Thermo-oxidative and Photo-oxidative Aging of Polypropylene Under Simultaneous Tensile Stress

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Synopsis

The effect of uniaxial tensile stress at constant load in the range of 0 to 6.86 MN/m² upon the behavior of stabilized and unstabilized types of isotactic polypropylene was investigated in the course of thermo-oxidative aging at 80° to 130°C and of photo-oxidative aging in the Xenotest 450 apparatus at 45° and relative humidity of 65%. From kinetic evaluation of the temperature dependence of weight changes of unstabilized polypropylene during thermo-oxidative aging, it was found that the weight losses of unstressed and tension-stressed specimens obey the kinetic equations for a reaction of the first order. The degradation of stressed specimens, however, proceeds at a considerably higher rate as compared with the unstressed state and is marked by a decrease in apparent activation energy as well as by an increased rate of crack development. The cracks develop in the direction perpendicular to the tensile stress and have the shape of hollow funnels widening outward. The tensile stressing of stabilized types of polypropylene in thermo-oxidative and photo-oxidative environments causes an accelerated embrittlement of the polymer, manifested particularly by a marked decrease of elongation at break. This accelerated embrittlement goes on under the action of tensile stresses exceeding the so-called safe stress, i.e., the stress below which no acceleration of aging (as measured by the relative decrease in the elongation at break of the stressed and unstressed specimens, can be detected. The values of this safe tensile stress decrease with the temperature and lie well below the tensile strength of the polymer. In the range of tensile stresses exceeding the safe stress, the dependence of the logarithm of time of a 50% decrease of the elongation at break on the applied tensile stress was found to be linear. The findings are in agreement with Zhurkov's kinetic concept of mechanical deterioration of polymers, where the effect of the applied mechanical stress is superimposed on the thermal fluctuation and leads to the scission of chemical bonds and to the formation of cracks in the polymer.

INTRODUCTION

The effect of external mechanical stressing upon the aging of polymers, although used for a number of years for accelerating the aging tests of polymers and of their stabilization systems,[1,2] has been systematically studied only recently. These studies have referred to the photochemical degradation of polyamide, poly(methyl methacrylate), poly(vinyl chloride), and natural silk,[3] and to the weathering of polyethylene.[4]

These investigations had for their basis Zhurkov's kinetic concept of the mechanical deterioration of polymers[5-8] defined by the general equation[5]:

$$\tau = \tau_0 \cdot e^{U_0 - \gamma\delta/kT} \tag{1}$$

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where τ = lifetime under load, i.e., time to rupture of the polymer; σ = applied mechanical stress; T = absolute temperature; τ_0 = period of thermal fluctuations of atoms; U_0 = energy of the rupture of an interatomic bond; γ = coefficient of overstress in the bond being ruptured; and k = Boltzmann constant.

The kinetics of the mechanical deterioration of polymers confirmed by Zhurkov's direct measurements using infrared spectroscopy,[9] electron spin resonance,[10] mass spectrometry,[11] and small-angle x-ray scattering[12] includes three stages: (a) deformation of atomic bonds in polymer chains by mechanical stress, where the initial binding energy U_0 is reduced by the value $\gamma \cdot \sigma$; (b) scission of excited bonds by thermal fluctuations; (c) formation of submicroscopic cracks and their coalescence into larger cracks, which lead to the fracture of polymer.[8]

It has been the aim of our studies to investigate the significance of applied tensile stress for the thermo-oxidative and photo-oxidative degradation of stabilized and unstabilized isotactic polypropylene. The behavior of polypropylene on these combined degradations has been studied using reaction kinetics, microscopic observations of crack development, and determination of changes in tensile properties.[13]

EXPERIMENTAL

Initial Polymers

Three types of Czechoslovak polypropylene produced by the Research Institute for Macromolecular Chemistry in Brno were used in the tests: unstabilized (PP-N), antioxidant-stabilized (PP-A), and carbon black-stabilized (PP-S) polypropylene. The properties of the initial types of polypropylene are summarized in Table I.

