

Solid-Phase Oxidation of Polyethylene Coatings on Metals

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SYNOPSIS

The paper considers the problem of solid-phase oxidation for cases of polyethylene coatings applied onto active (copper) and passive (aluminum) substrates. Oxidation of PE coatings on copper, unlike that of PE coatings on aluminum, is shown to develop in two stages separated by a time period of autoinhibition. During this time period the concentration of carboxyl groups does not in fact change. In a similar manner copper-containing compounds accumulate in the coating, which fact supports the relation between metal transfer and polymer oxidation processes. © 1994 John Wiley & Sons, Inc.

INTRODUCTION

The thermo-oxidation rate of polymers is known to depend on the kinetic parameters of the reaction and the process of oxygen transfer by diffusion, as well as on the low-molecular weight products of thermo-oxidative degradation.¹ Several researchers considered the variation in specimen thickness to find a critical value below which oxidative process no longer depend on the diffusion factors. For polyethylene (PE) film, the following thicknesses were found to be critical: 20 μm ,² 50 μm ,³ 100 μm ,⁴ and 125 μm .⁵ Iring et al.³ have pointed out, however, that critical thicknesses decreased with increasing degrees of oxidative conversion. The oxidative process, proceeding uniformly across the bulk specimen at the initial stage, was observed to be forced to the surface layer, i.e., the kinetic oxidative regime changed to the diffusive one.

A number of authors, who researched diffusion-restricted polymer oxidation in the solid phase, have presented data on the distribution of oxidation products (carbonyl⁶ and hydroxide⁷ groups, gel-fraction⁸) across the specimen's thickness. The highest content of the products has been detected in the surface layer, whereas their distribution throughout the specimen was of an exponential mode. The thickness of the specimen layer in which oxidation products were detected appeared to be dependent on the testing conditions, growing with the duration of oxidation.

The works referred to above had considered oxidation of free (i.e., self-supported) films. Solid-phase oxidation of PE in contact with metals (e.g., polymeric coatings on metal substrates) has been inadequately understood. Most of the data on PE contact oxidation found in literature refer to oxidation in the molten state. It had been revealed⁹⁻¹¹ that oxidation of molten PE in contact with catalytically active metals (e.g., copper, iron, zinc, etc.) was followed by metal transfer into the polymer, leading to homogeneous oxidation of the polymer by the metal. The catalytical action of the substrate makes corrections in the development of the oxidation process—localization of oxidation in the coatings' surface layer was observed to occur after accelerated oxidation had taken place in the layer bordering on the substrate.¹² It was of interest to see whether such regularities are typical of contact oxidation in the case of solid-phase PE coatings.

EXPERIMENTAL

Unstabilized high-density PE powder was used in the experiments. Metallic substrates were coated by the hot-forming process. Copper foil (active) and aluminum foil (passive) were the substrates.¹³ The applied coatings were oxidized in air at 100°C. The coating oxidation degree was assessed as a whole and also in the coat's layers at different distances from the surface. To do this, cuts for analysis were made parallel to the coat surface. The PE oxidation level was characterized by the optical density of the

