

Crosslinking in Polyethylene Films by Oxidation on Metals

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ABSTRACT: The kinetics of oxidative conversions, such as accumulation of carbonyl groups and crosslinks in polyethylene films that were subjected to oxidation on metallic substrates differing in activity (e.g., copper and aluminum), was investigated. It was learned that the rate and ultimate level of crosslinking in the polymer oxidized on copper were higher than those on aluminum. It is believed that this situation is related to the catalytic effect of the copper compounds transferred into the polymer volume at the regimes of contact oxidation. The amounts of transferred metal were approximately equal in both the soluble and the insoluble fractions of the polymer. © 2002 Wiley Periodicals, Inc. *J Appl Polym Sci* 84: 2776–2783, 2002

Key words: polyethylene film; crosslinking; catalytic effect; oxidation

INTRODUCTION

Complex physical and chemical transformations take place when polyethylene (PE) is oxidized in contact with metals.¹ These processes involve not only the polymer but the metallic substrate as well. The rate at which carbonyl groups accumulate in PE depends on the nature of the substrate on which oxidation is performed.^{2,3} In connection with this, metals were selected that are either active or inactive to oxidation of the polymer.¹

Oxidation of PE on active metals is accompanied by transfer of metal-containing compounds (product of contact reactions) into the bulk of the polymer.^{1–4} It was revealed that transferred compounds of metals cause a catalytic effect on the formation of carbonyl groups. That is why it was suggested to regard the catalysis of PE oxidation on active substrates as a homogeneous process, which is brought about by metal-containing compounds transferred into the bulk of the polymer. When PE is oxidized on inactive substrates (e.g.,

aluminum), no metal is transferred into the polymer film and the substrate does not cause any catalytic effect.^{1,5}

The above-mentioned studies treat oxidation of PE from the standpoint of accumulation of carbonyl groups therein. However, some other oxidative transformations occur in the polymer, such as oxidative crosslinking of macromolecules. Chemical crosslinking of PE during oxidation has long been addressed by some investigators as a means of controlling physical, mechanical, adhesional, and protective properties of polymers.⁶ In an earlier work devoted to oxidative crosslinking,⁷ it was reported that the strength and hardness of polymers increased along with adhesional bonding to steel, whereas the vapor permeability decreased after the linear polymer had changed to a three-dimensional product. The same authors had learned that the oxidative crosslinking of PE proceeds nonuniformly through the specimen thickness, that is, the polymer would undergo oxidative crosslinking at a higher rate in the outer surface layer than that in its deeper layers. Other researchers⁸ also investigated the development of the process of oxidative crosslinking through the specimen thickness. They stated that

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a deep reaction of crosslinking proceeded in the layer in which the thickness was less than 100 μm ; low molecular weight products of oxidation could transfer from the outer surface into the deeper layers of the oxidized polymer. In another work,¹⁰ the thickness of the crosslinked layer in PE samples was defined more exactly; it was also noted that this layer thickness decreased with increasing the temperature.

However, the studies conducted up to now on oxidative crosslinking of PE cannot be recognized as systematic because no comparison data on PE crosslinked on active and inactive substrates are available as yet; no influence of the polymer layer thickness on formation of crosslinked structure in the polymer was reported; the problem of distribution of the transferred metal-containing compounds between the gel fraction and sol fraction of a sample remains unsolved. In this connection, the present study was undertaken with copper as an active substrate and aluminum as an inactive substrate. The interest in copper stems from the fact that copper-containing compounds transferred into the polymer during contact oxidation exhibit a dual nature. At low concentrations, they catalyze the oxidation process, whereas at high concentrations they suppress the oxidation process, that is, they act as inhibitors.

