	120 000	395 000	1 045 000	740 000	127 000	578 000	5 635 000
N/N_{unaged}	1	> 3	> 8	> 6	1	> 4	> 46

According to the obtained results, a significant cyclic hardening is observed, which considerably depends on the aging program. Thus for program 1, exposure in ice during 4 and 11 days leads to increasing of number of cycles to fracture in 3 and 8 times correspondingly, compared for specimens without aging. Further exposure in ice leads to decrease of number of cycles to fracture. For 19 days, it is only 6 times more compared for unaged specimens. For 23 days, it is approximately equal to number of cycles to fracture for specimens without aging.

3. Influence of climatic and deformation aging on creep deformation of polyurethane specimens

To study the influence of climatic and deformation aging on the creep deformation of polyurethane, the specimens were tested according to the following program.

Program 3. Specimens were tested to 105 000 cycles at $\Delta l = 4$ mm and 10 Hz; then aged in laboratory conditions for 1 year; than tested to 105 000 cycles at noted loading parameters; then aged in laboratory conditions for 2 years; and then tested for creep at room temperature with various constant loads.

The obtained experimental creep curves according program 3 are compared with corresponding creep curves for the specimens without aging. These curves are shown on Figs. 1-3. Curves marked by number 1 corresponds to specimens without aging and marked by number 2 to specimens after aging according to program 3.

It follows from Figures 1-3 that for specimens after aging the creep time for fixed deformation was increased up to three times compared with specimens without aging.

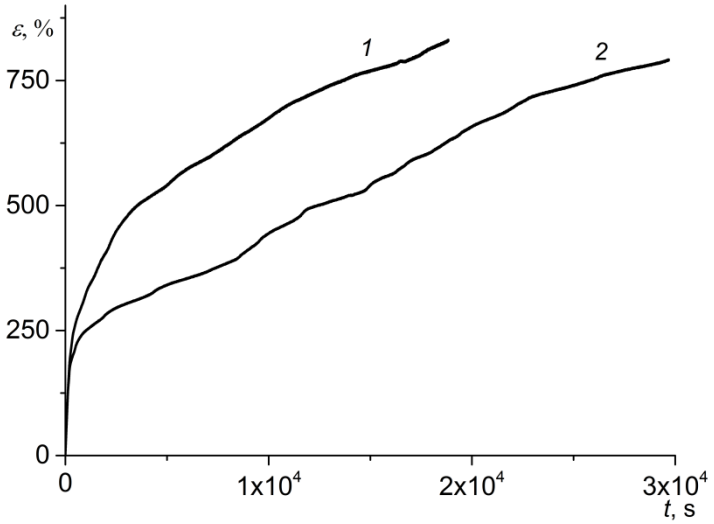

Fig. 1. Experimental creep curves under constant load of 80 N for polyurethane specimens without aging (curve 1) and after aging (curve 2)

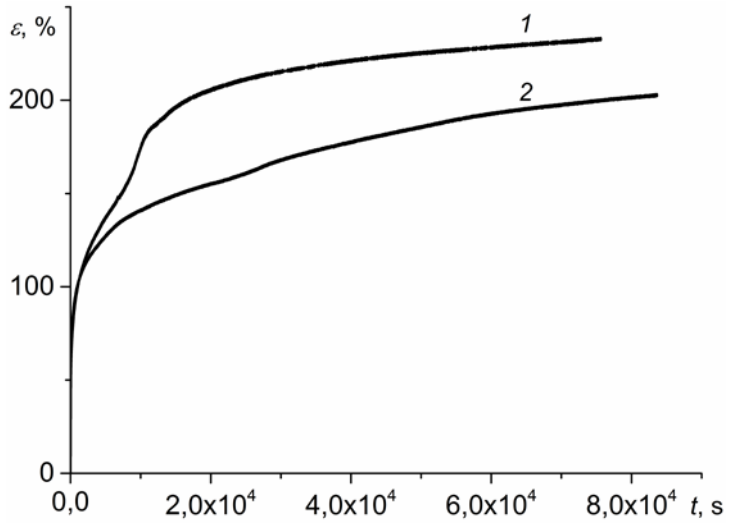

Fig. 2. Experimental creep curves under constant load of 70 N for polyurethane specimens without aging (curve 1) and after aging (curve 2)