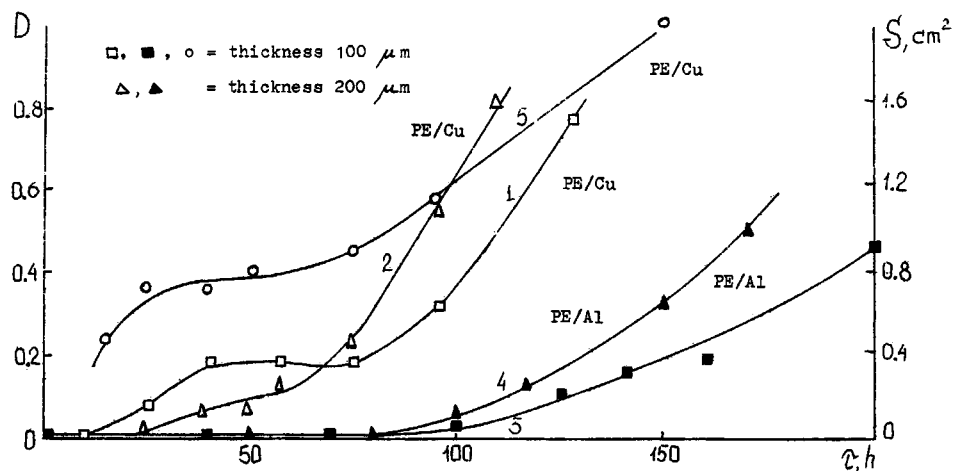


Figure 1 Optical density of absorption band 1720 cm^{-1} (1–4) and area of band $1550\text{--}1700\text{ cm}^{-1}$ (5) in IR-spectra obtained for PE coatings of thicknesses: $100\text{ }\mu\text{m}$ (1, 3 and 5) and $200\text{ }\mu\text{m}$ (2 and 4) versus oxidation duration on copper (1, 2 and 5) and aluminum (3 and 4).

band at 1720 cm^{-1} in the IR-spectra of PE, and also by the extinction index of this band. The absorption band at 1460 cm^{-1} was used as internal standard to calculate the optical density.

RESULTS AND DISCUSSION

The results obtained on oxidation of PE coatings of different thicknesses are presented in Figure 1. Oxidation of coatings on copper (thickness $100\text{ }\mu\text{m}$), unlike that of coatings on aluminum, proceeds in two stages; between them is a stage of autoinhibition,

i.e., the period during which carbonyl groups concentration does not change in the coating (Fig. 1, curves 1 and 3). In thicker coatings ($200\text{ }\mu\text{m}$) the two-stage feature is not very distinctive; nevertheless, it exists (Fig. 1, curve 2).

Figure 2 represents data on the accumulation of carbonyl groups in the PE coat surface layer and in that adjacent to the copper substrate (coating thickness, $300\text{ }\mu\text{m}$; the analyzed layer thickness, $50\text{ }\mu\text{m}$). The oxidation process is first registered in the layer adjacent to the substrate; here it also develops in two stages divided in time by an interval of oxidation stabilization (Fig. 2, curve 1). It can be seen

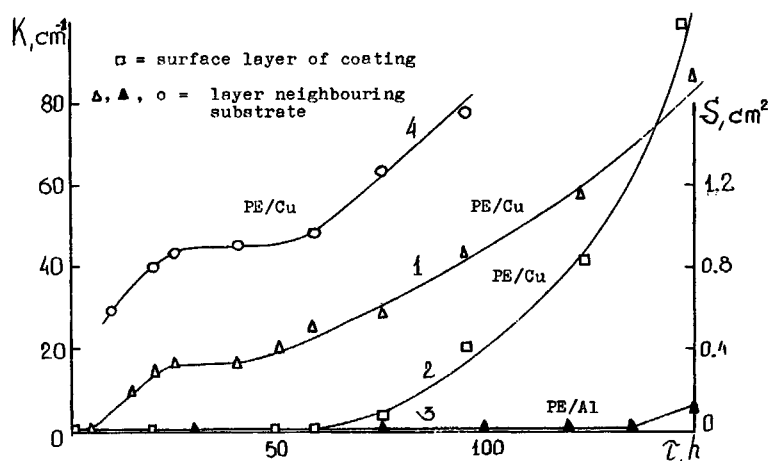


Figure 2 Extinction index for absorption band 1720 cm^{-1} (1–3) and area of band $1550\text{--}1700\text{ cm}^{-1}$ (4) in IR-spectra of surface layer (2) and that neighbouring to substrate (1, 3 and 4) for PE coatings versus oxidation duration: (1, 2 and 4) on copper; (3) on aluminum.

