Effects of Mechanical and Thermal Stresses on Electric Degradation of Polyolefins and Related Materials

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Summary: Degradation under the simultaneous effects of mechanical stress and temperature in polyolefins (PE, PP), composites on their basis (PE+PP fibre, PP+PP fibre, PP+glass fibre) and radiation low-density polyethylene (X-LDPE) used in high-voltage cables obeys the thermofluctuation theory of Zhourkov (in certain σ and τ_0 intervals) based on the theory of Arrhenius is presented in the following form:

$$\tau_\sigma = \tau_0 \exp[(U_0 - \gamma\sigma)/RT] \tag{1}$$

where τ is durability. τ_0 is a constant (10^{-12}-10^{-13}s) equal to period of vibrations of atoms around equilibrium position, U_0 is the activation energy of the mechanical destruction process (at $\sigma = 0$), γ is a structure-sensitive parameter, T is absolute temperature and R is universal gas constant. Electric degradation under the effects of electric field and temperature in the materials mentioned above obeys the equation:

$$\tau_E = \tau_0 \exp[(W_0 - \chi E)/RT] \tag{2}$$

Here, τ_E, W_0 and χ are analogous to τ_σ, U_0 and γ, respectively.
It is assumed that the following equation is valid under the simultaneous effects of E, σ and T:

$$\tau_{\sigma,E} = \tau_0 \exp[(U_0 - (\gamma\sigma + \chi E))/RT]. \tag{3}$$

Keywords: electric degradation; mechanical stress; polyolefins; termal stress; thermofluctuation theory

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Introduction

Polymers, polymer composites and crosslinked polymers are used extensively in all types of electrical power networks, devices and equipment, presenting attractive features such as excellent dielectric properties and good thermomechanical behaviour. However, being exposed to the external factors, such as electrical strength (E), mechanical stress (σ), and temperature (T), all the materials degrade and become unusable. There are some studies about the individual effects of these factors in the literature but the simultaneous effects are complex and their mechanisms are still being discussed. [1-5] Bagirov et al. have given an invalid equation in terms of units for polyethylene (PE) and polycaprolactam. Also the mechanism of the degradation is unclear. [6] In addition, although the experimental results may be correct, the mathematical expressions of the parameters in the equation presented are not examined.[7] Electric degradation of polymer materials, in particular those used in electric cables, are still subject to discussion. As to the mechanisms, exponential equations are given for electric degradation:

$$\tau_E = \tau_0 \left(\frac{E_0}{E} \right)^m , \tag{4}$$

and for temperature dependence

$$\tau_E = \tau_0 \, exp\left(\frac{\Delta W}{kT} \right). \tag{5}$$

Arrhenius equation is given for either the sum of the two or for individual mechanisms.

Experimental

In experiments, PP+PP fiber (0, 10, 20, 30, 40 and 50 %), LDPE (low-density polyethylene)+PP fiber (0, 10, 20, 30, 40 and 50 %), PP+glass fiber (0.1, 0.3, 0.5, 0.7, 1 and 5 %) and unaged XLPE transmission power cables having radiation-crosslinked low-density polyethylene (X-LDPE) insulation of 22 mm thickness are used. Composites samples of 50-100 μm thicknesses are prepared by hot pressing at 453 K and 15 MPa for 10 min. The dynamic mechanical characteristics (σ) are measured by a lever mechanism that keeps σ constant as the cross-section of the sample changes[1]. In order to measure the simultaneous effect of σ and E, and electric degradation of XLPE cable samples, an electric cell is added to the system. One of the electrodes (ϕ 30 mm) is grounded, while the other (ϕ 10 mm) is connected to the voltage source of 0 - 15 kV. The sample is sandwiched between two electrodes shaped in such a way that no electric discharge is likely to arise through the edges of the electrodes. X-LDPE samples of thicknesses 120 - 200 μm are cut with a microtome from the cables. Since the sample thicknesses and strengths are high, the measurements have been made after placing the samples between the electrodes immersed in transformer oil. The structure variations have been observed using a Mattson 1000 Fourier transform spectrometer and polarization microscope.

Experimental results and discussion

Typical graphs for PP+PP fiber, LDPE+PP fiber, PP+glass fiber and X-LDPE cable samples are given (Figures 1-5). Most of them contain PP+20 % PP, because the best results for all properties of the composites are obtained at this composition.

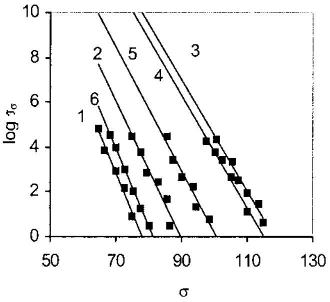

Figure 1. The dependence of log τ_σ on σ (at 183 K) for PP + PP fiber composites (1 - neat PP; 2 – PP + 10 % PP fiber; 3 – PP + 20 % PP fiber; 4 – PP + 30 % PP fiber; 5 – PP + 40 % PP fiber; 6 – PP + 50 % PP fiber).

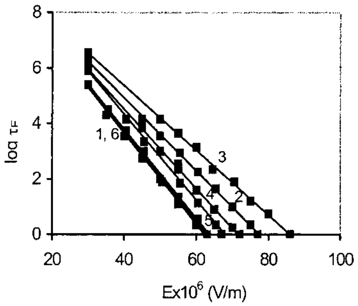

Figure 2. The dependence of log τ_E on E (at 293 K) for PP + PP fiber composites (1 - neat PP; 2 – PP + 10 % PP fiber; 3 – PP + 20 % PP fiber; 4 – PP + 30 % PP fiber; 5 – PP + 40 % PP fiber; 6 – PP + 50 % PP fiber).

