

Relationship Between Thickness of Polymer Films and Their Oxidation on Copper Substrate

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ABSTRACT: This research was undertaken to understand how the thickness of polyethylene films oxidized on a copper substrate influences the accumulation of carbonyl groups (measured by an IR-spectroscopy technique) and of metal from the substrate (determined by polarography analysis). It was found that the whole polymer became inhibited by the time the copper stopped transferring into the specimen. Plots of copper concentration versus film thickness have two thickness sections: section I is found between 0 and 70 μm and section II between 80 and 170 μm . Between these two sections the metal concentration varies drastically. This situation can be explained by two schemes by which PE changes to inhibited condition. According to Scheme I (for section I, short oxidation time) this change has only one step: the inhibited layer gradually becomes thicker beginning from the interface and moving toward the outer surface. The

second scheme (for section II) shows that the polymer becomes inhibited in two steps. It is typical of thicker films. In this case the oxidation process shifts and localizes in the outer surface because of longer treatment. As a result, transfer of metal and formation of an inhibited layer are interrupted for some time. The metal accumulation in the film only resumes when low-molecular-weight products of thermooxidative degradation—formed in the specimen outer surface—enter the region of adhesional contact. A so-called second transfer stage for metal is realized during which the whole polymer becomes inhibited. © 2002 Wiley Periodicals, Inc. *J Appl Polym Sci* 87: 671–675, 2003

Key words: unstabilized high-density polyethylene; thickness of polymer films; copper substrate; contact oxidation.

INTRODUCTION

Biggs and Hawkins¹ studied the effects of polymer film thickness on the course of oxidation. They reported that oxidation of polyethylene (PE) in air basically developed in the outer surface of the specimen but that in deeper layers the oxidation of PE depended on penetration of oxygen into those layers (diffusion).

Some investigators² have recognized two regimes for oxidation, kinetic and diffusive, each of which is realized through the access of oxygen to the reaction zone. In the outer surface of the specimen, where no limitations for oxygen exist and where products of oxidation are free to leave, the rate at which the treated polymer undergoes conversions depends only on the kinetic factors. A so-called kinetic regime of oxidation is realized in this instance; on the contrary, for deeper layers of the specimen, oxygen enters in limited amounts, and the polymer undergoes oxidation in diffusive conditions. The location of the boundary between the kinetic and diffusive regions of oxidation is usually determined from the test results obtained for films of different thicknesses. The highest

thickness of a polymer film at which oxidation of the specimen does not depend on diffusion factors determines the kinetic regime of oxidation. This approach of determining the thickness of the layer that is oxidized at kinetic conditions can be applied when experiments are run with films supported on inert substrates.

Introduction of some metals or their compounds into PE essentially changes the kinetics of PE oxidation.^{3–5} In contact with active metals, it is followed by transfer into the polymer bulk—first into the layer bordering the substrate—of metal-containing compounds that catalyze the oxidation process.^{6–10} Because of this, oxidation of the polymer in the initial stage is localized in the boundary layer, that is, it proceeds nonuniformly through the cross section (thickness). In our opinion it makes no sense to speak about the kinetic nature of oxidation if polymers are tested on active substrates because the coat film has a transversal gradient of oxidation from the very onset of the process. It should be mentioned that, on subsequent oxidation of the films, the region of high-rate oxidation of the polymer is forced into this area of the specimen because of the higher consumption of oxygen by the outer surface. The low-molecular-weight products of oxidation formed here penetrate the region of adhesional contact and further stimulate the access of metal-containing compounds into the bulk

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film. A second stage of active transfer of the metal begins.¹¹ The oxidation details for polymers treated on active substrates, described above, are in the main qualitative. Systematic studies are required to understand how the thickness of a polymer film influences the development of oxidative conversions in the polymer and the metal transfer. This article discusses these problems for adhesively joined PE-copper systems.