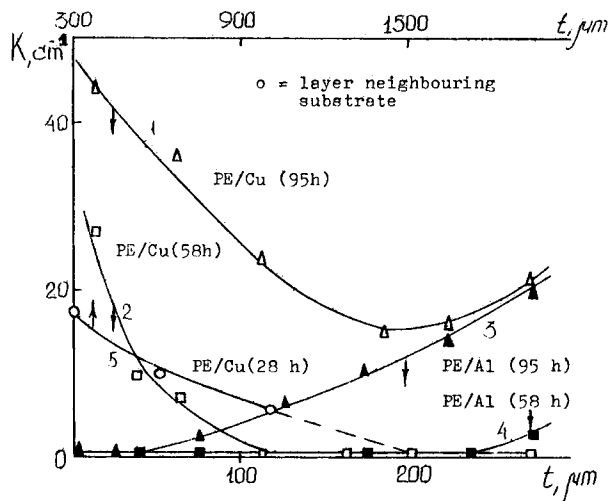


Figure 3 Distribution of carbonyl groups throughout PE coat thickness on copper (1 and 2) and aluminum (3 and 4) oxidized at 100°C during 58 h (2 and 4) and 95 h (1 and 3). Thickness was measured from the substrate. Curve 5 illustrates dependence of extinction index for 1720 cm^{-1} absorption band in IR-spectra of PE coat layer bordering on copper substrate vs. coat thickness. Oxidation lasted 28 h.

that the first oxidation stage for PE coatings on copper is related to the catalytical effect of the substrate. Oxidation of the PE coating's surface layer has an autocatalytical character (Fig. 2, curve 2). As a result, with time, the carbonyl group concentration becomes higher in the surface layer of the coating than in the boundary layer. In the case of coatings on aluminum, oxidation of the PE layer adjacent to the substrate begins much later (Fig. 2, curve 3) than oxidation of the coating as a whole (Fig. 1, curves 3 and 4). This supports the fact that aluminum substrate is inactive to oxidation.

The oxidation rate for PE in the layer neighboring the copper substrate was observed to decrease as the coat thickness increased, which was probably related to the diffusive limitations of oxygen supplied to the reaction zone. The predicted coating thickness, above which no catalytical effect of the substrate was observed, makes ca. 1500–1600 μm (Fig. 3, curve 5). It is conceived that the ultimate thickness of coatings whose oxidation follows the diffusion mechanism is found within these limits.

Figure 3 also represents data on the distribution of carbonyl groups across PE coat depth (thickness