TABLE I
Properties of Initial Types of Polypropylene

Property	PP-N	PP-A	PP-S
Melt flow index[a]	0.48	1.2	0.87
Logarithmic viscosity number,[b] ml/g	306	232	254
Volatile fraction,[c] %	0.009	0.04	0.030
Thermal stability,[d] min	5	880	920
Tensile strength, MN/m²	36.28	40.31	37.96
Elongation at break, %	230	322	268

[a] Ten minutes; 21.18 N; 230°C.

[b] In tetralin at 140°C; c = 0.1 g/100 ml.

[c] Five hours at 80°C.

[d] Induction period at 180°C, in which no absorption of oxygen occurs.

Testing Equipment Used

The testing equipment for constant-load uniaxial tensile stressing consisted of upper and lower grips made of stainless steel weights and securing

rods for catching the weight in case of rupture of the stressed specimen. The specimens were suspended on the suspension frame of the exposure space. Exposure of loaded specimens was in drying boxes with forced hot-air circulation (Type ST 23) or in the Xenotest 450 apparatus.

Weight Changes During Thermo-oxidative Degradation of Unstabilized Polypropylene Under Simultaneous Tensile Stress

Rods 3 mm in diameter were made of granulated PP-N polypropylene on a Czechoslovak screw-extrusion machine of the type VUGPT E 542. Twenty-cm lengths of these rods were drawn three times in succession through graduated sizing dies heated at about 180°C. They were cut into test specimens of 40-mm length and then annealed for 1 hr in boiling distilled water, dried at 60°C to constant weight, and stored in a desiccator over solid sodium hydroxide. The measurements consisted in the determination of weight losses of the test specimens (three pieces for each test) after exposure in hot-air drying boxes at temperatures of 100°, 120°, 140°, and 160°C under simultaneous action of tensile stresses of 0, 0.775, 1.550, and 3.138 MN/m² (referred to the initial cross section of the test specimens).

Crack Development in Test Specimens of Unstabilized Polypropylene from Weight Change Measurements

To investigate the crack development in brittle porous surface layers of PP-N polypropylene from the previous procedure, the test specimens were coated with a film of electrically conductive silver paint. After drying, a copper coating about 0.2 mm thick was applied electrolytically from an acid copper-plating bath. The copper-plated test specimens were cut to half-length, and the cut surfaces were ground for microscopic examination. The thickness of the well-defined porous layer, which showed the depth of cracks formed during the degradation, was measured on ground sections, using a Meopta D polarizing microscope at a 25× magnification with side lighting of the specimens.

To check the correctness of the microscopic method of the crack depth measurement and to find the character of the cracks, the following method of autoradiographic investigation of the cracks was 1% used on some of the specimens: A drop of sulfuric acid with radioisotope ^{35}S having a specific activity of 2.2 mCi/ml was placed on the surface of a ground section of a degraded test specimen. The surface was then cleaned with methyl alcohol and coated with a protective layer of a 1% solution of polystyrene. The autoradiographs were taken using the ORWO K 106 stripping film; and the autoradiographs thus made as well as the original ground sections of the test specimens were photographed on a Reichert Me-22F-microscope in transmitted and reflected light, respectively, at a 25× magnification (Figs. 1 and 2).
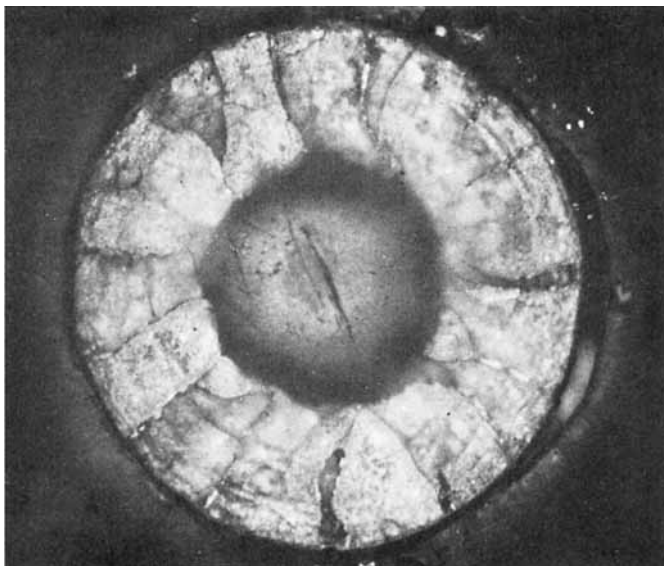
Fig. 1. Structure. Magnification 25×.

