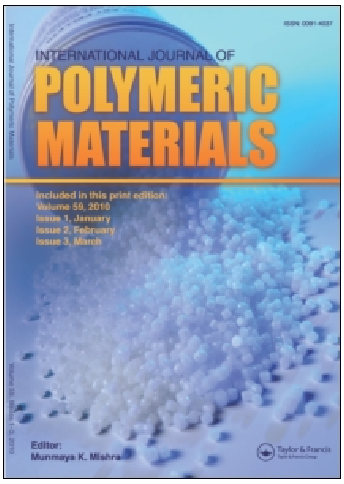

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Variation of Antioxidant Effectivity with Copolymer Composition

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The variation of inhibited oxidation parameters with the composition of ethylene-propylene and ethylene-vinyl chloride copolymers is studied. In both cases the antioxidant effectivity is minimal in copolymers containing small amounts of the second monomer groups.

KEY WORDS Antioxidants, copolymers.

INTRODUCTION

The variation of inhibited oxidation parameters with the composition of ethylene-propylene and ethylene-vinyl chloride copolymers is studied. In both cases the antioxidant effectivity is minimal in copolymers containing small amounts of the second monomer groups.

In polymers, the efficiency of antioxidants depends not only on chemical properties of compounds used as antioxidants, but also on the specificity of the polymer matrix including the character of antioxidant molecule distribution in it. One of the methods of regulating polymer matrix properties is to introduce heterogeneous elements into the polymer chain, i.e., transition from a homogeneous to a mixed polymer. This approach is the subject of investigation of the present study.

EXPERIMENT

The investigation uses copolymers of ethylene with propylene, and ethylene with vinyl chloride, preferably with low content of propylene and vinyl chloride groups, and the following antioxidants: phenyl-β-naphthylamine and 2,2′-methylene-*bis*-(4-methyl-6-*tert*-butylphenol).

Oxidation is studied using equipment described in Reference 1. In this paper, the length of the induction period τ is registered by determining the change in the oxygen pressure (the pressure is reduced by 2.5 mm Hg, the system volume being 12 cm^3 and sample mass being 0.05 g). The antioxidants are extracted from the sample by vacuum evaporation and are analyzed by spectrophotometry.[2]

RESULTS AND DISCUSSION

A. Inhibited oxidation of copolymers of ethylene with propylene

The oxidation of copolymers of ethylene with propylene (CEP) is studied at 180°C and standard oxygen pressure of 300 mm Hg. Phenyl-β-napthylamine is used as an oxidant. The relation curves of the induction period versus phenyl-β-napthylamine concentration are presented in Figure 1. As is evident from Figure 1, up to a certain lower critical concentration $i_{cr.1}$ the antioxidant has practically no effect on the induction period, but further up, its influence grows rapidly, the value of critical (nonworking) concentration quickly rising with the content of propylene groups: increase in the content of propylene groups leads to a marked reduction of antioxidant efficiency.

Figure 2 shows the curves of antioxidant concentration change in (CEP) during the induction period time (i.e., the time of fast reaction delay) of ethylene with propylene copolymer oxidation. Two or three regions can be seen on these curves: rapid decrease of concentration at the initial part of induction period (absent in curves for pure polyethylene); the region of relatively slow consumption, which obeys the first-order law; and the region of rapid consumption at the end of the induction period.

The appearance of the first region can be explained by the fact that the initial antioxidant concentration is higher than at certain upper concentration $i_{cr.2}$, and the last region by the fact that it drops lower than the lowest $i_{cr.1}$. The mechanism of critical phenomena is discussed in Reference 3, and in brief, can be understood from the different changes in certain branching and termination rates.

Figure 3 shows the relation of $i_{cr.1}$ and $i_{cr.2}$ upon the composition of mixed polymer. It can be seen that with increasing content of propylene groups these concentrations approach each other and the region of slow (stationary^3) antioxidant consumption is significantly narrowed.