EXPERIMENTAL

Test specimens

GOST 16338-85 unstabilized high-density polyethylene grade 20306-005 (Russia) with the following characteristics was used: density of 0.950–0.959 g/cm³; average melt flow index of 7.5 g/10 min; and molecular weight of 150 000–200 000. The PE was prepared at low pressure with complex organometallic catalysts that were used in the experiments. Copper foil (Grade M1) was used as the substrate. For comparison, polymer films on window glass were tested. Window glass is inert to PE oxidation.⁶ PE powder was hot-molded on substrates at 150°C for 5 min to get test specimens. Thus, prepared specimens were oxidized in air in ovens (the oxidation temperature was 150°C, oxidation lasted up to 10 h). Then they were cooled at ambient temperature, and the polymer films were separated from the substrate and used in the experiments.

Test methods

The degree of oxidation of PE was determined using IR transmission spectra and the multiply violated complete internal reflection (MVCIR) spectra of the polymer films. The optical density of the 1720 cm⁻¹ absorption band attributed to carbonyl groups and the extinction rate—the ratio of optical density to film thickness in centimeters—were used as oxidation characteristics of the material. The spectra were recorded on a Specord 75IR spectrophotometer; the MVCIR spectra were recorded using KRS-5 ($\theta = 45^\circ$, $n = 2.4$, $N = 14$, where θ is the angle of incidence, n is the index of refraction, and N is the number of reflections).

The metal-containing compounds accumulated in the polymer were estimated by the copper amount found in the film. To do this, the treated films were separated from the substrate and reduced to ash by a two-step heat treatment in air.¹² The ash residue was used to prepare working solutions. The copper concentration in the solutions was determined by the polarography method. This method is described in detail elsewhere.¹³ The copper content in the film was evaluated for the weight-percent (wt %) concentration of the metal and surface density, that is, the metal

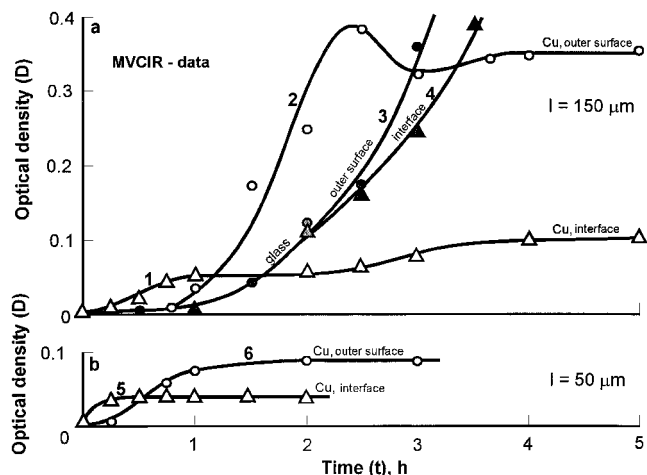


Figure 1 Optical density of 1720 cm⁻¹ absorption band in IR spectra of MVCIR for (2, 3, and 6) outer surface layer and (1, 4, and 5) interface of PE-copper systems oxidized at 150°C against time of oxidation. Film thicknesses: (a) 150 μm, (b) 50 μm.

content by weight per 1 sq m of the specimen area (g/m²).

RESULTS AND DISCUSSION

The accumulation of carbonyl groups in the PE outer surface and at the interface with glass is shown in Figure 1(a), curves 3 and 4. These data were obtained from IR spectra of MVCIR; the thickness of the analyzed layer was about 2 μm. Figure 1 shows that at an early stage of oxidation the kinetic curves run as one, implying inertness of the glass substrate to PE oxidation.⁶ The coincidence of the plots also indicates that the film has undergone oxidation at kinetic conditions through the whole cross section (150 μm). At the point where the curves separate (after 2 h of oxidation) the kinetic region equals the film thickness. With further oxidation a region of diffusive oxidation appears in addition to the kinetic oxidation; its thickness (cross section) gradually increases. In other words, a region of high-rate oxidation developed in the polymer film; this region gradually contracted and was forced toward the outer surface. Such a situation can be explained as follows. The oxidation process is autocatalytic, and oxygen consumption must continuously increase for the reactions to take place. As the film has limited permeability, the oxygen entering the polymer by diffusion is more and more consumed in the specimen's outer surface (bound diffusion). As a result, the deeper layers of the film consume an inadequate amount of oxygen, that is, their oxidation is influenced by diffusion limitations. That is why, as the oxidation develops, the boundary that separates the kinetic region from the diffusion region shifts toward the outer surface of the specimen, that is, the diffusion region

