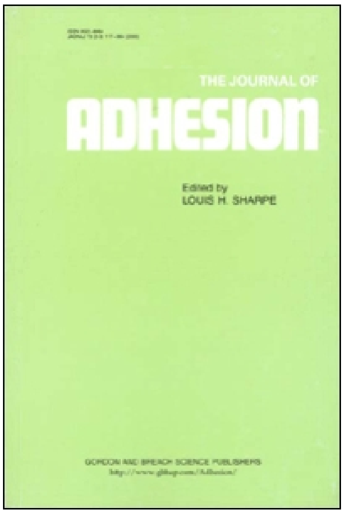

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Kinetics of Adhesion Interaction of Polyolefins with Metals under Conditions of Contact Thermooxidation. II. Dissolution and Diffusion of Iron Compounds into the Bulk of Polymer

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Kinetics of Adhesion Interaction of Polyolefins with Metals under Conditions of Contact Thermooxidation. II. Dissolution and Diffusion of Iron Compounds into the Bulk of Polymer

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The kinetics of dissolution and penetration of iron compounds (IC) into the bulk of a polyethylene layer during oxidation in contact with steel as a function of contact temperature and thickness of a polymer layer has been studied by X-ray spectral fluorescence analysis (XSFA). The measured intensity of dissolving species correlates with the rate of contact oxidation. Small amounts of IC dissolve in the absence of oxygen. The depth profiles of IC content were determined by electron probe microanalysis (EPMA). It was observed that the depth of penetration of IC does not exceed 15 μm up to a contact time of 3.6 ks at a temperature of 473 K. Judging from the value of the effective diffusion coefficient of IC, the process of transfer of IC is diffusion controlled. The results of some model experiments show that the most likely reaction for IC generation is the formation of iron carboxylates by the interaction of iron oxide with the products of contact oxidation of the polymer (carboxyl groups).

Keywords: Polyethylene; steel; adhesion interaction; contact thermooxidation; iron compounds; dissolution; diffusion

1. INTRODUCTION

In our previous article, we have discussed the main kinetic features of contact oxidation of polyethylene during adhesion interaction with steel [1]. The catalytic effect of the steel surface on the oxidation process was revealed. It was of special interest to answer the question: Is there only a heterogeneous catalysis or does some transfer of iron compounds into the bulk of the polymer melt occur and, as a result, homogeneous catalysis takes place? Experimental evidence for the latter case is discussed in our work.

Transfer of metal compounds into the bulk of a polymer during contact oxidation of polyolefines might be considered as a known phenomenon. From a wide variety of transition metals (only these metals efficiently catalyze thermooxidation of polyolefins) the transfer process of copper was investigated by M. Chan and D. Allara. Cu ions were detected in PE samples by these authors at a comparatively great distance from the interface after prolonged oxidation on the metal surface (for 10 hours at temperatures up to 180°C) using several experimental methods: IR reflection spectroscopy [2, 3], electron probe microanalysis [4] and Rutherford back-scattering [5, 6]. On the basis of these studies it was proved that dissolution of Cu is a result of the interaction of somewhat low-molecular-weight products of PE contact oxidation (containing mainly carboxyl groups) with surface compounds of metal oxide. These products are removed from the oxide phase and, by subsequent diffusion, they move into the bulk of polymer as copper carboxylates [2, 3].

As far as we know, similar diffusion of iron compounds has not yet been studied, except the discussed in Reference 7. In this article, attention is focused on the study of the kinetics of transfer of iron compounds and its correlation with other kinetics of contact oxidation.

2. EXPERIMENTAL DETAILS

2.1. Materials

Unstabilized low-density polyethylene of trade mark 108-02-20 (obtained from Novopolotsk Chemical Enterprise) with the following characteristics was used (the same as in Ref. 1): density, 0.919 g/cm^3; average values of molecular weight $M_\eta = 31200$, $M_w = 36500$, $M_n = 19500$); degree of branching, 4.5 (number of tertiary substituted C atoms per 100 C atoms of chain); melting temperature, 378 K;

temperature of intensive oxidation, 488 K (both according to DTA data). A 70 μm thick steel foil (approximately corresponding to USA AJS 1010 steel) was used as a substrate.