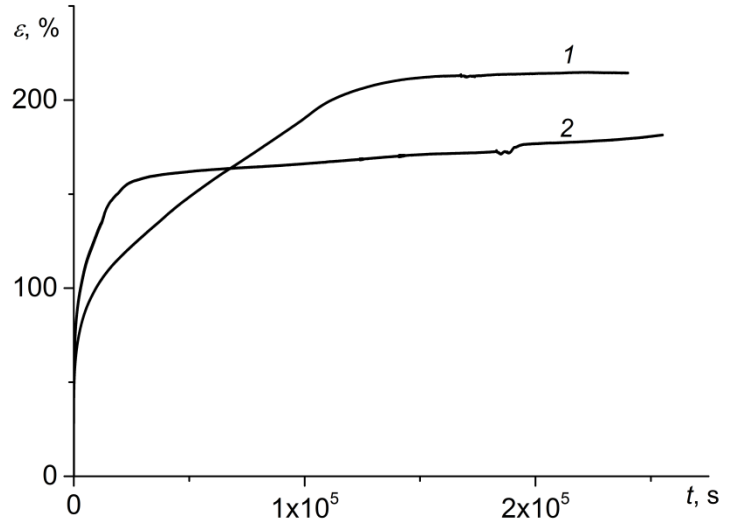

Fig. 3. Experimental creep curves under constant load of 60 N for polyurethane specimens without aging (curve 1) and after aging (curve 2)

4. An effective time parameter

To describe the process of deformation aging parameter α is introduced [2]

$$d\alpha = f_1(\alpha,\varepsilon,T,t)dt + f_2(\alpha,\varepsilon,T,t)d\varepsilon, \quad (1)$$

where ε is the value of deformation, t is the real time, T is temperature.

Parameter α will be considered as an effective time, which is capable to describe the aging (deformation and quench). According to relation (1) in the instantaneous active loading this parameter can be considered as 'deformation time' ε. In unloading state $d\varepsilon = 0$ and α reduces to the real time t. We may call it as the 'chemical time'.

For the Maxwell equation, we will receive the following modified relation

$$\frac{d\varepsilon}{d\alpha} = \frac{d}{d\alpha}\left[\frac{\sigma}{E(\alpha)}\right] + \frac{\sigma}{\eta(\alpha)}. \quad (2)$$

Further, we will consider the simple version of elastic viscous model (2) expressed in scale of effective time (1)

$$\frac{d\varepsilon}{d\alpha}=\frac{1}{E}\frac{d\sigma}{d\alpha}+\frac{\sigma}{\eta}, \tag{3}$$

$$d\alpha = k(\alpha_\infty - \alpha)t^m dt, \tag{4}$$

where E, η, k, α_∞, m are constants, α is a parameter of material degradation ($\alpha = N / N_0$, N_0 is the initial number of chemical bonds, N is the current number of fractured chemical bonds).

So the equation (4) can be considered as an equation of chemical reaction and parameter α has a meaning of chemical time. With the initial conditions $t=0$, $\alpha=\alpha_0$, $\varepsilon=\sigma_0/E_0$, the solution of the system (3)-(4) can be written in the form

$$\varepsilon=\frac{\sigma_0}{E_0}\left[1+\frac{\alpha_\infty-\alpha_0}{\tau}\left(1-exp\left(-\frac{k}{m+1}t^{m+1}\right)\right)\right]. \tag{5}$$

The theoretical creep (compliance) curves according relation (5) and experimental creep curves (marked by curves with circle points) under constant load of 60 N for polyurethane specimens without aging and after aging according to program 3 are shown on Figs. 4 and 5.