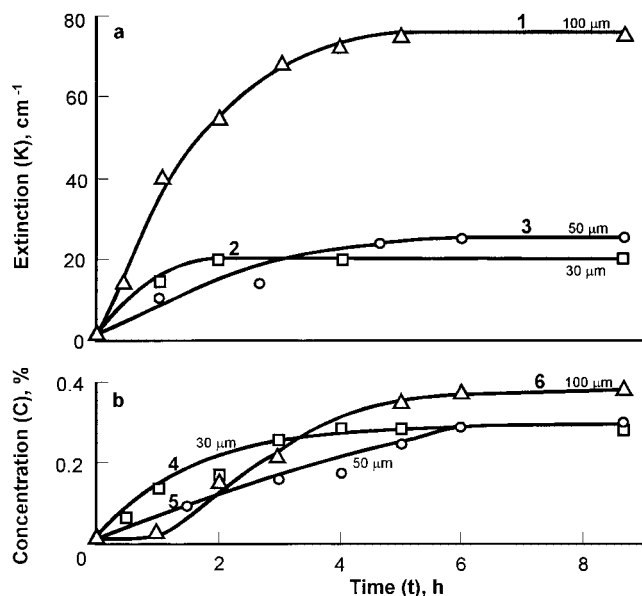


Figure 2 (a) Extinction rate for 1720 cm^{-1} absorption band in IR-transmission spectra; (b) metal concentration in PE films against time of oxidation on copper substrate at 150°C . Film thicknesses: (2 and 4) $30\text{ }\mu\text{m}$, (3 and 5) $50\text{ }\mu\text{m}$, (1 and 6) $100\text{ }\mu\text{m}$.

becomes wider at the expense of the narrowing kinetic region. Apparently, this circumstance can explain different thicknesses reported by numerous researchers for PE layers that are oxidized at kinetic conditions. Only those thickness values that were determined under equivalent test conditions can be correct.

Figure 1 shows the IR spectroscopy (MVCIR) data on the accumulation of carbonyl groups in PE films oxidized on copper. Regardless of film thickness (50 or $150\text{ }\mu\text{m}$), the interface polymer began to oxidize earlier than the outer surface polymer (Fig. 1, curves 1 and 5), that is, at an early stage of oxidation there was an oxidation gradient through the film cross section, and the oxidation regime was not kinetic. As time passed, the oxidation rate in the outer surface polymer increased because of free access of oxygen (Fig. 1, curves 2 and 6), that is, the oxidation process was localized within this part of the specimen.

A characteristic feature of PE oxidation on copper is the change from an active condition of oxidation to its suppression, that is, to stabilization or inhibition. For $50\text{-}\mu\text{m}$ -thick PE films, the kinetic curves of carbonyl groups accumulated in the outer surface and at the interface of the polymer had the shape of curves with saturation [Fig. 1(b)]. The ultimate values of optical density of the 1720 cm^{-1} absorption band, as well as the time required to reach stabilization, were higher for the outer surface than for the interface. For films treated on glass there were no signs of stabilized oxidation. (Fig. 1, curves 3 and 4).