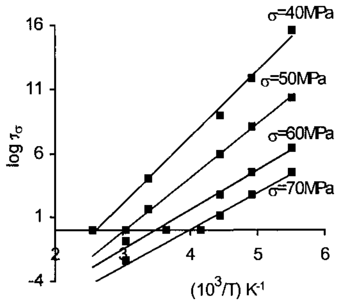

Figure 3. The dependence of log τ_σ on $1/T$ for neat PP sample.

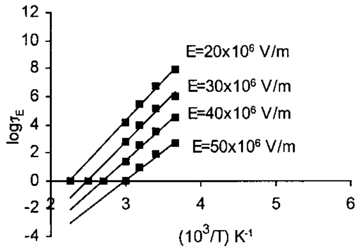

Figure 4. The dependence of log τ_E on $1/T$ for neat PP sample.

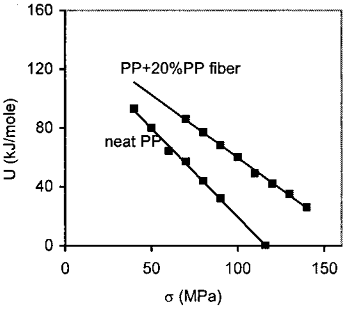

Figure 5. The dependence of activation energy of degradation on σ.

As can be seen in the figures, it is possible to write the following equations for the electric degradations similar to the equation for mechanical degradations:

$\tau_\sigma = \tau_0\exp[(U_0 - \gamma\sigma)/RT]$ an $\tau_E = \tau_0\exp[(W_0 - \chi E)/RT]$.

The equations are supported by the following results:

(1) The graphs log $\tau_\sigma - f(\sigma)$, log $\tau_E - f(E)$, log $\tau_{\sigma,E} - f(1/T)$ are linear in certain σ and E intervals; (2) τ_0 and U_0 values are constants for all cases, i.e., the thermofluctuation theory is valid; (3) while the mechanical stress (σ) and electric strength (E) are increasing, τ decreases and also structure-

sensitive parameters (γ and χ) increase. The equation for degradation of the polymer materials mentioned above, occurring while two or more factors change simultaneously is

$$\tau_{\sigma,E} = \tau_0 \exp[(U_0 - (\gamma\sigma + \chi E))/RT]$$

The equation may be expressed as the products of two exponents $\left(\tau_{\sigma,E}\right) = \tau_0 \exp\left(\frac{W_0 - \chi E}{RT}\right)\exp\left(\frac{U_0 - \gamma\sigma}{RT}\right)$; probably $W_0 \cong U_0$ if assumed that the mechanisms of electric and mechanical degradations are similar, one of them belongs to degradation under a long-term electric field and the other belongs to the degradation caused by mechanical stress. In this case, the temperature dependence may be written as the Arrhenius equation. In long-term degradation, variations in the composite structure can be observed. This result is observed both in microphotographs and IR spectra (Figures 6a, b and 7), in which the intensities of the peaks at 1680 cm^{-1} (C = C vibrations) and at 1715-1780 cm^{-1} (C – O and C = C vibrations) belong to amorphous regions. As can be seen from Figure 7, burning of the material and then deterioration of the fibrous structure arise in the broken area. The mechanism of breaking in an electric field following a long-term degradation can be based on the above results. In this process, the role of electric degradation in the instantaneous breaking is a decrease in the breaking potential energy (ΔU).

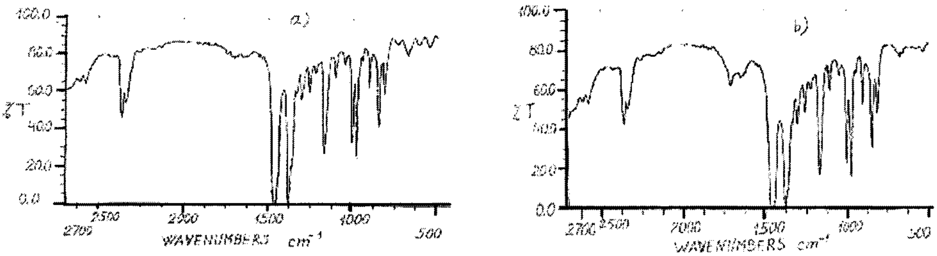

Figure 6. The changes in the IR spectrum of PP+20 % PP composite during long-term degradation in electric field. (a) $t = 0$ and $U = 0$, (b) $t = 5$ h and $U = 9$ kV.

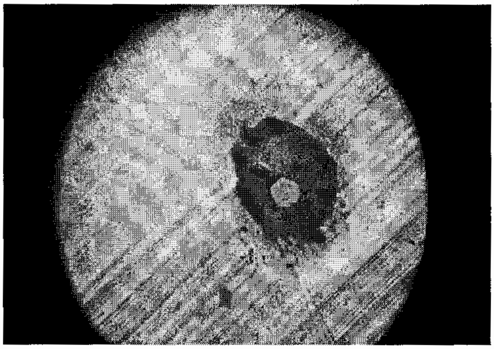

Figure 7. a) Carbonization region; b) complete disorder of fiber structure; pure fibrous structure in the ordered region.

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