EXPERIMENTAL

Materials and Specimens

The following materials were used to carry out the experiments. Powdered unstabilized low-density polyethylene (PE), prepared with complex organometallic catalyst [PE Grade 21006-075, GOST 16338-85, Russia; density 0.950–0.959 g/cm^3 ; melt flow index (MFI) 7.5 $\text{g}/10$ min], was compressed between the plates of the laboratory press to obtain films of required thicknesses. The molding temperature was 150°C; the residence time was between 30 and 300 s. The molded films were used as coatings. Copper foil (GOST 5638-51, Russia) and aluminum foil (GOST 618-62, Russia) were used as substrates for coatings. Test specimens were prepared as follows. A polymer film/metallic foil system was placed in an oven to oxidize at a temperature above the melting point of PE (150–180°C). Then the system was removed from the oven and cooled to room temperature, after which the film was separated from the foil and examined. To investigate the distribution of

the products of oxidation through the film thickness, cuts were made in parallel to the outer surface and examined. The cuts, 20 to 50 μm thick, were microtomed using the TESLA BS 490A instrument (Czech Republic). *O*-Xylene (Grade pure for analysis, TU-6-09-3325-88, Russia) served as organic solvent for PE when the amount of insoluble fraction was determined.

Analysis

Our purpose was to determine the degree to which PE films oxidize and crosslink when oxidized on metals, and also the amount of metal transferred into these films from the substrate.

The degree of oxidative crosslinking of macromolecules was evaluated from the gel fraction (both weight and percentage) of PE. To do this, film samples were boiled in *O*-xylene for 2 h. The undissolved portion (gel fraction) of the film was removed from the solution and weighed.

To estimate the oxidation degree of the polymer, IR spectra of the film were recorded using a Specord-75IR instrument (Zeiss, Jena, Germany). The optical density of the absorption band at 1720 cm^{-1} in the spectra, related to carbonyl-containing compounds, was the measure of the degree of oxidation.¹¹ Additionally, the extinction rate (cm^{-1}), that is, the ratio of optical density to sample thickness (in cm), was used.

The quantity of copper transferred into the polymer was determined by the polarography method.¹² To prepare a solution for this analysis, a sol residue of the polymer was first prepared. The separated polymer film was weighed, put in a porcelain crucible, and heated in the muffle furnace (IP20, Russia). The heat treatment was conducted in two steps. Conditions of the first step were 350°C for 40 min, and those of the second step were 350°C for 120 min.¹³ The formed ash was cooled to room temperature, dissolved in 0.1M HCl (HCl, TU 2642-001-07500602-97; St. Petersburg, Russia), and subjected to polarography analysis on a PU1 instrument (Gomel, Belarus) using the dropping mercury electrode. The metal content in the sample was estimated using calibration curves. Besides the coating films, experiments were run with gel fractions extracted from the films. The metal content in these gel fractions was also estimated. The content of the metal in the soluble part of the sample was determined as the difference in content of the metal contained in the whole sample and that in its undissolved portion.