For $150\text{-}\mu\text{m}$ -thick PE films oxidized on copper, the process was observed to stabilize both in the outer

surface and at the interface (Fig. 1, curves 1 and 2). The interface acquired this stabilization through a short intermediate period (there is a small horizontal plateau in the middle part of curve 1, Fig. 1). As for the outer surface layer, it reached stable oxidation after a small cyclic variation in the carbonyl group concentration (there are a maximum and a minimum in the middle part of curve 2, Fig. 1). The outer surface and the interface of $150\text{-}\mu\text{m}$ -thick specimens actually simultaneously reached a stable level of oxidation. Thus, on increasing PE film thickness, the oxidation mode of the polymer in contact with the copper differed a lot. The causes of these differences are discussed below.

Variations in the extinction of the 1720 cm^{-1} absorption band and the copper concentration of PE films of different thicknesses treated on copper substrate are shown in Figure 2. Extinction as well as metal concentration in the film are specific variables characterizing, respectively, an average amount of carbonyl groups and metal in a unit of bulk polymer. The relationships shown in Figure 2 look like the curves that have a region of stabilization. For films of equal thickness, the extinction and metal concentration values actually stabilized simultaneously (Fig. 2, curves 3 and 5), that is, the PE oxidation and metal transfer in them are interrelated. It was found^{5,6} that copper-containing compounds influenced the PE oxidation process in two ways. At low concentrations they catalyzed oxidative conversions, but at high concentrations they acted as inhibitors. That is why change to oxidation suppression (Fig. 2, curves 1, 2, and 3, the stabilization zone on kinetic curves showing carbonyl groups accumulation) can be explained by a critical amount of metal-containing compounds being reached in the bulk polymer, that is, an amount adequate to suppress the oxidation process (Fig. 2, curves 4, 5, and 6).

Figure 3 shows the summarized data of the effects of film thickness on the ultimate values of extinction and metal concentration in PE oxidized on copper. For the test range of film thicknesses, two sections can be highlighted. Section I runs from 0 to $70\text{ }\mu\text{m}$, section II

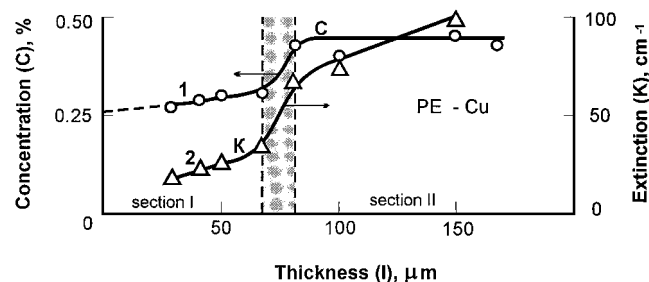


Figure 3 (1) Copper concentration in PE films against their thickness; (2) extinction rate of 1720 cm^{-1} absorption band in IR-transmission spectra. Treatment time for film on copper: 9 h at 150°C .

from 80 to 170 μm . Extinction increased at a relatively slow rate within these sections. There is a narrow intermediate region between them (shaded region in Fig. 3), over which the extinction rate grew drastically, from 34 to 64 cm^{-1} . The relationship for the ultimate amount of metal transferred into the polymer had a similar appearance (Fig. 3, curve 1). The minimum amount of copper required to change the PE oxidation process to inhibition can be determined by extrapolating Figure 3, curve 1, to zero film thickness. This yields about 0.25 wt %. The polymer oxidation level appears extremely low. Figure 3, curve 2, extrapolated to zero thickness of the film shows the extinction rate as being between 8 and 10 cm^{-1} . We think this division of the thickness range into two sections (Fig. 3) is related first to the details of oxidative conversions, which occur at different depths of the polymer specimen.

Referring to the data in Figure 1, it can be understood that even with thin films (curves 5 and 6) the change to inhibition of PE films oxidized on copper does not occur simultaneously through the whole film cross section. First, the interface becomes inhibited; after some time the outer surface becomes inhibited. Thus, the boundary separating the inhibited part of the polymer from the uninhibited part gradually shifts toward the outer surface of the specimen. Naturally, the thicker the polymer film, the longer is the time required to change the film to an inhibited condition. This statement was corroborated by the data available on the accumulation kinetics of carbonyl groups and metal (Fig. 2). The thinner the film, the faster were the ultimate concentrations of metal-containing compounds, as well as the products of oxidation, reached.

