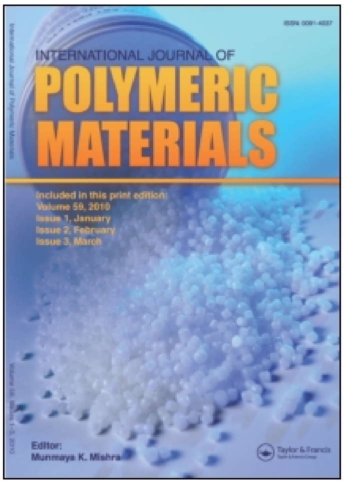

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The Initiation of Polypropylene Oxidation

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The rate of primary initiation of PP oxidation with catalytic centers containing transition metals was evaluated. The rate was determined from the retardation period of the oxidation reaction in the fracture sites of stressed PP films with an inhibitor when the retardation period was close to the value of durability. The number of initiation centers was taken into account. For this purpose, the predicted durability of samples was calculated for the concentration of initiation centers of the polymer without additives. Inhibited PP films with various complexone contents introduced to the polymer to deactivate the catalytic centers were studied. The rate of initiation was shown not to change in the presence of the complexone, while the number of centers changed. The comparison of the oxidation kinetics of samples derived from the oxygen absorption using data from this study showed that the macrokinetic parameters were dependent on the number of the initiation centers. Thus, the kinetic regularities were shown to be related to the catalytic activity of initiation centers and also to their concentration.

Keywords: Polypropylene; oxidation; catalysis; metal ions; films; oxidation kinetics

INTRODUCTION

It was demonstrated in [1] that the initiation of the oxidation of PP involves the metals ions of the catalytic systems for polymerization of the monomer and iron particles from equipment. During polymerization the particles of the catalyst are ground to subparticle size and randomly distributed in the polymer globules [2]. It was assumed in [1] that the rate of oxidation initiation can be decreased by introducing a complex formation agent binding the metal ions. In fact, the complexones of various nature mixed with phenolic inhibitors demonstrate the strong synergistic effect essentially decreasing the rate of the thermooxidative degradation of PP. In [1], this fact was explained by a decrease in the rate of the primary initiation by metal impurities in the presence of complexones. The objective of the present study was to check this assumption.

EXPERIMENTAL

The specimens used in this study were oriented PP films with a melt index of 2.2 g/min (without purification). The complexone pentadione-2,4 (PDO) and Irganox-1076 inhibitors (without preliminary purification) were introduced to the polymer powder in the presence of a small amount of a solvent. The films were pressed on the laboratory press at 230°C and $p = 150$ atm and orientationally drawn at 130°C to draw ratio $\lambda = 7$ using the local heating technique. The durability of the samples was determined on a setup described in [3] at 140°C, $\alpha = 15$ MPa, and $p_{O_2} = 20$ kPa. The overall rate of the oxidation of the polymer sample of the 0.05 g mass was determined from the oxygen absorption on the static manometric device [4] in non-isometric conditions; the water absorber was at 140°C and $p_{O_2} = 20$ kPa. The induction period was defined as the time necessary for consumption of 0.07 moles of O_2 per 1 kg of polymer. For the fractured samples, the number of nucleation sites "n" crossed by the ultimate crack has been determined microscopically from the shape of the fracture cross section [5]. From the number of nucleation sites and durability of the sample, the average propogation rate of the oxidation reaction from the center of primary oxidation in the direction transverse to the orientation or the rate of growth of nucleation sites was calculated [5]: $\omega_g = l/(\tau_{\text{dur}} n)$, where l is the sample width. From this dependence, the durability of a sample for a given nucleation sites density in PP without additives τ_{dur} was found. Using the inhibitor method [6], as the retardation time of the oxidation reaction in nucleation sites was close to the durability value [7], the rate of primary initiation on impurities of metals was evaluated in accordance with average rate of inhibitor comsumption in the nucleation sites of the fracture as $\omega_c^{\text{nuc}} = f[\text{InH}]/\tau_{\text{dur}}$, where f is the number of chains terminated with one inhibitor molecule.