The antioxidant consumption rate is the sum of the rates of its direct oxidation and the rate of consumption in chain termination. The latter rate near the $i_{cr.}$ becomes commensurable or even greater than the rate of oxidation. This explains

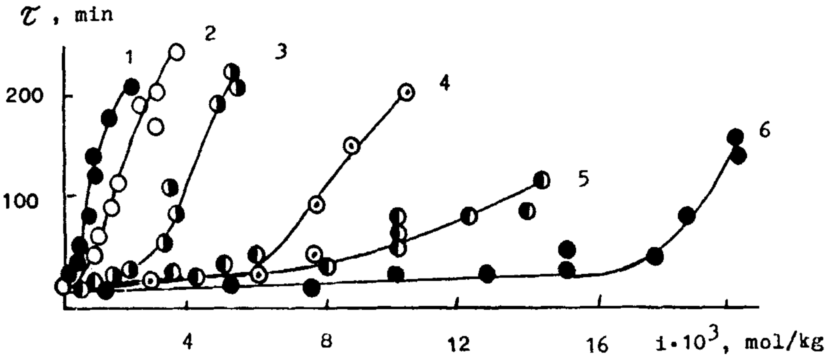

FIGURE 1 Induction period of the oxidation of ethylene-propylene copolymers and homopolymers as a function of initial phenyl-β-naphthylamine concentration at 180°C and oxygen pressure 300 mm Hg. (1) polyethylene; (2) 0.6; (3) 1.5; (4) 5.1; (5) 24 weight percent; (6) polypropylene.

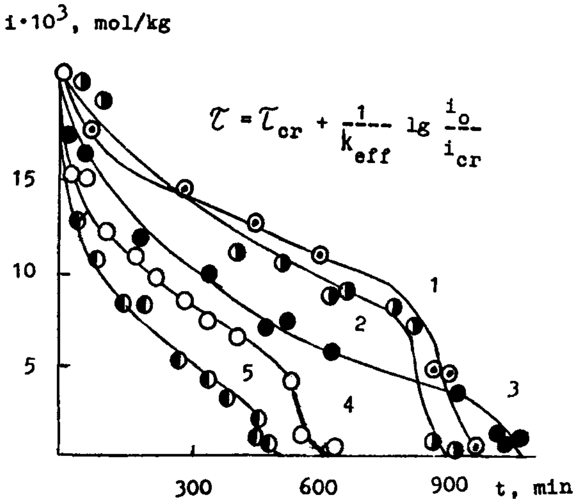

FIGURE 2 Antioxidant phenyl-β-napthylamine consumption during the induction period of the oxidation of ethylene-propylene copolymers: (1) 0; (2) 0.6; (3) 1.5; (4) 24; (5) 5.1 weight percent; C_3H_6 at 180°C and oxygen pressure 300 mm Hg.

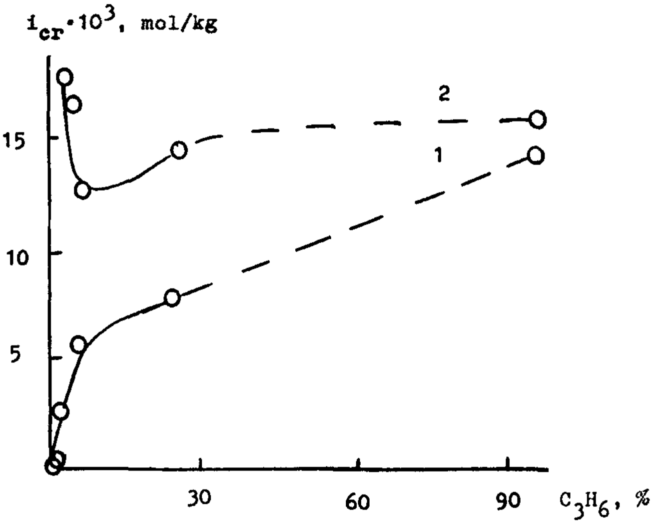

FIGURE 3 Upper (1) and lower (2) critical concentrations of phenyl-β-naphthylamine as a function of the composition of ethylene-propylene copolymers at 180°C and oxygen pressure 300 mm Hg.

the significant rise of the apparent constant of the consumption rate of phenyl-β-napthylamine with the increase in the content of propylene groups in the 0–10% interval.