Changes in Mechanical Properties of Stabilized Types of Polypropylene during Thermo-oxidative and Photo-oxidative Aging Under Simultaneous Tensile Stress

Tensile test specimens with dimensions defined by the French testing standard NFC-32-100 (thickness 1 mm, overall length 75 mm, length of narrow parallel portion 25 mm, width of narrow parallel portion 4 mm, width at ends 12.5 mm, radius 8 mm) were used for the investigation of aging of polypropylene. The test specimens were prepared from plaques of dimensions 90 mm × 40 mm × 1 mm, made by injection molding granulated polypropylene on an Engel injection-molding machine using a film gate. From the central portion of the polymer plaques thus made, the tensile test specimens were cut out using a punching device specially made for this purpose. They were annealed in boiling distilled water for 1 hr, dried at 60°C to constant weight, and stored over solid sodium hydroxide.

The effect of tensile stress in the range of 0 to 6.86 MN/m² on the aging was investigated as follows: After weighing and measuring their dimensions, the specimens were clamped between the grips of the loading device and, after suspending them in hot-air drying boxes or in the Xenotest 450, were loaded with the appropriate weight. The exposed specimens (about five pieces for each measurement) were taken out of the testing space and placed for 16 hr in a desiccator over solid sodium hydroxide and again weighed and measured. The specimens taken from the tests in the Xeno-test 450 were previously dried at 60°C to constant weight.

Tensile tests employed the Instron TTDM machine with simultaneous recording of the stress–strain curve at a temperature of 23° ± 2°C. The
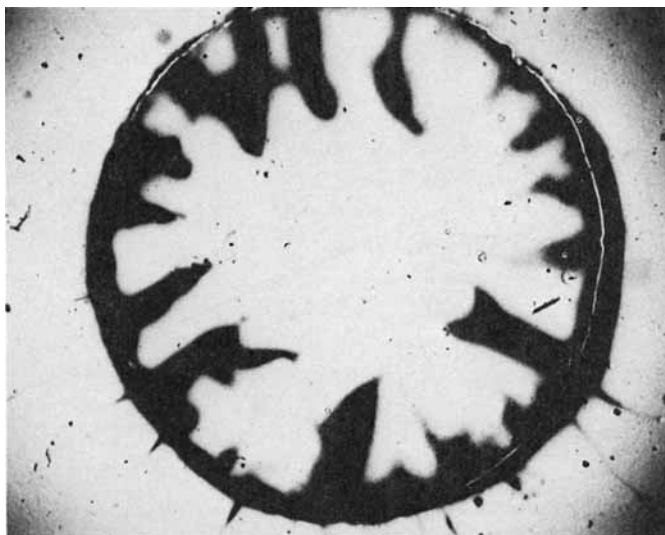
Fig. 2. Autoradiograph of cross section of unstabilized polypropylene subjected to thermo-oxidative degradation under simultaneous tensile stress. Magnification 25×.

yield point, tensile strength, and elongation at break were measured at a speed of 1 cm/min. The Young's modulus in tension was determined form measurements of the linear part of the stress–strain curve at a speed of testing of 0.05 cm/min.

RESULTS AND DISCUSSION

The study of the effect of applied tensile stress upon the thermo-oxidative and photo-oxidative aging of polypropylene was aimed at an approximate simulation of the actual conditions of aging of polymers in technical practice. To simulate these conditions, we used a range of external stresses up to about 6.86 MN/m² and we applied an uniaxial tensile stress to the specimens at constant load. This pure mode of stressing (i.e., free from combination with other types of stress) occurs frequently in technical practice and ensures an approximate constancy of the level of the applied mechanical stress with respect to time. It also enables aging tests to be carried out with simple loading devices and currently available exposure equipment which require the use of test specimens having a substantially smaller cross section than the cross section of test specimens currently used. This is met by specimens to the French standard NFC-32-100. To reduce the occurrence of dangerous orientations and internal stresses, the test specimens were cut from injection-molded plaques made in a mold with a film gate and were subsequently annealed to relieve residual stresses.

