

STRESS RELAXATION PROCESS IN CROSS-LINKED POLYETHYLENE

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Fittings used to connect pipes to each other, to connect bends or branch junctions, or to join valves, are an important part of a pipeline. Compression fittings made of metal which trap the pipe between an insert mandrel and an outer sleeve are widely used for multilayer pipes and nowadays, for reinforced multi-layer plastic pipes. To ensure that the pipe and fitting combination provide good reliability in service it is important that they are well designed.

Plastic pipe systems have a stress relaxation mechanism [1] which is well understood and considered when designing compatible pipe and fitting systems. This mechanism is temperature dependent, as well as time dependent, and the method of setting optimal compression of pipes in joints of this type must consider this effect.

This paper considers the mechanical behavior of peroxide cross linked polyethylene (PE-Xa) in response to temperature. This material is the primary core used in the G-PEX-AMT reinforced multi-layer pipes manufactured by the POLYPLASTIC Group.

In order to understand the relaxation properties of the PE-Xa material, tests have been performed on dumb bell samples (type 1 of the GOST 11262) taken from production quality pipe (85% degree of cross linking). An IPT tensile creep tester (MOD 1598) has been used to load samples with constant tensile deformation to observe stress relaxation, having the following measurement attributes:

- accuracy of temperature, $\pm 1^\circ\text{C}$;
- deformation, $\pm 0.1\%$;
- force, $\pm 2\text{ N}$.

Special software has been developed by the Institute of Organoelement Compounds of Russian Academy of Sciences. This software predicts stress relaxation dependent behaviours according to the Boltzman – Volterra equation based on consideration of thermodynamic behavior of the material during the relaxation process [2]. Optimal parameters of relaxation, including initial and quasi-equilibrium stress, can be calculated using this tool. The potential also exists to define the relaxation process, i.e. to understand whether it is diffusion controlled (where the limit state of the process is the diffusion of kinetic units), or kinetic controlled (where the limit state is the rate of interaction of relaxators).

$$\sigma = \sigma_0 \left[1 - \int_0^t T(\tau) d\tau \right] \quad (1),$$

where σ is the stress after relaxation, σ_0 is the initial stress, which is developed in the sample when the constant deformation is settled, $T(\tau)$ is a relaxation core, τ is the current moment of time, t is the ending time.

During this study, it was discovered that the limiting parameter of the relaxation process is the rate of interaction of particles (relaxators). Disregarding the complicated transformations, one may express the core of kinetic relaxation process as follows [3]:

$$T_1(\tau) = \frac{S_0}{k_B m_1} \left[\frac{1}{(\alpha - \alpha_0)(\ln(\alpha - \alpha_0)) + (1 - \alpha + \alpha_0)\ln(1 - \alpha + \alpha_0)} - \frac{1}{\ln 0.5} \right]$$

$$m_1 = m_1^* \int_0^1 T_1(\tau) d\tau;$$

$$\alpha = \frac{1}{(1 + k\tau/\beta)^n}$$

$$k = \frac{S_0}{k_B m_1}$$

$$\beta = 1/(n-1)$$

$$k^1 = k C_0^{n-1}$$

where m_1^* is the number of heterogeneities (relaxators) that interact with each other in the course of relaxation process in the polymer; α is the part of the total number of particles presented by relaxators; k_B is Boltzmann constant; S_0 is the initial entropy of the system, T^* is a variable part of the core described in square bracket, τ is the time; k is the rate constant of relaxator interaction; C_0 is the initial concentration of relaxators; n is the order of a kinetic reaction of relaxators.

As the first step, an approximation of the data obtained at 7% deformation and different values of temperature was conducted. The test results are presented at Pic. 1 and the results of calculation of parameters of relaxation cores are shown in Table 1. When core $T_1(\tau)$ was used, the correlation coefficient r was equal to 0.997. Rate constant of relaxator interaction is the same for all temperature values and is equal to 0.01 min^{-1} . The order of reaction n is equal to 6, i.e. 6 relaxation units co-operate in the single act. The A value is

proportional to the number of heterogeneities in the material and it grows with the increase of the temperature.

The most important aspect for evaluation of material properties are the values of initial (σ_0) and quasi-equilibrium (σ_∞) stress. These stresses retain high values in the temperature range 50 up to 90°C, thus providing one with the opportunity to predict the material mechanical performance (Pic. 2).