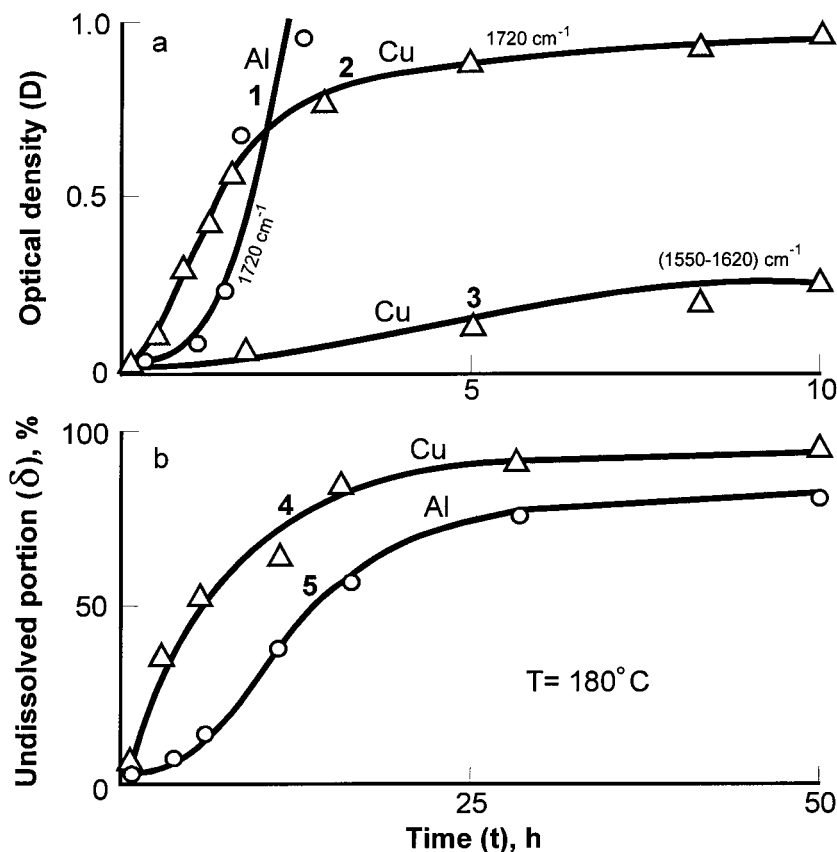


Figure 1 Optical density of absorption bands at 1720 cm^{-1} (1 and 2) and $1550\text{--}1620\text{ cm}^{-1}$ (3); percentage of undissolved fraction (4 and 5) in PE films $100\text{ }\mu\text{m}$ thick against length of oxidation at 180°C on copper (2, 3, and 4) and aluminum (1 and 5) backings.

RESULTS AND DISCUSSION

Accumulation of Gel Fraction During Oxidation of PE Films

The data on accumulation of carbonyl groups and gel fraction in PE films of thickness $100\text{ }\mu\text{m}$ oxidized on copper and aluminum backings are shown in Figure 1. Some investigators reported the kinetic conditions of oxidation for films below $120\text{ }\mu\text{m}$,¹⁴ that is, the process variables are independent of the diffusion factors. On the initial stage of oxidation, in our experiments, the polymer films oxidized at a higher rate on copper than that on aluminum (Fig. 1, curves 1 and 2). Further oxidation of PE in contact with copper reduced the accumulation rate of carbonyl groups to negligibly low values. This development of oxidative conversions is explained by transferred and accumulated copper-containing compounds in the polymer bulk, the critical concentration of which results in autoinhibition, that is, oxidation be-

comes suppressed.¹⁻⁴ Transfer of copper compounds is corroborated by variations in the optical density of the absorption band at $1550\text{--}1620\text{ cm}^{-1}$ (this band refers to metal-containing compounds like salts) in the IR spectra of PE (Fig. 1, curve 3), and also by polarography findings on metal concentration in the films (Fig. 2, curve 1).

We next consider polymer crosslinking by oxidation. The first traces of undissolved fraction in the polymer film were detected as early as the induction period of oxidation had ended; on the initial stage of oxidation, the rate of crosslinking in PE films on copper was much higher than that in PE films on aluminum (Fig. 1, curves 4 and 5). For PE films on copper, the ultimate level of undissolved fraction reached by thermal treatment was also higher. It is likely that these differences in crosslinked structures (higher rates and ultimate levels of crosslinking) in PE films on copper result from the catalytic effect of copper com-