RESULTS AND DISCUSSION

Earlier, the nucleation character of the fracture of stressed PP films in an oxidizing medium was demonstrated [5, 7–9], and the dependence of durability on the number of initiation centers in the cross section of the fatal crack was considered [9]. It was shown in [1, 9] that the topology of the impurity particles distribution was changed during the orientational drawing of the isotropic film and the topology anisotropy was noted: the distance between centers increased by l/l_0 (l and l_0 are the final and initial lengths of the film) along the stretching axis and decreased twice in the lateral direction. The fracture of a film proceeds as a result of the junction of nucleation sites of thermoxidative degradation around the initiation centers during their growth in a direction transverse to the applied stretching force [5, 7, 9]. The duration of oxidation before fracture at a standard sample size, other conditions being equal, depends on the number of centers (or nucleation sites), i.e., on the distance between them. When the number of nucleation sites of the fracture is the same, the durability should depend on the rate of primary initiation. If complexones block the catalytic centers on the surface of particles, as is assumed in [1], a decrease in the rate of initiation or a change in the number of centers should be observed. The calculation presented below was performed to investigate this assumption. Let us first explain some assumptions on which this calculation is based.

The evaluation of the initiation rate from the durability value, i.e. on the rate of inhibitor consumption in the nucleation sites of the fracture of inhibited films can only give approximate values. Oxidation is the chain process with degenerate chain branching. Inhibitor is consumed in both termination of primary kinetic chains, of chains initiated by hydroperoxide decomposition, and in direct reactions of inhibitor with oxygen. For this reason the inhibitor consumption in nucleation sites is only approximately proportional to the rate of chain initiation. As well as the known disadvantages of the inhibition method [10], the calculated rate of the initiation is affected by the nonuniform distribution of the low-molecular-mass additives in a polymer and by the fact that fracture occurs in the areas depleted of the nucleation sites additives.

According to [11], up to 60–80% of an inhibitor remains in the fractured samples as a result of a strong localization of the oxidation in the nucleation sites and because of the irregularity of the distribution.

The overestimation of the calculated value is partially compensated because the time of the reaction retardation by an inhibitor is less than the durability. The difference is equal to the time necessary for the development of the thermooxidative and mechanical degradation of all chains in nucleation sites and for their connection in the interfibrillar layers. According to [7, 12], this time is equal to ~ 20% of the durability. The combination of these opposing effects should give satisfactory results.

In Table I, the following data are presented: the number of nucleation sites "n" and their growth rate ω_g, the finite size of the average statistical nucleation site d_f, the number of nucleation sites per 1 mm of the cross section length (per 1 mm) and the average rate of inhibitor consumption in the nucleation ω_c^{nuc} sites ωnucin inhibited PP films with various concentrations of Irganox at the density of catalytic fracture centers characteristic of PP without additives and equal to 2.4 nucleation sites per 1 mm of the film width. Analogous data are presented in the Table II for samples with complexone.

It follows from Table I that, in the presence of an inhibitor, the number of oxidation nucleation sites increases threefold. This can be explained by the initiation of the oxidation both by an inhibitor and the products of its transformation [13] and by an increase of the localization of the reaction in nucleation sites [7] resulting in a more irregular contour of the fracture cross-section. The dependence of the calculated rate of initiation on the concentration of an inhibitor is apparently related to the insufficient efficiency of the inhibition with a weak antioxidant at a low concentration (10^{-3} mole/kg). The initial concentration of inhibitor in nucleation sites of fracture appears to be close to the critical value.

Because, in the presence of an inhibitor, there are nucleation sites of various origins, the calculated rate of initiation is an average value. A comparison of the data in Tables I and II shows that, in the presence of the complexone, the number of initiation centers changes while the initiation rate remains unchanged. At a relatively high concentration (2×10^{-3} mol per kg Irganox) complexone and inhibitor provide effective termination of the kinetic chains. When high concentrations of the complexone and inhibitor are introduced, the number of initiation centers decreases 7–9 times as compared with inhibited samples (Tabs. I and II) and 2.4 times as compared with the initial PP. The rate of initiation by metal ions and by an inhibitor is practically the same. An

TABLE I Durability, the amount of initiation centers, the average propagation rates of nucleation sites W_g, their average finite size d_{fin} and the rate of inhibitor consumption in the nucleation sites W_c^{nuc} at various an inhibitor concentrations in oriented PP films