For the generally accepted estimation of long-term stress relaxation the principle of time-temperature superposition (TTS) was used [4]. According to the TTS principle, the stress relaxation curves, built for different test temperatures, can be shifted horizontally along the time logarithm axis ($\lg t$) to form the general curve. The average shift of the curve, obtained at the higher temperature, to the general curve is used as the shift factor $\lg a_T$. This principle is successfully applied to various polymeric systems, examined at different strain values. Naturally, the higher the temperature, the larger is the shift factor $\lg a_T$. For heat-resistant polymers in the whole glass state the shift factor temperature dependency can be described by this relation:

$$\lg a_T = C(T - T_0)^n$$

The general curve of relaxation module is shown on Pic. 3, the shift factor temperature dependency, ruled by equation $\ln a_T = 0,511(T - T_0)$ is presented on Pic. 4.

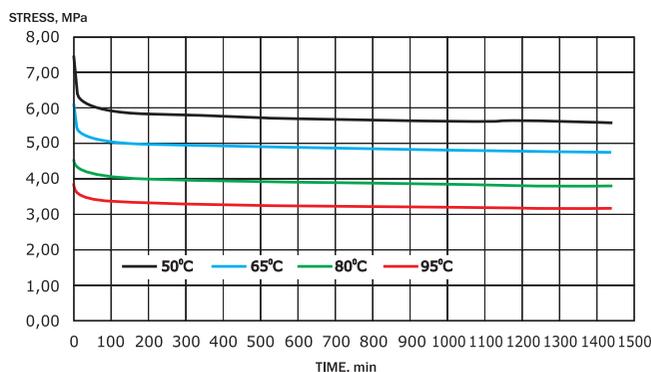
$T_1(\tau)$ core describes stress relaxation processes well in the linear area of mechanical behavior, when the material parameters do not depend on stress or deformation. It becomes clear in the further analysis that polymers often exhibit non-linear behavior though, in this case the relaxation core parameters depend on stress or strain value.

When the strain value is small, the relaxation time dependencies settle in one narrow batch with small dispersion (for instance, 5%). This fact establishes that the polymer mechanical behavior is linear. Nevertheless, when the deformation reaches a certain value, these dependencies shift to smaller relaxation modulus values, proving that the mechanical behavior is non-linear.

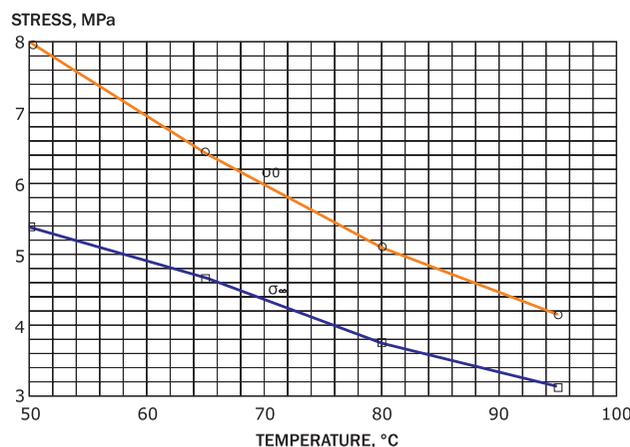
Modified $T_1(\tau)$ core, considering the dependency of k^* of relaxation modulus [3, 5], was used for the approximation of non-linear mechanical behavior.

Table 1. Parameters of relaxation core $T_1(\tau)$

T, °C	Core $T_1(\tau)$						
	Strain, ε_0 , %	k, мин ⁻¹	r	A, J·kg·degree/m ³	n	σ_0 , MPa	σ_∞ , MPa
50	7	0,01	0,997	$1,07 \cdot 10^{25}$	6	7,97	5,39
65		0,01	0,997	$1,45 \cdot 10^{25}$	6	6,43	4,65
80		0,01	0,997	$1,89 \cdot 10^{25}$	6	5,10	3,76
95		0,01	0,997	$2,44 \cdot 10^{25}$	6	4,15	3,13



Pic. 1. Stress relaxation curves at constant strain value (7%) and varied temperature

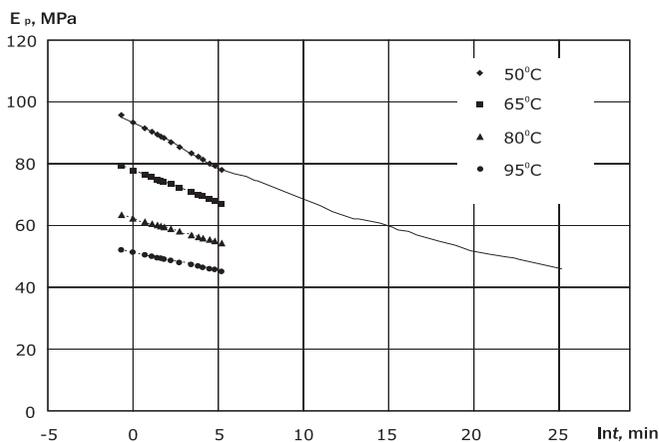


Pic. 2. Temperature dependencies of initial and quasi-equilibrium stresses at 7% strain