2.2. Steel Surface Preparation

The steel surface was subjected to electro-chemical degreasing in an alkaline solution (composition of solution in g/l: Na_3PO_4-60, Na_2CO_3-30, NaOH-15) at temperature 343–363 K and current density 10 A/dm^2 as a cathode for 2.5 min., then as an anode for 0.5 min). Specimens were rinsed in hot (363 K) distilled water and then dried in a filtered warm air flow (353 K). Steel specimens were kept in a desiccator over dehydrated $CaCl_2$ for no more than 24 hours before use. The value of wetting angle of the prepared steel surface by water was less than 8–10°.

2.3. Preparation of Polymeric Films

Films of thickness 50–500 μm were prepared by hot pressing at a temperature of 408 K and under a pressure of 40 KPa for 2.5 min. between Teflon films. Specimens were cooled to room temperature between steel plates (average rate of cooling about 1°C/sec.), then rinsed with acetone, dried in a warm air flow and stored in the desiccator.

2.4. Preparation of Samples of Adhering Systems

Laminated polymer-steel (open systems) and metal-polymer-metal (closed systems) samples were made. The polymer films were bonded with the substrate by direct hot-pressing at a fixed temperature under a pressure of 40 kPa for a specified time in different environments (pressure and content of oxygen in parentheses): oxygen (100 kPa, 99.7%), air (100 kPa, 21.0%), argon (100 kPa, 7×10^{-4}%), vacuum (1.33 dPa, 27×10^{-5}%), high vacuum (1.33 mPa, 2.7×10^{-7}%). For this purpose, specially designed membrane-type and tubular reactors were used [8]. These reactors made it possible to hold samples under fixed pressure and also to heat open samples (free access of environment of polymer layer) without pressure.

2.5. Studies of Kinetics of Accumulation of Iron Compounds and Oxygen-Containing Groups

The laminated polymer-substrate specimens after contact with metal in the noted media for a specified time and temperature were debonded using an electrolytic method (a kind of forced cathodic delamination). The specimen served as a cathode in Na_2CO_3 aqueous solution (2%) with current density of 2 A/dm^2. Interfacial debonding of the polymer film occurred [9]. The films obtained were used for analysis.

The average content of iron compounds in debonded polymer films was determined by X-ray spectral fluorescence analysis (XSFA) [10] (spectrophotometer VRA-2).

The quantitative XSFA analysis was based on an external standard. Calibration curves were obtained for specially-prepared standard polyethylene samples with a known content of a model iron compound, iron stearate. The range of Fe content was: 10^{-6}–10^{-2}g/g of PE. Special powdered low-density polyethylene with initial iron content less than 10^{-5}% was mixed with the appropriate amount of iron stearate solution in toluene. After drying in a vacuum over compositions were prepared by mixing in laboratory rolls at 403 K for 0.6 ks. Films of appropriate thickness were pressed at 408 K for 90 s. PE films without iron stearate were prepared similarly. Discs of 40 mm diameter were cut out for XSFA.

The intensity of fluorescence, I_ϕ, at diffraction angle $2\theta = 58°47''$ (characteristic irradiation of polyethylene) was measured for several thickness (in the range from 30 to 300 μm) of pure polyethylene films. The values of I_ϕ were a linear function of thickness of the polymer layer (film) and were used as an external standard.

The intensity of fluorescence of Fe (the analytical line FeKα), I, at $2\theta = 57°47''$ was measured for the iron-containing samples used as standard. Calibration curves of relative intensity of fluorescence, I/I_ϕ, as a function of iron content, c_{Fe}, were plotted for three film thicknesses: 50, 100 and 300 μm. The total average content (ignoring the presence of gradient of content) of iron in films delaminated from the metal after contact at definite contact temperature and time was determined from these curves with an accuracy not less than 1.7%.