In the course of polymer oxidation, as the depth of the inhibited polymer increases, a second process begins developing, namely, the oxidation process is forced from the bulk film and localized in the outer surface. It was mentioned above that localization of the oxidation process in the specimen's outer surface is attributed to oxygen consumption, whose rate grows with time and results in its inadequate supply into the specimen's depth. As a result, oxidation reaction is suppressed in the bulk film, as shown by the intermediate plateau on the kinetics plots describing the carbonyl groups' accumulation in the PE interface (Fig. 1, curve 1). Simultaneously, severe oxidative conversions occurred in the outer surface layer. The low-molecular-weight products formed in this area because of thermooxidative degradation of the polymer move by the diffusion mechanism into the bulk film, and after some time those products entered the zone of adhesional contact. This led to a repeated increase in the amount of carbonyl groups in the interface (the rise in Fig. 1, curve 1, following the intermediate plateau) and to some decrease in the number of carbonyl groups in the outer surface (a small minimum in Fig.

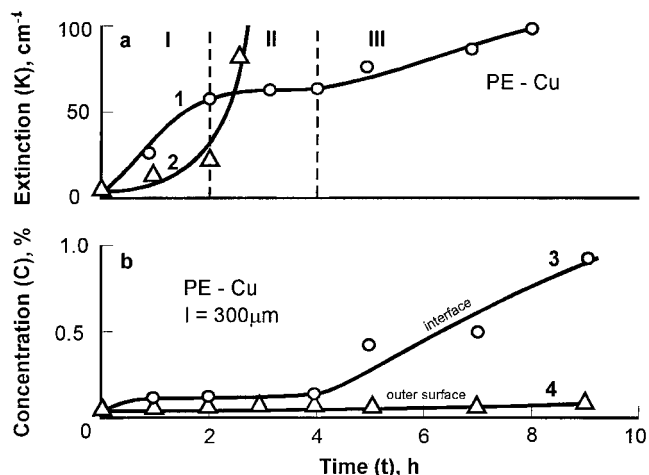


Figure 4 (a) Extinction rate of 1720 cm^{-1} absorption band in IR-transmission spectra and (b) metal concentration in: (2 and 4) outer surface; (1 and 3) interface of 300- μm -thick films against treatment time on copper at 150°C.

1, curve 2). Then followed the final conversion stage, at which the film acquired its inhibited condition.

The oxidation pattern described above for PE films treated on copper was corroborated by research into the transfer kinetics of metal for 300- μm -thick polymer films (Fig. 4, curves 3 and 4). On the plot of copper accumulation in the interface (the analyzed layer was between 10 and 15 μm) two transfer stages for metal can be seen. These stages are separated by a time interval during which no marked variations occurred in the amount of metal present in the analyzed layer. A similar plot was obtained for carbonyl groups in the interface (Fig. 4, curve 1). By the completion of the first accumulation stage for carbonyl groups (Fig. 4, curve 1, section I) the oxidation level of the polymer outer surface is relatively low (the extinction rate is about 20 cm^{-1}). However, traces of transferred metal were detected in this layer (Fig. 4, curve 4). When the interface material is at section II of its oxidation (Fig. 4) the carbonyl content increases but slowly. This is because the interface polymer is in fact inhibited. The second accumulation stage for carbonyl groups in the interface (Fig. 4, curve 1, section III) can be attributed to the transfer of low-molecular-weight products from the thermally oxidized outer surface. At that time the polymer oxidation in the outer surface is rather high (the extinction rate is much higher, 100 cm^{-1}). A second transfer stage for metal into the PE film begins as soon as products of oxidation start entering the interface (Fig. 4, curves 1 and 3). At this stage metal continues transferring until the oxidation process is stabilized through the whole polymer cross section. It is clear that the concentration of the metal transferred into the film will be higher in this case than in thin films.