[InH] mol/kg	*dur* × *10*^{3} *s*	*1, mm*	*n*	$W_g \times 10^{-5}$ *mm/s*	d_{fin}*, mm*	*dur* × *10*^{3} *s*	$W_c^{nuc} \times 10^{-8}$ *mol/(kg s)*	*n (per 1 mm)*
–	4.14	5.1	12	10	0.4	4.14	–	2.4**
10^{-3}	18.24	6.1	53	0.6	0.1	60.02	3.3	8.8
10^{-3}	19.92	6.0	53	0.6	0.1	65.79	3.0	8.8
10^{-3}	26.40	5.2	38	0.5	0.1	76.92	2.6	7.3
10^{-3}	33.60	5.9	39	0.5	0.2	81.90	2.4	6.6
10^{-3}	48.72	6.8	35	0.4	0.2	85.00	2.3	5.1
	(29.38)*		(44.6)*	(0.5)*	(0.14)*		(2.7)*	(7.3)*
2×10^{-3}	48.00	5.0	47	0.2	0.1	189.40	2.1	9.4
2×10^{-3}	92.64	6.0	51	0.1	0.1	288.46	1.4	8.5
2×10^{-3}	95.46	5.6	27	0.2	0.2	195.80	2.0	4.8
2×10^{-3}	104.40	6.4	30	0.2	0.2	188.20	2.1	4.7
2×10^{-3}	122.40	4.1	32	0.1	0.1	410.00	1.0	7.8
2×10^{-3}	159.84	4.2	29	0.1	0.2	466.60	0.9	6.9
	(85.08)*		(36)*	(0.2)*	(0.2)*		(1.6)*	

*Average values. **This data coincides with average data.

TABLE II Durability, characteristics of initiation centers and nucleation sites, and the average rate of inhibitor consumption in the fracture spots in oriented PP films in the presence of the complexone

[InH] *mol/kg*	*[PDO]* *mol/kg*	$\tau_{dur} \times 10^{-3}$ *s*	*n*	$W_g \times 10^{-5}$ *mm/s*	d_{fin} *mm*	$\tau_{dur}^{w/a}$ $\times 10^3$, *s*	$W_c^{nuc} \times 10^{-8}$ *mol/(kg s)*	*n* *(per 1 mm)*	τ_{ind} $\times 10^{-3}$, *s*	$t_{ac} \times 10^{-3}$ *s*	$W_{max} \times 10^{-4}$ *mol/kg s*
		4.14	12	10	0.4	4.14		2.4	7.02	1.50	2.2
	10^{-2}	2.46	13	17	0.4	2.46		2.4	1.50	0.30	2.4
	5×10^{-2}	3.60	18	7	0.3	5.90		2.3	1.68	0.36	2.7
	10^{-1}	4.02	15	9	0.4	4.63		2.8	1.74	0.54	2.5
10^{-3}		26.40	38	0.5	0.3	76.92	2.6	7.3	33.60	7.20	1.0
10^{-3}	5×10^{-2}	99.42	12	0.4	0.4	99.42	2.0	3.8	15.48	9.12	0.5
10^{-3}	10^{-1}	79.38	13	0.5	0.4	86.88	2.3	2.7	13.50	9.30	0.5
2×10^{-3}		48.00	47	0.2	0.1	189.40	2.1	9.4	47.00	0.30	1.7
2×10^{-3}	10^{-2}	698.34	6	0.1	0.8	340.30	1.2	1.2	94.20	46.20	0.2
2×10^{-3}	10^{-1}	540.00	4	0.2	1.0	210.50	1.9	1.0	84.00	378.00	0.7

increase in the number of centers of initiation by an inhibitor and by the products of its transformation is accompanied by a slight increase in the calculated rate of the initiation (Tab. I). It can be concluded that, in the conditions under study (T = 140°C), the inhibitor used has the same initiating activity as a catalyst. This fact can be explained as follows. The number of kinetic chains appearing in the active sites of the catalyst surface depends not only on the catalytic activity of the metal, but is also limited by the possibility of forming the reactive complexes with the participation of a polymer. In the polymer matrix, especially in the solid state, when the diffusional displacements of solid particles and polymer chains are limited by low segmental mobility, and the conformational prohibitions are in effect, a limited number of polymer radicals can appear. In this sense, the mobile molecules of the low-molecular-mass initiator have some advantages and can be of the same efficiency as the immobile catalyst particles.