To elucidate the nature of the effect of tensile stress on the thermo-oxidative degradation of polypropylene, weight changes (down to a weight
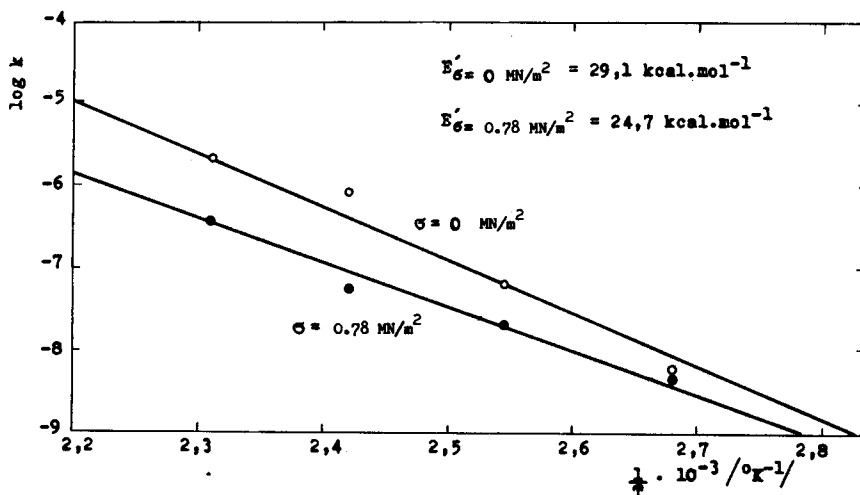
Fig. 3. Apparent activation energy of thermo-oxidative degradation of unstabilized polypropylene in the unstressed state and under the action of tensile stress of 0.78 MN/m².

loss of about 5%) and development of cracks in stressed specimens of unstabilized polypropylene were investigated at 100° to 160°C at an applied tensile stress in the range of 0 to 3.14 MN/m². It was found that weight losses of unstabilized polypropylene increase at constant temperature with the magnitude of the applied tensile stress. The temperature dependence of weight changes of the polymer in the unstresses state and under a stress of about 0.78 MN/m² both obey the kinetic equation for a reaction of the first order, which would indicate a common mechanism for the two degradations. In the case of stressed polypropylene, however, the degradation occurs at a considerably higher rate. Whereas the apparent activation energy of the thermo-oxidative degradation of unstressed polypropylene, calculated from these measurements, amounts to 29.1 kcal/mole, the apparent activation energy of the analogous degradation, proceeding under a tensile stress of 0.78 MN/m² is only 24.7 kcal/mole, i.e., a 15% decrease (Fig. 3). For comparison, the activation energy of the thermo-oxidative degradation of polypropylene, calculated from the oxygen sorption, equals 21.8 kcal/mole.[14]

An analogous accelerating influence of mechanical stressing was found in the investigations of crack development in the thermo-oxidative degradation of unstabilized polypropylene. The increase in mechanical stress applied to the specimen has the same effect as an increase in environmental temperature in accelerating the rate of crack development. The cracks form in a direction perpendicular to the tensile stress and have the shape of hollow funnels widening outward, probably providing the transport of volatile degradation products from the polymer (Figs. 1, 2, and 4).

