Experimental and theoretical studies of the effect of long-term natural aging on the mechanical properties of high impact polystyrene

A R Arutyunyan
Saint Petersburg State University, St. Petersburg, Russia
E-mail: a.arutyunyan@spbu.ru

Abstract. Effect of prolonged natural aging in the laboratory conditions at room temperature during 40 years on the mechanical properties of six different marks of high impact polystyrene (HIPS) was investigated. The deformation curves in tensile experiments were obtained. These curves indicated that the hardening effect is observed for all marks of HIPS after aging. The HIPS were also tested for creep at room temperature and constant tensile force. Specimens of most marks of HIPS does not fractured during 30 days. After natural aging during 40 years, the specimens were fractured in a time-to-fracture range from 10 minutes to 30 hours depending on the mark of HIPS. A modified version of the Maxwell equation written in the effective time scale is used to describe the obtained experimental creep curves. A good agreement between theoretical and experimental creep curves is observed.

1. Introduction
Polymer and composite materials based on them are widely used in various fields of engineering, aircraft, rocket science, as well as in medicine. These applications frequently have a very high performance demand, which makes their long-term characteristics of paramount importance. At the same time, the physical and mechanical characteristics of polymer and composite materials changed after long-term operation, which is largely induced to the aging process [1–6]. Therefore, studies of the aging processes of these materials are needed.

In this paper, the effect of prolonged natural aging in the laboratory conditions at room temperature during 40 years on the mechanical properties of six different marks of HIPS was investigated. HIPS are polymer-polymer matrix composites with a polystyrene matrix, in which there are rubber inclusions with size 0.5–5 microns and a concentration volume in the range of 20–40%. These polystyrene at room temperature are in a glassy state and under such conditions are able to experience significant deformations, as well as much higher toughness and other fracture characteristics compared to conventional polystyrene [7]. HIPS has a wide range of applications, for example, they are used in the manufacture of doors, packaging containers, interior lining of railway cars and aircraft, sheets and parts of the interior lining of refrigerators, freezers and their components, technical products and consumer goods, various products and containers intended for contact with food. Therefore, the study of the long aging process of such composite materials is relevant.
2. Investigation of the effect of long-term natural aging on mechanical properties of HIPS under tension

The experiments on HIPS specimens with a total length of 60 mm, width 10 mm, thickness 4 mm and a working length of 50 mm were carried out. Specimens without aging were tested on a tearing test machine MR–500T–2 in 1979. Then specimens were stored in the laboratory conditions at room temperature during 40 years, and then was tested on a tearing test machine TINIUS OLSEN H10K–T. Experiments were conducted under loading rates equal to 5 mm/min and 50 mm/min.

![Figure 1](image1.png)

**Figure 1.** Tension stress-strain diagrams for specimens of HIPS grade UPS 0803 at loading speeds equal to 5 mm/min (a) and 50 mm/min (b): 1 – without aging, 2 – with aging during 40 years

![Figure 2](image2.png)

**Figure 2.** Tension stress-strain diagrams for specimens of HIPS grade UPS 0804 at loading speeds equal to 5 mm/min (a) and 50 mm/min (b): 1 – without aging, 2 – with aging during 40 years

The obtained results indicate that for all marks of HIPS after 40 years of natural aging, a hardening effect is observed. Almost for everyone mark value of deformation to fracture has decreased and for all marks, the yield strength has increased.

3. Investigation of the process of long-term natural aging of HIPS in creep experiments

In the next part of research, the HIPS specimens were tested for creep at room temperature and constant tensile force. Specimens were conducted on a tearing test machines MR–500T–2 and TINIUS OLSEN H10K–T.
Figure 3. Tension stress-strain diagrams for specimens of HIPS grade UPM 0612 at loading speeds equal to 5 mm/min (a) and 50 mm/min (b): 1 – without aging, 2 – with aging during 40 years

On the figure 4, the experimental creep curves for specimens of HIPS grade UPM 03L without aging (a) and with aging during 40 years (b) are shown. The experiments were carried out under constant load equal to 438 N.

Figure 4. Experimental creep curves for specimens of HIPS grade UPS 03L without aging (a) and with aging during 40 years (b)

Specimens without aging were fractured at times of order 600 minutes, whereas specimens after aging were fractured after 13 minutes. Thus, experiment results show that for specimens after prolonged aging, the time to fracture during creep decreased by more than 35 times.