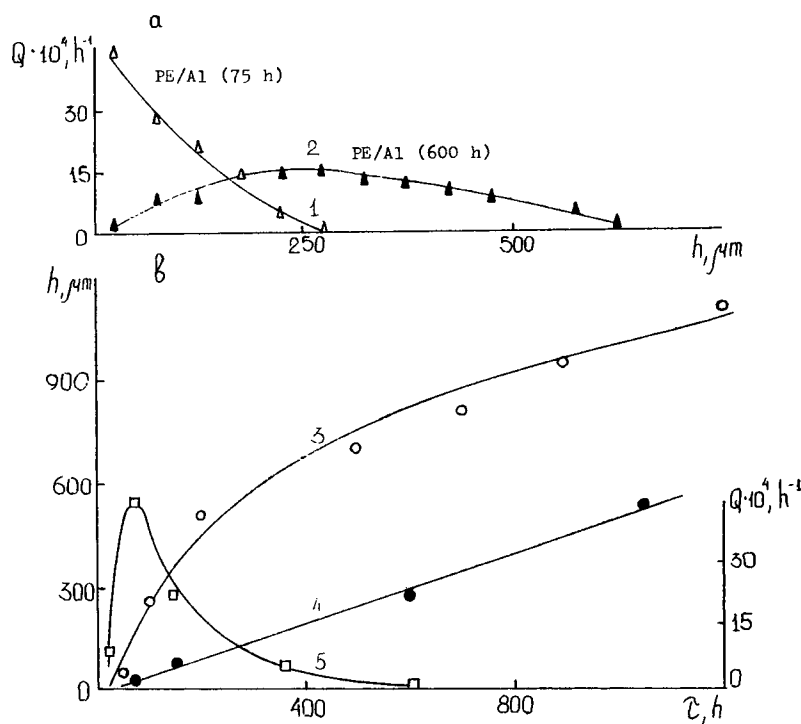


Figure 4 (a) Carbonyl groups accumulation rate vs. coating thickness oxidized on aluminum during 75 h (1) and 600 h (2); (b) Time dependence of polymer layer thickness (3) in which carbonyl groups were detected, surface layer oxidation rate (5) and depth of the layer (4) in which highest oxidation rate was measured.

of 300 μm); the coatings were oxidized on different substrates. In the case of coatings on copper, the oxidation process was localized in the region neighboring the substrate (Fig. 3, curve 2), while the surface layer remained actually unoxidized. Further thermal treatment of coatings on copper was observed to lead to oxidation developing throughout the whole bulk specimen, whereas the surface layer's oxidation rate became the highest. As a result, the middle section of the coating appeared less oxidized (Fig. 3, curve 1). Under the same conditions, the carbonyl group concentration in the coating on aluminum discussed above was gradually becoming lower with the approaching substrate (Fig. 3, curves 3 and 4), i.e., the oxidation process was localized only in the surface layer.

It should be noted that the oxidation rate of the coating's surface layer being determined by the expression $Q = dD/dt$ varies in the course of trials; its dependence on time can be described by a curve with a maximum (Fig. 4, curve 5). However, this is

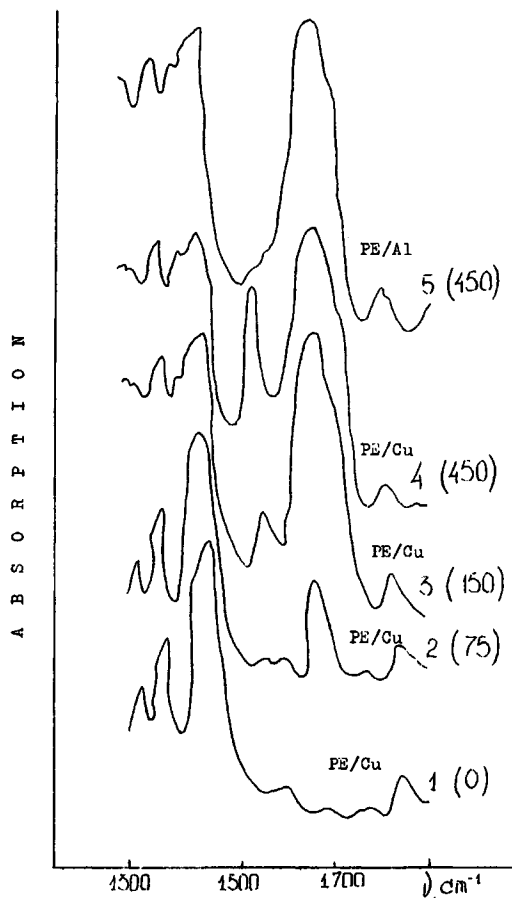


Figure 5 IR spectra of PE coatings oxidized on copper (1-4) and aluminum (5). Numbers in parentheses indicate PE duration in hours.