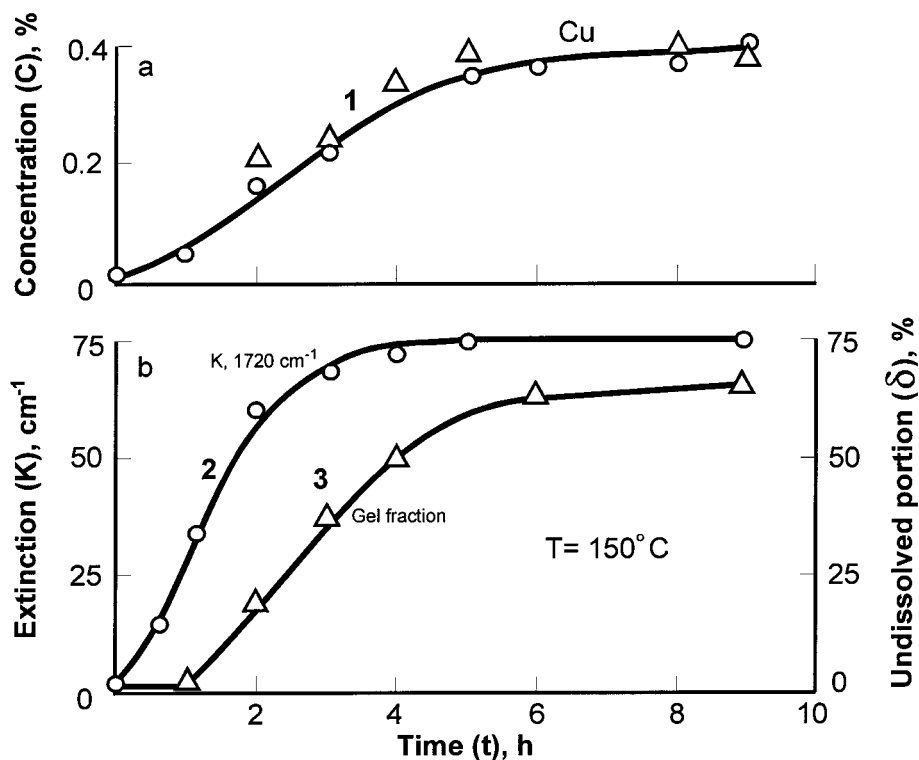


Figure 2 Concentration of metal (curve 1, \circ), rate of extinction for absorption band at 1720 cm^{-1} , and percentage of gel fraction (3) in PE films $100\text{ }\mu\text{m}$ thick against length of oxidation at 150°C on copper backings. Curve 1, \triangle shows concentration of metal in gel fraction.

pounds (transferred into polymer bulk) on the crosslinking process.

The kinetic relationship of copper accumulated in the film is a curve with saturation, although the amount of the metal is not constant. Prolonged thermal treatment makes the metal move slowly into the film (Fig. 2, curve 1). The relationships between carbonyl groups and crosslinks accumulated in the film yield similarly shaped plots (Fig. 2, curves 2 and 3). The similarity in the plots of Figure 2 confirms that copper transfer and accumulation of products of oxidation (i.e., carbonyl groups and gel fraction) are mutually related. It was learned that the metal concentration in the gel fraction isolated from the polymer differs only slightly from the total concentration of metal in the specimen (Fig. 2, curve 1). It can be inferred that the transferred metal is uniformly distributed between the gel and sol fractions.

A further step in our investigations was to assess the effect of polymer film thickness on generation of crosslinks by oxidation.

Figure 3 shows data on the accumulation of gel fraction in relatively thin films ($100\text{ }\mu\text{m}$), films of

intermediate thickness ($400\text{ }\mu\text{m}$), and thick ($800\text{ }\mu\text{m}$) films. In this case the crosslinked product was determined as the ratio of gel-fraction weight to unit area of the sample, that is, $\mathfrak{S} = \Delta m/S$, where Δm is the weight of the gel fraction in the sample and S is the area of the sample.

The kinetic dependencies of the accumulated insoluble fraction in the films become stable on a constant level (Fig. 3, curves 1, 3, 4, and 6). The thicker the film, the more time is required to reach stable values and the higher the amount of the crosslinked product. For $800\text{ }\mu\text{m}$ films, the time lengths chosen were inadequate for reaching this level (Fig. 3, curves 2 and 5). The experimental results indicate that some restrictions arise (in generation of crosslinks in PE) related to oxygen conveyed into the film volume.