On figure 5 the experimental creep curves for specimens of HIPS grade UPM 0612L without aging (a) and with aging during 40 years (b) are presented. The experiments were carried out under constant load equal to 355.5 N. For specimens without aging, the time to fracture was 20 days (28800 minutes), whereas for specimens after aging time to fracture was equal to 45 minutes. Thus, it can be seen that for specimens after prolonged aging, the time to fracture during creep decreased by more than 625 times.

On figure 6 the experimental creep curves for specimens of HIPS grade UPM 0703 without aging (a) and with aging during 40 years (b) are presented. The experiments were carried out under constant load equal to 376.2 N. Specimens without aging were tested for 30 days (43200 minutes) and do not fractured. Specimens with aging during 40 years fractured already after 53 minutes.
4. Maxwell’s equation, written in the effective time scale
To describe the obtained experimental creep curves, let’s consider the problem of stretching a specimen of an elastic-viscous aged material under the influence of a constant load $P$. As a rheological equation, we use the modified Maxwell equation, written in the scale of effective time $\alpha$ [6]

$$\frac{d\varepsilon}{d\alpha} = \frac{1}{E} \frac{d\sigma}{d\alpha} + \frac{\sigma}{\eta},$$
$$d\alpha = f_1(\alpha, \varepsilon, T, t)dt + f_2(\alpha, \varepsilon, T, t)d\varepsilon,$$

where $\varepsilon$ is deformation, $\sigma$ is true stress, $T$ is temperature, $E$ is modulus of elasticity, $\eta$ is coefficient of viscosity.

The parameter $\alpha$ is considered as an effective time by which it is possible to describe the processes of climatic and deformation aging. According to equation (2) for instant, active loads, the parameter $\alpha$ corresponds to the ‘deformation time’ $\varepsilon$. In the discharge state, this parameter describes the kinetics of chemical aging processes and is reduced to usual time $t$. With this interpretation, the concept of ‘chemical time’ can be introduced. Thus, the effective time parameter is in generally able to describe the interrelated deformation and physic-chemical processes and define their development in the scale of deformation and chemical time. This is the difference between this parameter and the well-known temperature-time and polarization parameters used in mechanics of polymer [8–10].
When calculating using formula (2), the effective time parameter is given in the form
\[ \frac{d\alpha}{t} = k(\alpha_{\infty} - \alpha) t^m dt \] (3)
where \( k, \alpha_{\infty}, m \) are constants, \( \alpha \) is material degradation parameter (\( \alpha = N/N_0 \), \( N_0 \) is initial number of chemical bonds, \( N \) is current number of destroyed chemical bonds).

Thus, equation (3) can be considered as the equation of a chemical reaction, and the parameter \( \alpha \) has the meaning of chemical time.

The solution of the system of equations (1) and (3) under initial conditions \( t = 0, \alpha = \alpha_0, \varepsilon = \sigma_0/E_0 \), can be written as
\[ \frac{\varepsilon}{\sigma_0} = \frac{1}{E_0} \left\{ \left[ 1 + \frac{\alpha_{\infty} - \alpha_0}{\tau} \left[ 1 - \exp \left( - \frac{k}{m} t^{m+1} \right) \right] \right] \right\} \]  \hspace{1cm} (4)

On figures 7 and 8 the compliance curves \( (D = \varepsilon/\sigma_0) \) according to relation (4) and experimental creep data for specimens of HIPS grade UPM 03L with aging and without aging are shown.

From figures 7 and 8 can be seen that the obtained curves are in good agreement with the corresponding experimental data on the creep of HIPS grade UPM 03L.
Conclusions
In the paper the effect of long-term natural aging at room temperature during 40 years on the mechanical properties of six marks of high impact polystyrene (HIPS) was investigated. Deformation curves in tensile experiments at loading speeds equal to 5 mm/min and 50 mm/min are obtained.

The obtained results indicate that for all marks of HIPS after 40 years of natural aging, a hardening effect is observed. Almost for everyone mark value of deformation to fracture has decreased and for all marks, the yield strength has increased.

The HIPS also was tested for creep at room temperature and constant tensile force. Specimens of most marks does not fractured during for 30 days. After natural aging during 40 years, the specimens fractured in a time-to-failure range from 10 minutes to 30 hours, depending on the HIPS mark. Thus, experiment results show that for, example, for specimens of HIPS grade UPM 03L after prolonged aging, the time to fracture during creep decreased by more than 35 times.

To describe the experimental creep curves of HIPS specimens after aging and without aging, a modified version of the Maxwell equation recorded in the effective time scale was used. A good agreement between theoretical and experimental creep curves is observed.

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