On the basis of these as well as other findings, the probable mechanism of such degradations of polypropylene may be assumed as follows: Under
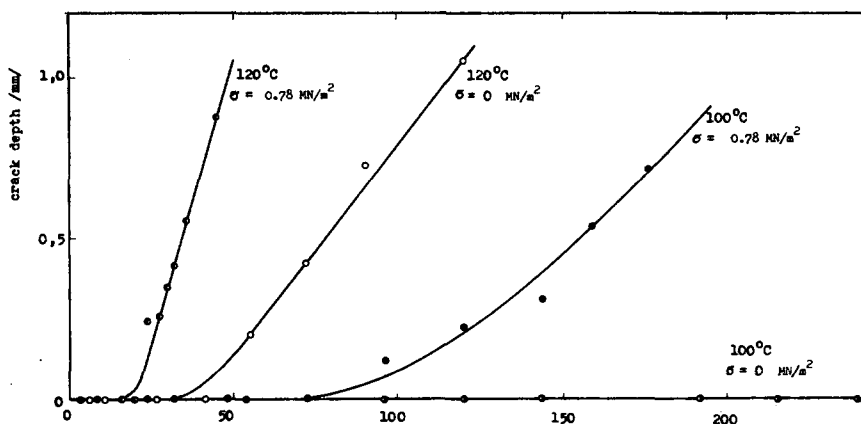
Fig. 4. Crack development during thermo-oxidative degradation of unstabilized poly-propylene in unstressed state and under tensile stress of 0.78 MN/m².

the action of external mechanical stress, high stress concentrations arise in the polymer body even at low values of mechanical stress at various defects, which lie probably in the region of supermolecular structure of the polymer. These mechanical stress concentrations produce the scission of chemical bonds in polymer chains and cause the initiation of cracks at the spots of bond scissions. This results in an acceleration of the total deg-radation process, which proceeds with lower activation energy and with enhanced crack development.

Particularly characteristic are the changes in the mechanical behavior of stabilized types of polypropylene that have been subjected to tensile stresses in the range of 0 to 6.86 MN/m² under simultaneous action either of a thermo-oxidative environment of 80° to 130°C for periods up to 4000 hr or of a photo-oxidative environment at 45°C and relative humidity of about 65% for periods up to 1200 hr. It was found that the tensile stress causes an appreciable acceleration of the embrittlement of the polymer as compared with the unstressed state. This becomes manifest particularly by a marked drop in elongation at break and to a lesser extent by a decrease of tensile strength and a rise of Young's modulus and proceeds in a quite analogous manner both in thermo-oxidative and in photo-oxidative en-vironments. The acceleration of polymer embrittlement as a function of the applied tensile stress occurs only under the action of tensile stresses exceeding the so-called safe stress, which decreases with the temperature of the degrading environment and lies well below the tensile strength of the polymer. Thus, at 80°C the safe stress for antioxidant-stabilized polypropylene (PP-A) amounts to some 2.45 MN/m². Below this value, embrittlement proceeds as in the unstressed state. Above this safe stress the embrittlement of the polymer rapidly rises with the magnitude of the applied mechanical stress.
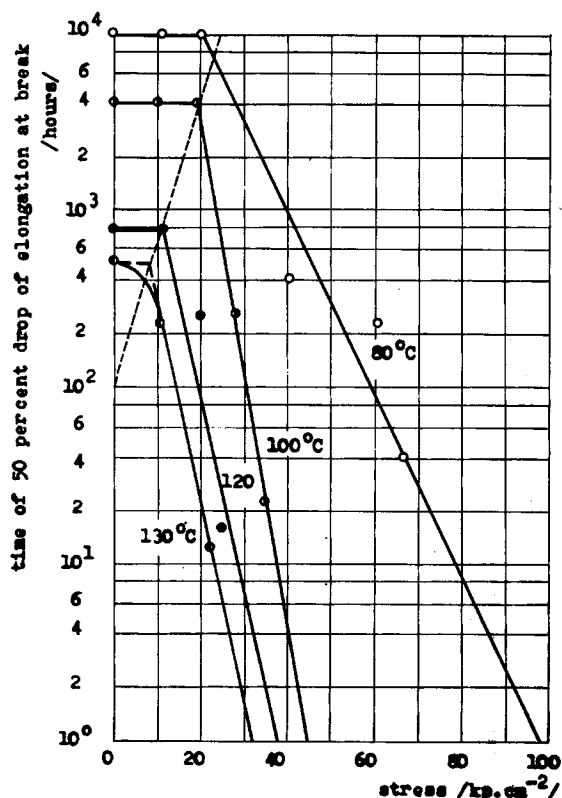
Fig. 5. Time dependence of 50% drop in elongation at break vs. tensile stress during thermo-oxidative degradation of tension-stressed polypropylene (antioxidant-stabilized).