B. Oxidation of copolymers of ethylene with vinyl chloride

Oxidation of copolymers of ethylene with vinyl chloride (CEVC) is studied using 2,2′-methylene-*bis*-(4-methyl-6-*tert*-butylphenol) as an antioxidant. Analogous to mixed ethylene-propylene copolymers the increase in the content of vinyl chloride groups is accompanied by a rise of the apparent rate constant of antioxidant consumption, which reaches its maximum at 10% C_2H_4Cl (the two curves presented in Figure 4 correspond to different ways of estimation; the upper curve is obtained from the relation of the induction period as a function of the initial concentration; the second curve, from the antioxidant consumption curves). The upper critical concentration changes in a more complicated manner, the curve of which has two minimums and one maximum. At 4–5% vinyl chloride group concentration $i_{cr.}$ is not detected.

Sophistication of curves in comparisons to the curves for copolymers of ethylene with propylene can be explained by the polarity of vinyl chloride groups, capable of forming stationary, therefore nonreactive with regard to fixed macromolecules, complexes with polar antioxidant molecules, as well as by the lower reactivity of vinyl chloride groups.

The reactivity of a separate copolymer molecule should monotonously increase (CEP) or decrease (CEVC) with the rise in the content of the second monomer. In reality, small amounts of second monomer groups lead to the increase in the lower and to the decrease in the upper critical concentrations, thus indicating an increase in the oxidizability of the polymer as a whole. The most likely reason for the increase in reactivity is the loosening of the structure, which causes the enhancement of group mobility and oxygen dissolubility in the melted polymer. Unfortunately, it is impossible to measure the dissolubility of oxygen in the polymer.

Thus, in the case under consideration, the physical effects connected with the alteration of the polymer matrix structure exert a significantly greater influence on

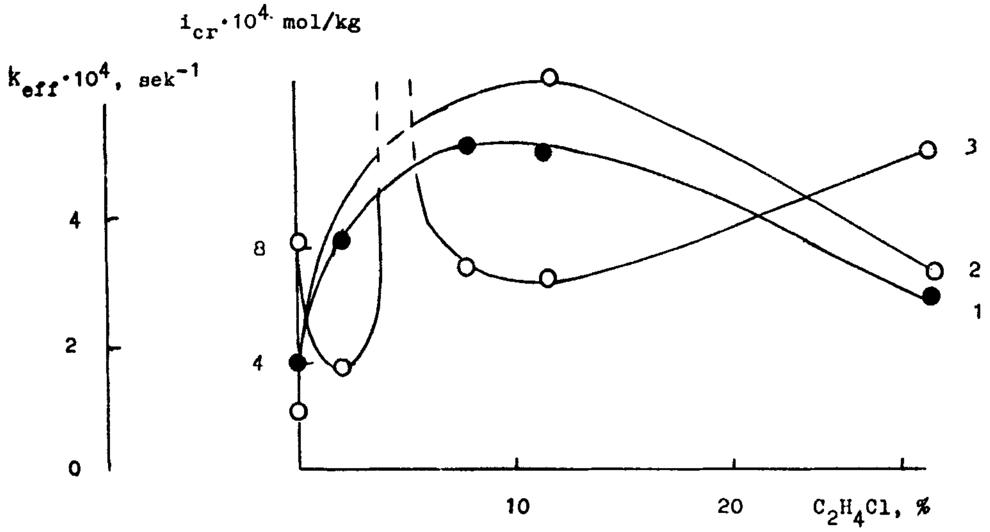

FIGURE 4 The apparent rate constant of antioxidant consumption calculated from formula versus [IH] (1) and from antioxidant consumption (2) as a function of the composition of copolymers ethylene-vinyl chloride. 180°C, oxygen pressure 300 mm Hg, antioxidant 2,2'-methylene-*bis*-(4-methyl-6-*tert*-butylphenol).

the parameters of inhibited oxidation as compared to the changes in the reactivity of separate polymer macromolecules.

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