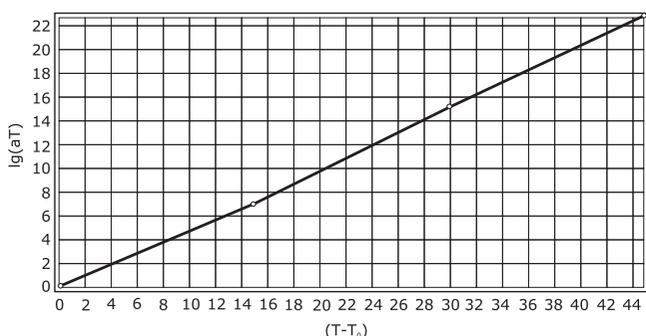
The relaxation modulus dependencies at 95°C and varied strain values are shown on Pic. 5, the results of initial and quasi-equilibrium stresses calculation are given in Table 2.

Time dependent modulus do not fit the same graph and shift to lower values with the strain growth, thus proving the non-linear behavior of the polymer. The non-linearity is even more obvious from the dependency of PE-Xa equilibrium modulus at different strain values and 95°C (Pic. 6).

Therefore, as a result of experiments it has been shown that the stress relaxation in PE-Xa occurs under kinetic control, when the limitation is the rate of relaxator interaction. The non-linear behavior of the material at high strain values



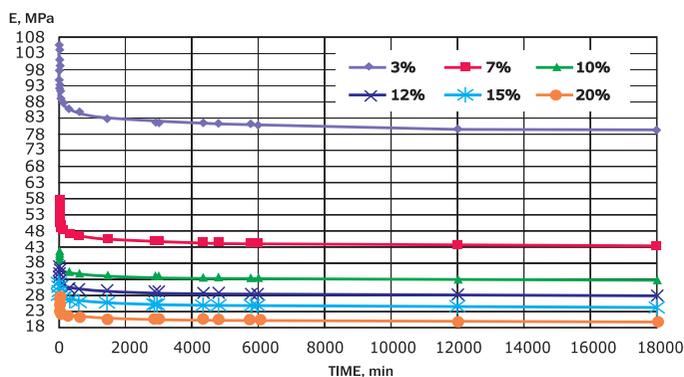
Pic. 3. General curve of relaxation module for PE-Xa



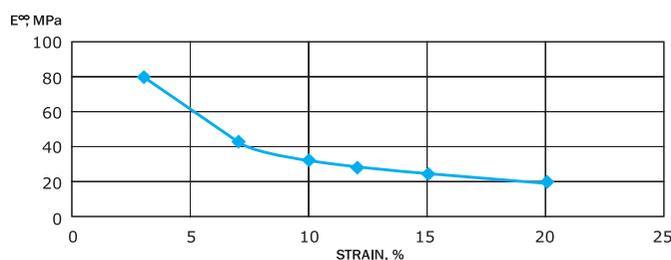
Pic. 4. Shift factor ($\lg a_T$) dependency on temperature difference ($T - T_0$)

is shown. As a result of highly accurate approximation the relaxation core parameters and quasi-equilibrium stresses at different temperatures and strains were determined. It was shown that cross-linked polyethylene retains the stress level developed during deformation. The stress doesn't go lower than its quasi-equilibrium value for any given period of time.

The relaxation modulus dependencies obtained in this work allow one to estimate the residual stresses in PE-Xa at various values of strain, temperature and time, thus giving one the opportunity to design fitting units more carefully and with greater reliability.



Pic. 5. Dependencies of PE-Xa relaxation modulus at 95°C and different strain values on relaxation time



Pic. 6. Dependency of equilibrium module of PE-Xa at 95°C on strain

Reference list

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4. Gul' V.E., Kuleznev V.N. Structure and Mechanical Properties of Polymers. – Moscow, Labirint, 1994. – 367 p.
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Table 2. Calculated values of initial and quasi-equilibrium stress values

Temperature, °C	Strain, %	Stress σ_0 , MPa	Stress σ_∞ , MPa	Correlation coefficient r
95	3	3,057	2,380	0,993
	7	3,935	3,033	0,990
	10	4,129	3,245	0,985
	12	4,300	3,351	0,982
	15	4,636	3,659	0,992
	20	4,990	3,942	0,993