From the time dependence of the decrease of elongation at break of stabilized polymers at various stresses and temperatures, the so-called life-time curves for the elongation at break of polymers were plotted. These curves exhibit the dependence of the logarithm of the time corresponding to a 50% drop in the elongation at break of the polymer on the applied tensile stress at various temperatures and are linear above the safe stress (Figs. 5 and 6).

The principal findings of the study of the effect of applied tensile stress on the thermo-oxidative and photo-oxidative aging of polypropylene are in agreement with Zhurkov's general kinetic theory of mechanical deterioration of polymers.[5–12] This theory is based on the concept that the effect of the applied mechanical stress is superimposed on thermal fluctuations in the polymer and leads to the scission of chemical bonds and to the development of cracks in the polymer. The theory is defined by the fundamental equation (1), according to which the lifetime, i.e., time to rupture of the mechanically stressed polymer, is a negative exponential function of the applied stress.[5]
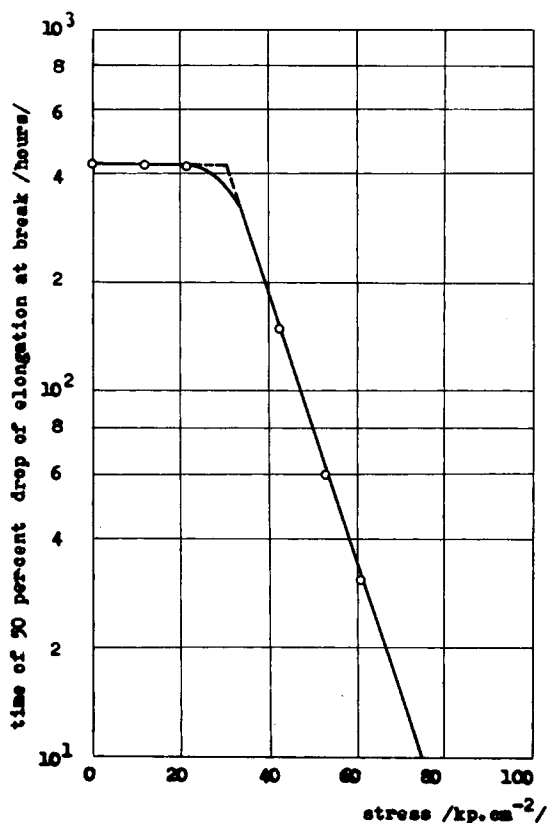
Fig. 6. Time dependence of 50% drop in elongation at break vs. tensile stress during photo-oxidative aging of tension-stressed polypropylene (carbon black-stabilized) in Xenotest 450 apparatus.

The occurrence of the so-called safe stress for embrittlement of polypropylene found in our investigation corresponds to the conclusions of Bartenev,[15,16] who has modified the original kinetic theory of mechanical deterioration[5,6] of materials by elaborating the so-called reversible brittle crack model. This model is based on the concept that, owing to thermal fluctuations, the existing cracks in the polymer are alternately closed and widened, with the probability of crack growth increasing with applied mechanical stress. On the basis of derived equations for the rate of crack propagation, two characteristic values of external stress have been defined: (a) the so-called safe stress, under which no crack propagation occurs either by the action of thermal fluctuations or of the applied stress, and (b) the so-called critical stress, under which the material breaks down at an instantaneous rate. Equation (1) for the lifetime under load, which has been independently derived by Bartenev on the basis of the above concept and confirmed using some polymers, is valid in the range delimited by these two marginal stresses.[15,16]

The actual mechanism of thermo-oxidative and photo-oxidative degradation of polymers under simultaneous action of mechanical stress still remains unclarified, and at present we are engaging in research aimed at elucidating it by using direct methods.

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