It was observed that the yield of gel fraction in the course of oxidation depends considerably on the film thickness (Fig. 3). The plot of \mathfrak{S} against thickness passes through the maximum (the time length of oxidation of the polymer was constant). The maximum corresponds to critical thickness l_{cr} , at which a maximum quantity of crosslinked

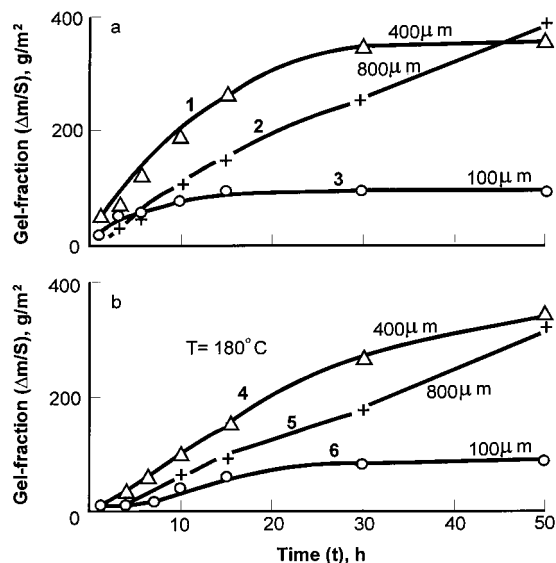


Figure 3 Weight of gel fraction from films of varying thickness (in μm): 100 (3 and 6), 400 (1 and 4), and 800 (2 and 5) against length of oxidation at 180°C on copper (1, 2, and 3) and aluminum (4, 5, and 6) backings.

product is formed in the sample. We explain this extreme dependency of \mathfrak{S} on sample thickness as follows. The values of \mathfrak{S} increase with increasing film thickness up to l_{cr} attributed to higher amounts of oxygen entering the polymer. However, the diffusive permeability of coatings cannot be unlimited. Therefore, beginning from thickness l_{cr} , the amount of oxygen penetrating into the sample becomes constant. It is interesting that with films whose thickness is above l_{cr} , the value of \mathfrak{S} does not stabilize on a constant level, but decreases instead. We believe this to be connected with the fact that oxygen is distributed in the polymer volume; hence, partial pressure of the oxygen drops. As a result, the crosslinking degree of the polymer declines in local areas of the sample, thus leading to a reduced total yield of gel fraction.

Comparing the data on accumulation of gel fraction in films of different thicknesses, the effect of catalytic activity of the substrate on the process of oxidative crosslinking of PE can be observed. We took the relative activity index of the copper substrate (δ/δ_0), that is, the ratio of weight (or percentage) content of the gel fraction in the PE film oxidized on a copper substrate to the same parameter of the film oxidized on an aluminum substrate. The higher the relative activity index, the stronger the effect of substrate on the crosslinking degree of the polymer during oxida-

tion. The data on variations in δ/δ_0 values against time lengths of oxidation (same film thickness) and against film thickness (same time length of oxidation) are shown in Figure 4. The catalytic effect of substrate on PE crosslinking is most strongly shown in the early stage of oxidation of thin films (Fig. 4, curve 1). In this case, metal-containing compounds are rapidly accumulated and catalyze the oxidative conversions in the polymer. No diffusion limitations caused by ingress of oxygen are shown. The extrapolation of $\delta/\delta_0(t)$ to $\delta/\delta_0 = 1$ level (crosslinking degree of PE is the same on copper and aluminum substrates) indicates the film thickness ($950 \mu\text{m}$) above which the substrate does not cause any catalytic effect on crosslinking during oxidation (Fig. 4, curve 3). This can be explained by the limited amount of oxygen that can enter the contact zone because the film is rather thick.

Distribution of Gel Fraction Through Film Thickness

The data on accumulation of carbonyl groups and insoluble fraction in the outer surface layer and the interface (adjoining the substrate) obtained for PE films of intermediate thickness ($400 \mu\text{m}$) are shown in Figure 5. Polymer layers of $50 \mu\text{m}$ thick were analyzed in our studies.