Thus, two schemes are possible for polymer treated on copper to change to the inhibited condition,

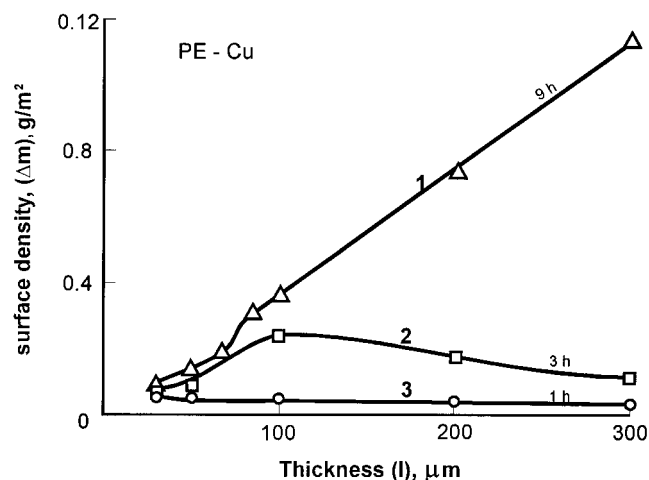


Figure 5 Surface density of copper in PE film outer surface against film thickness. Treatment time on copper at 150°C: (1) 9 h, (2) 3 h, (3) 1 h.

namely, the one-step and two-step schemes. The one-step scheme is realized for films below 70 μm . For such films carbonyl groups accumulate in the interface in one step when the oxidation process is not interrupted in the bulk. The two-step change of PE to an inhibited condition takes place in films more than 70 μm thick. In this case a longer time is required to change the polymer to an inhibited condition. During this time the oxidation process shifts and localizes in the specimen's outer surface, where PE oxidation and metal transfer processes are suppressed. As the low-molecular-weight products of oxidation accumulate in the outer surface and enter the zone of adhesional contact, metal resumes transferring into the polymer film, and the whole polymer changes to an inhibited condition. The accumulation kinetics for carbonyl groups of the metal in the polymer interface prompts the regime at which PE acquires an inhibited condition. If an intermediate plateau of stabilization appears on the kinetics plots, then the two-step regime is realized. If no such plateau is present, the one-step change of the polymer to an inhibited condition is realized.

The details reported above about copper transfer into the polymer interface influence the weight content of metal in the film. Figure 5 shows data on the effect of film thickness on the surface density of copper in the specimen (the amount of metal in grams transferred into the film having an area of 1 sq m). The experiments were conducted at three oxidation regimes, which corresponded in time to sections I, II, and III in Figure 4. If an experiment lasted for a short time (1 h), the plot of the copper surface density against specimen thickness went down (Fig. 5, curve 3). In this case the oxidation time was too short for the

thinnest 30 μm film used in our experiments to acquire an inhibited condition. After a 3-h oxidation such plots have a maximum (Fig. 5, curve 2). In this case thin films, which undergo oxidation at the one-step regime, have already acquired an inhibited condition (the ascending section in curve 2, Fig. 5) and metal discontinues transferring. At these conditions the oxidation of thicker films was localized in the outer surface, and the transfer of metal was highly restricted (descending section of Fig. 5, curve 2). As a result, there was an extreme relationship between the metal surface density and film thickness. The maximum on the plot corresponds to the largest film thickness that was found at an inhibited condition during a given oxidation time. In the case of prolonged film treatment (the regime corresponds to section III, Fig. 4), a different relationship was observed (Fig. 5, curve 1). In this case the density of copper in the polymer outer surface only increased, thus corroborating the data on metal transfer in Figure 3.

CONCLUSION

The investigation showed that, depending on the thickness of PE films oxidized on copper, the polymer can change to an inhibited condition by one of two regimes: (1) a one-step regime typical of films having thicknesses up to 70 μm and (2) a two-step regime typical of films having thicknesses between 80 and 170 μm . A mechanism was described in this article by which the oxidation process develops through the film cross section. This mechanism explains the two variants of polymer change to an inhibited condition.

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