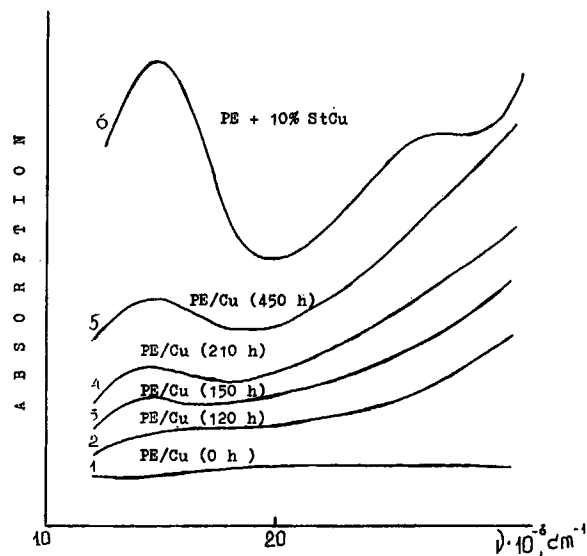


Figure 6 Visible-light spectra of PE coatings oxidized on copper during 0 h (1), 120 h (2), 150 h (3), 210 h (4) and 450 h (5). (6) PE containing 10% of copper stearate.

not indicative of oxidation suppression if tests last for longer periods. Figure 4, curves 1 and 2, represent data on variations in the oxidation rate for the polymer depending on the depth of the layer analyzed; the intensive oxidation region can be seen to shift into the coating bulk with time. Simultaneously, the maximum values of oxidation were noticed to have decreased. The polymer layers containing carbonyl groups appear much thicker than the depth at which they are found, which oxidation rate is the highest at a given moment (Fig. 4, curves 3 and 4). (The data in Fig. 4 were obtained for 2000- μm -thick coatings oxidized on aluminum substrate.)

Solid-phase oxidation of PE in contact with copper was accompanied by metal transfer into the polymer bulk. In IR-spectra of the coatings oxidized on copper substrates there appeared and grew an absorption band at 1550-1700 cm^{-1} typical of metal-containing compounds (carboxylates), i.e., products of contact reactions between the substrate and low molecular weight carboxylic acids formed by polymer oxidation (Fig. 5). The polarographic analysis gave the ultimate copper content in the coatings in question, somewhat above 10⁻¹%. The coatings that were oxidized on copper substrates during a long period acquired a greenish color. These data were supported by absorption spectra recorded in the visible light region (Fig. 6, spectra 1 through 5). The PE films doped with copper stearate had the same colour (Fig. 6, spectrum 6). Transfer of copper into PE bulk was first discovered when studying contact oxidation of

Table I Dependence of Area S (cm²) of Absorption Band 1720 cm⁻¹ in IR-Spectra of PE Coatings on Copper and Aluminum Substrates on Period of Oxidation T (h)

Substrate	Time T, h	30	90	120	210	300	450	600	750
Copper		1.2	2.6	4.2	7.0	6.6	6.5	6.5	6.5
Aluminum		0	0	1.6	5.2	9.8	10.8	11.0	11.6

molten polymers;⁹ later, Japanese investigators¹⁴ supported the existence of a similar phenomenon for solid-phase oxidation of PE on copper.

Two stages of metal accumulation, divided by a time period during which the concentration of metal in the layer does not actually change, can be seen from the kinetic relationships illustrating the accumulation of metal-containing compounds in the coating layers neighboring the substrate (similar to thin coatings on copper) (Fig. 2, curve 4). As mentioned above, the same appearance is typical of kinetic relationships describing accumulation of carbonyl groups; this is indicative of a relation existing between metal transfer and polymer oxidation.

If PE coatings on copper were subject to prolonged oxidation, the oxidation process was observed to stop. This is supported by the constant area of the absorption band at 1720 cm⁻¹, while in case of coatings on aluminum the area of this band continued growing Table I. Stabilization of the oxidation process in coatings on copper was also observed if polymers underwent oxidation in the molten state;⁹ the ultimate content of carbonyl groups was much lower than in the case of solid-phase polymer oxidation.

CONCLUSION

To conclude, the two-stage mode of molten polyethylene oxidation in contact with copper¹² was observed as well at contact oxidation of PE in the solid phase. Such a common feature probably results from a homogeneous catalytic action of copper compounds transferred into the polymer. Transfer of copper into

coat bulk should be accounted for when developing formulations for coatings to be operated at elevated temperatures. Ingredients capable of neutralizing the harmful effects of the metal should be used to prepare coating compositions.

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