In coatings on aluminum, carbonyl groups first accumulate almost uniformly through the whole volume (initial sections of curves 2 and 4 in Fig. 5). As time goes on, diffusion limitations begin to show in deep-seated layers of the specimens and oxidation takes place mainly in the outer surface

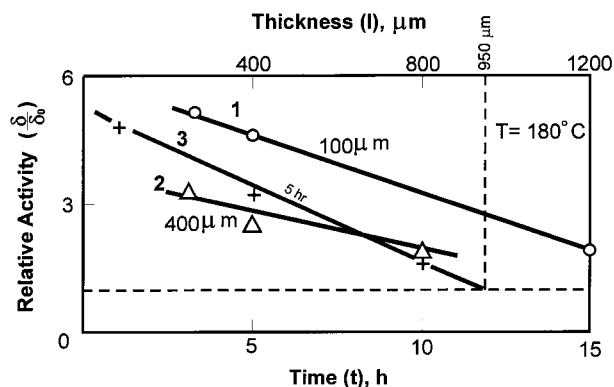


Figure 4 Relative activity of copper backing against length of oxidation of PE films: $100 \mu\text{m}$ thick (1) and $400 \mu\text{m}$ thick (2) and thickness of coating film oxidized for 5 h (3).

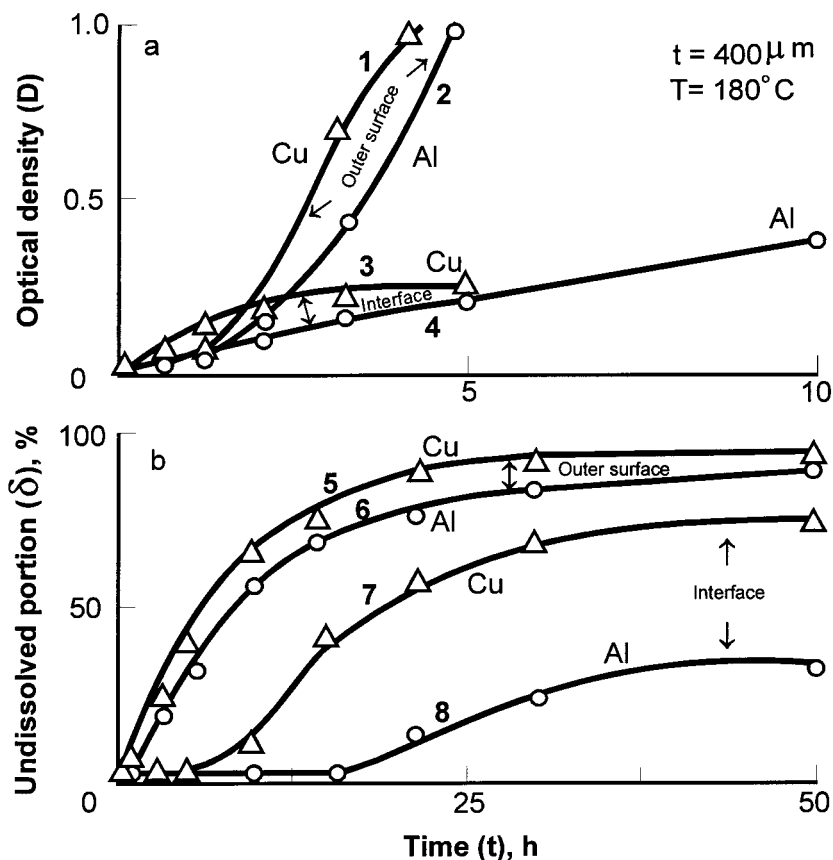


Figure 5 Optical density of absorption band at 1720 cm^{-1} (1, 2, 3, and 4), insoluble fraction (5, 6, 7, and 8) in the outer surface (1, 2, 5, and 6), and interface layers (3, 4, 7, and 8) of PE films $400 \mu\text{m}$ thick against length of oxidation at 180°C on copper (1, 3, 5, and 7) and aluminum (2, 4, 6, and 8) backings.

layer. Later on, PE oxidizes more rapidly in the outer surface layer than in the layer adjoining the substrate. The kinetic plot of accumulation of carbonyl groups in thin films oxidized on aluminum resembles that for the outer surface layer of thicker films (Fig. 1, curve 1; Fig. 5, curve 2).