The data obtained agree with the estimates that the number of active sites on the catalyst surface does not exceed 1% of the surface content of metal atoms [14]. The number of active sites on each catalyst particle can be evaluated. In [15], the number of defects in the amorphous phase of PP was calculated from the solubility of phenyl benzoate. In the oriented PP films drawn to a stretch ratio equal to 9, the concentration of the defects is equal to $\sim 10^{-3}$ mol/kg. The assumption that the complexone is equally distributed in the polymer permits us to obtain up to 10 molecules of pentadione-2,4 in one defect at a concentration of 10^{-2} mol/kg. Since the number of centers of initiation depends only slightly on the concentration of the complexone (Tab. II), one can assume that this concentration is sufficient for deactivation. Thus, apparently, the number of active sites on the catalyst particles does not exceed three [16]. Because of the nonequal distribution of the complexone, some centers are not blocked by it.

The number of kinetic chains depends on the concentration of the catalyst particles, their catalytic activity and the molecular structure of the polymer. The rate of propagation of the free-radical process from the nucleation sites into the polymer bulk depends on the morphology of the sample and on the molecular dynamics of the polymer matrix.

It can be seen from Table II that macrokinetic parameters of polymer oxidation: the induction period τ_{ind}, the duration of acceleration t_{ac} and the maximum oxidation rate W_{max} depend on concentration of initiation centers. Decrease of induction period observed in the presence of complexone at low inhibitor concentration and considerably reduced value of τ_{ind} in comparison with durability τ_{dur} of all samples may be explained by strong plasticizing action of the complexone PDO, especially because the oxidation has been studied in non-isomeric conditions and was followed by shrinking. According to [7] the induction period may be considered as the time the reaction is restricted to the zones containing the particles of initiator. Induction period is over when the reaction spreads into the polymer volume and its rate becomes high enough to be registered by manometric methods. In [18] the oxygen consumption was measured by high-sensitive device. It is obvious from these data that during induction period the oxidation proceeds in the few nucleation sites around the particles of catalyst [7]. In presence of PDO plasticizer the level of localization of oxidation in the nucleation sites is considerably reduced as a result of changes in microstructure of the amorphous zones and, therefore, τ_{ind} decreases. This effect gets stronger during oxidation of oriented films in non-isometric conditions because of internal tensions relaxation.

Despite these uncertainties it is possible to note that in the case of a relatively effective inhibition of the reaction (i.e. when the concentration of Irganox is equal to 2×10^{-3} mol/kg) a decrease in the number of initiation centers is accompanied by an increase in the induction time of oxidation of PP τ_{ind} and by an increase of the duration of acceleration t_{ac} until a steady rate of oxidation W_{max} is attained. Thus, the decrease of PP thermooxidation rate in the presence of complexone is not due to a decrease in the rate of initiation, but to a decrease in the number of initiation centers from which the oxidation process propagates into the entire volume of the polymer. The change in macrokinetic parameters of the polymer oxidation is related to the volume effect: a decrease in the concentration of the catalytic centers in the unit volume of PP.

The greater is the distance between the sources of free radicals, the smaller is the average propagation rate of the reaction front in the polymer matrix and the longer is the duration of oxidation before the steady rate W_{max} is attained. Apparently, the kinetic parameters should be compared in samples with similar structural parameters and the same amount of inhibitor.

If the number of nucleation sites is not taken into account when calculating W_i^{nuc}, the calculations show a decrease in the initiation rate in the presence of complexone. Thus, the initiation rate determined assuming the concentration of the initiating centers is not taken into account represents an "effective" value.

Thus the kinetic regularities of PP oxidation depend not only on the initiation rate related to the initiator nature [1, 17, 19–21], but also on the initiation centers concentration.

Predicting the durability of stressed polymer materials in an oxidative medium is possible only when these factors are taken into account.

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