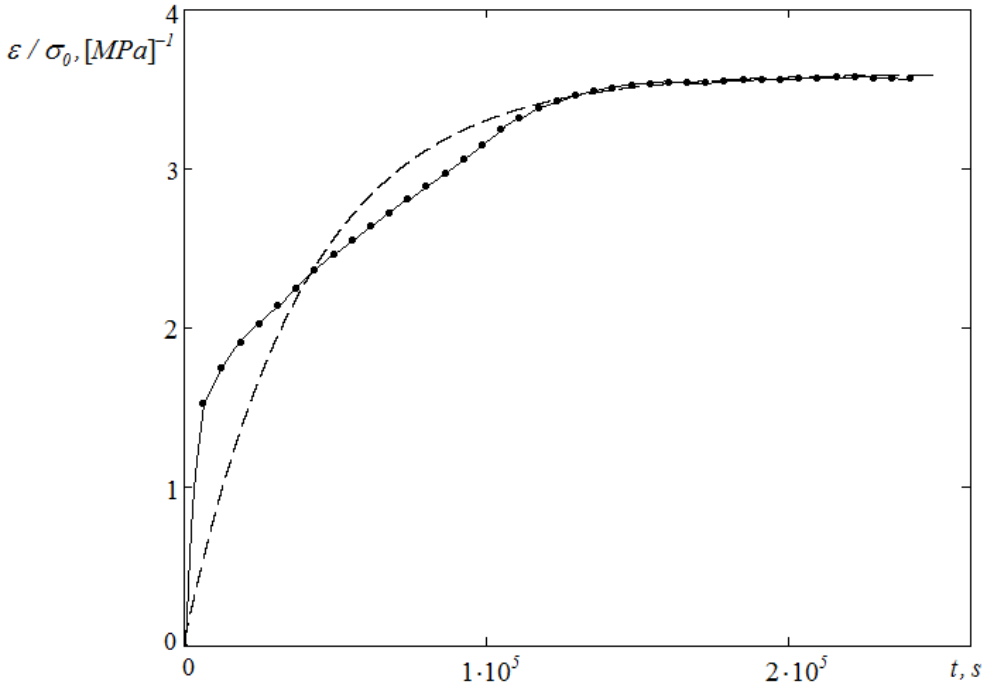

Fig. 4. The theoretical creep (compliance) curves according (5) and experimental points for polyurethane specimens tested on creep under constant load of 60 N without aging

In calculations the following coefficients were used: $\alpha_0=0$, $\alpha_\infty=1$, $m=0$, $k=2{,}5\cdot10^{-5}\ s^{-1}$, $\tau=8\cdot10^{-3}\ s$, $E_0=35\ MPa$ (for specimens without aging) and $\alpha_0=0$, $\alpha_\infty=1$, $m=0$, $k=9\cdot10^{-5}\ s^{-1}$, $\tau=9{,}65\cdot10^{-2}\ s$, $E_0=4\ MPa$ (for specimens after aging according to program 3).

From Figures 4 and 5 can be seen, that relation (5) well describes the experimental creep curves for polyurethane specimens without aging and after aging.

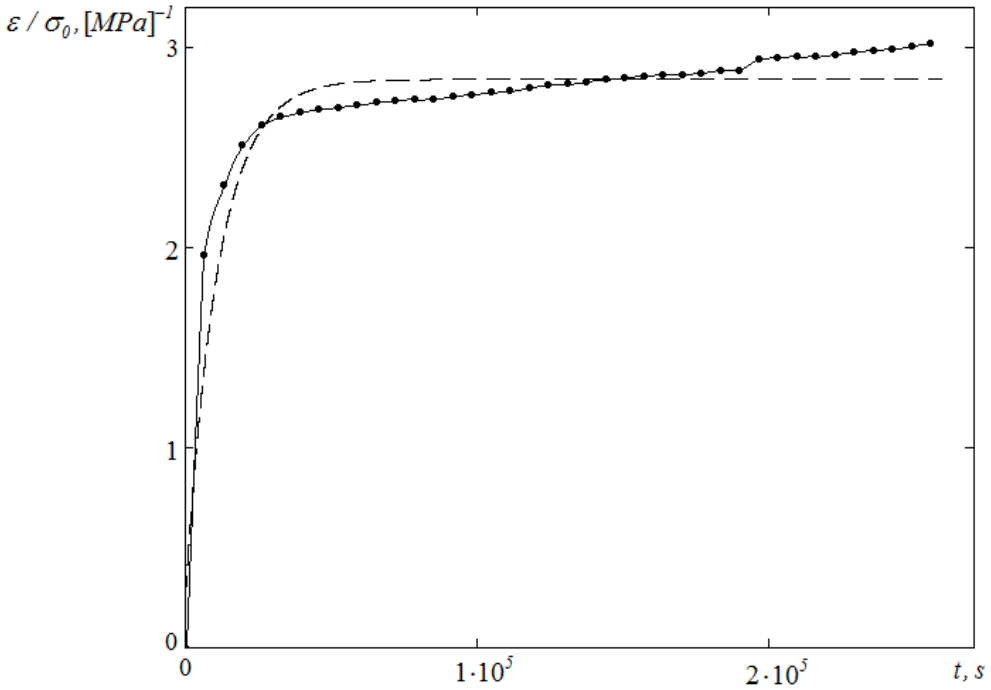

Fig. 5. The theoretical creep (compliance) curves according (5) and experimental points for polyurethane specimens tested on creep under constant load of 60 N and after aging according to program 3

5. Conclusions

Experiments for alternation of cyclic loadings and climatic aging during one year of the unloaded specimens are carried out. Results have shown the effect of considerable hardening and embrittlement depends on aging program. Some specimens were tested on creep at room temperature after cyclic loadings and climatic aging. Experimental creep curves for aged specimens and specimens without aging are received. For aged specimens the creep time for fixed deformation was increased up to three times compared with specimens without aging. To describe the process of deformation aging effective time parameter is introduced. The system of equations consists of equation of chemical reaction for effective time parameter and modified Maxwell equation is formulated. A good agreement of theoretical and experimental creep curves obtained for specimens without aging and after aging is observed.

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