The metal-containing compounds transferred into PE films, which are oxidized on copper substrates, change the kinetics of accumulation of

carbonyl groups in the outer surface and interface layers of PE. First of all, carbonyl groups are detected in the polymer layer bordering on the substrate into which metal transfers from the very beginning of oxidation (Table I).

The shape of the kinetic curve describing the accumulation of carbonyl groups in the polymer layer bordering on the substrate (Fig. 5, curve 3) follows the shape of the respective curve for thin

Table I Concentration (%) of Copper in the Outer Surface and Interface Layers of PE Films Against Length of Their Oxidation at 150°C on Copper Backing^a

Layer	Length of Oxidation (h)								
	0	1	2	3	4	5	7	9	
Outer surface layer	0.000	0.000	0.015	0.015	0.025	0.02	0.04	0.05	
Interface layer	0.000	0.017	0.085	—	0.09	0.38	0.5	0.84	

^a Film thickness was $300 \mu\text{m}$.

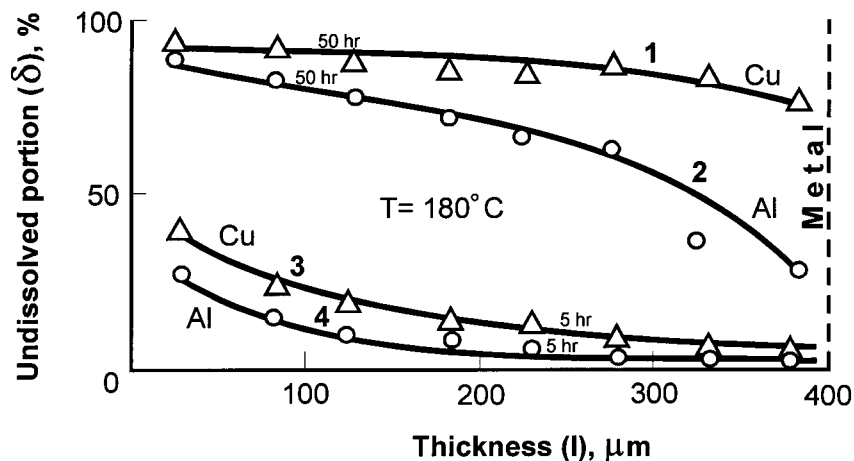


Figure 6 Distribution (%) of insoluble fraction through thickness of PE films on copper (1 and 3) and aluminum (2 and 4) after they were oxidized at 180°C for 5 h (3 and 4) and 50 h (1 and 2).

films on copper (Fig. 1, curve 2). This resemblance in the curves can be explained by the fact that copper compounds transferred into the polymer volume influence polymer oxidation. The transferred copper-containing products also influence the oxidation of the outer surface layer. The rate at which polymer oxidizes in this part of the specimen is at first lower than that in the interface layer, although it rapidly increases with time. As a result, the oxidation process becomes bound to the outer surface layer because there are no diffusion limitations, that is, feed of oxygen and discharge of gaseous products of oxidation. The polarography findings confirm that small quantities of copper-containing compounds reach the outer surface layer of the specimen. It is the low concentrations of copper compounds that catalyze polymer oxidation.^{1,5}

The data on PE structuralized by oxidation appear less sensitive toward conditions of oxidation in the early period of film-on-copper oxidation. The first traces of the insoluble fraction were detected in the outer surface layer of the film, and not in the interface layer. At the same time, PE crosslinks on copper more quickly than it does on aluminum (Fig. 5, curves 6 and 8). Films oxidized on copper contained higher ultimate amounts of insoluble fraction (90% on copper against 85–87% on aluminum). In the interface layer, the polymer begins to crosslink later (Fig. 5, curves 7 and 8), with a distinctive induction period (5 h for the film on copper; 15 h for the film on aluminum). The ultimate levels of insoluble fraction achieved in this layer differ significantly: in coatings on copper it is about 75%; on aluminum, only 30%.

The distribution of the insoluble fraction through the coating film thickness is shown in Figure 6. The difference in the amounts of insoluble fraction for films oxidized on copper and aluminum can either decrease (Fig. 6, curves 3 and 4, short length of oxidation) or increase (Fig. 6, curves 1 and 2, long length of oxidation), when moving from the outer surface layer to the interface layer.

The low degree of crosslinking during oxidation in deep-seated layers of the film on aluminum can be explained by the protective action of the outer surface layer, which it acquired as the result of deep oxidation and macromolecular crosslinking.¹ Besides, the ingress of oxygen into the films is limited because of its consumption during reactions of oxidation and crosslinking in the outer surface layer. These two actions (protective action of the outer surface layer and absorption of oxygen that enters the coating) cause PE oxidation in deep-seated layers of the films on aluminum to discontinue with time. Oxidation there can be renewed (e.g., by ingress of oxygen) only after the deeply oxidized outer surface layer is removed.

Crosslinking in films oxidized on copper proceeds in a different manner. Prolonged oxidation makes deep-seated layers of the polymer crosslink rather deeply (Fig. 6, curve 1). This can be explained as follows. The outer surface layer of films on copper acquires the condition of autoinhibition (suppression of oxidation) as a result of the critical amounts of copper-containing compounds accumulated therein. The oxygen absorption by the layer decreases and the gas can penetrate the film volume. As a result, oxidation con-

versions continue in deep-seated layers of the polymer, among them crosslinking.

CONCLUSIONS

Comparative studies were conducted to understand crosslinking of PE films oxidized on copper and aluminum. The copper substrate exerts a catalytic effect on this process. This finding is confirmed by the high rate of crosslinking and amounts of crosslinks in PE. This situation results from the catalytic effect of copper-containing compounds that are transferred into the polymer volume during its oxidation on copper.

REFERENCES

1. Lin, D. G. Ph.D. Thesis, Gomel, Belarus, 1993.
2. Egorenkov, N. I.; Lin, D. G.; Bely, V. A. *USSR Acad Sci (Doklady AN SSSR)* 1972, 207, 397.
3. Egorenkov, N. I.; Lin, D. G.; Bely, V. A. *USSR Acad Sci (Doklady AN SSSR)* 1974, 214, 1376.
4. Lin, D. G. *J Appl Polym Sci* 1994, 54, 1789.
5. Egorenkov, N. I.; Lin, D. G.; Bely, V. A. *J Polym Sci Polym Chem Ed* 1975, 13, 1493.
6. Sirota, A. G. *Modification of Structure and Properties of Polyolefins*; Khimia: Moscow, 1974.
7. Grinberg, A. Ya.; Demchenko, N. S. *Russ J Appl Chem XXV* 1952, 1, 57.
8. Bal'tenene, Ya. Yu.; Bal'tenas, R. A. *Polymeric Materials and Their Investigation: Collected Papers*, Kaunas 1971, 12, 11.
9. Lozenene, B. I.; Bal'tenas, R. A.; Bal'tenene, Ya. Yu. *Polymeric Materials and Their Investigation: Collected Papers*, Kaunas 1971, 12, 17.
10. Bal'tenas, R. A.; Bal'tenene, Ya. Yu.; Stinskas, A. B.; Kevyalaitis, Z. K. *Modification of Structure and Properties of Polymerizable Plastics; Collected Papers*, Leningrad, 1984; p 88.
11. Stolyarov, B. V. *Russ J Appl Chem* 1961, 34, 2726.
12. Sviridenko, V. G.; Lin, D. G.; Eliseeva, I. M. *Russ J Anal Chem* 1987, 8, 1525.
13. Lin, D. G.; Sviridenko, V. G.; Evmenov, V. V.; Egorenkov, N. I. *Russ Bull Invent* 1986, 15.
14. Iring, M.; Hedvig-Lastbo, Zs.; Kelen, T.; Tiidos, P. in *Thermal Analyses, Proceedings of the Fourth International Conference on Thermal Analysis*, Budapest, 1974; Vol. 2, pp 127-135.
15. Lin, D. G.; Kapshai, M. N.; Kachamin, A. N.; Egorenkov, N. I. *Russ J Appl Chem* 1983, 8, 1836.