The profiles of iron content (gradient of content) for PE films after contact with steel were determined by electron probe microanalysis

(EPMA) [11], using a scanning electron microscope (Philips EM-500) combined with an X-ray spectrometer "EDAX". The specimens of films (5 × 10 mm) with gradient of Fe content were encapsulated in an epoxide block (holder). Several layers of the prepared sample were cut off along the gradient (normally to the contact surface with the metal) by a microtome LKB 8800 A to guarantee a smooth cross-sectional surface. A carbon layer was sputtered on the surface of the cross-section to provide the necessary electrical conductivity.

The intensity, I, of the characteristic X-ray radiation of the sample (the analytical line FeKα) initiated by a narrow (0.1 μm) electron beam was registered by the scanning of the sample along the gradient of Fe content. The resolution of the method was characterized by the average dimensions of the zone in which micro X-ray radiation had been initiated: 2.0–2.5 μm. The calibration curves were used (obtained in the same way as for XSFA) for quantitative calculations.

The profiles of content of carbonyl groups and Fe carboxylates in the polymer layer were evaluated by infra-red spectroscopy (spectrophotometer IR-75) for 3–5 μm thick layers gradually cut off by a special device from the contact surface of the polyethylene adhesive (after interfacial delamination of adhesive joints) which was cooled to the temperature of liquid nitrogen.

IR spectra for adhesive films of thickness 50 μm were obtained by pressing of the scraps at 403 K under a pressure of 40 kPa for 1 min. The ratio (D^*_{cg}) between the values of optical density of carbonyl groups absorption (in the region 1710–1740 cm^{-1}), and the optical density of absorption in the region 4350 cm^{-1} (internal standard) was determined. A similar ratio of optical density values (D^*_{Fec}) was determined for iron carboxylates (a comparatively wide region: 1570–1620 cm^{-1} which corresponds to various forms of carboxylates [12]). Standard deviation of measurements was less than 10%.

The process of oxidation of the polymer layer on the surface of the metal was simultaneously studied by differential thermal analysis (DTA) and thermogravimetry (DTG). For this purpose a derivatograph (F. Paulik, I. Paulik and I. Erdei system, Hungary) was used. The heat effect, ΔH, and change in weight of the oxidizing polymer layer, Δm, at a constant rate of heating (20°C) were studied. Laminated polymer-substrate-polymer specimens of dimensions 25 × 115 mm coiled into a helix were used. The standard deviation of measurements was less than 5% for DTA and about 6% for DTG.

Time curves of parameters ΔH and Δm were recorded automatically.

2.6. Evaluation of Peel Strength of Adhesive Joints

Polymer-metal (steel foil) laminated specimens (10 mm wide and 100 mm long) were cut from the laminate panel (100 × 100 mm). The thickness of the steel foil was 70 μm and of the polymer adhesive layer 500 μm. The peel strength, A, of samples was determined in a tensile testing mechine ZT-20, at a cross head speed of 0.8 mm/s at room temperature. Standard deviation of the measurements was from 10 to 15%.

In all cases, a cohesive failure mode (fracture in the weak boundary layer of polymer) occurred. The thickness of the residual layer of polymer on the metal surface (determined by reactive (pyrolytic) gas chromatography [13]) was 10 nm, on the average.

The size of the experimental points on the figures corresponds to the respective error bars (where error bars are not present).

3. RESULTS AND DISCUSSION

The kinetic curves of accumulation of iron-containing compounds in the polymer layer during contact under the conditions of free access of air are shown in Figure 1. There is an obvious increase in the rate of accumulation with increasing contact temperature and decreasing thickness of the polymer layer. This tendency could be more clearly seen from the data of Figure 2 and Table I, where the values of the initial variation of iron content ($\dot{c}_{\mathrm{Fe}} = \lim(dc_{\mathrm{Fe}}/dt)|_{t\to 0}$) (plotted in the coordinates of the Arrhenius law), and also the data of iron content, c_{Fe}, as a function of contact time, t, were used as kinetic characteristic.

The kinetic characteristics of the dissolution process of iron into the polymer, and of the formation of strength of adhesive joints under the conditions of various oxygen content in the environment during primary and subsequent contact and different access of the medium, were compared (see Tabs. I, II and Fig. 3). There are at least four types of

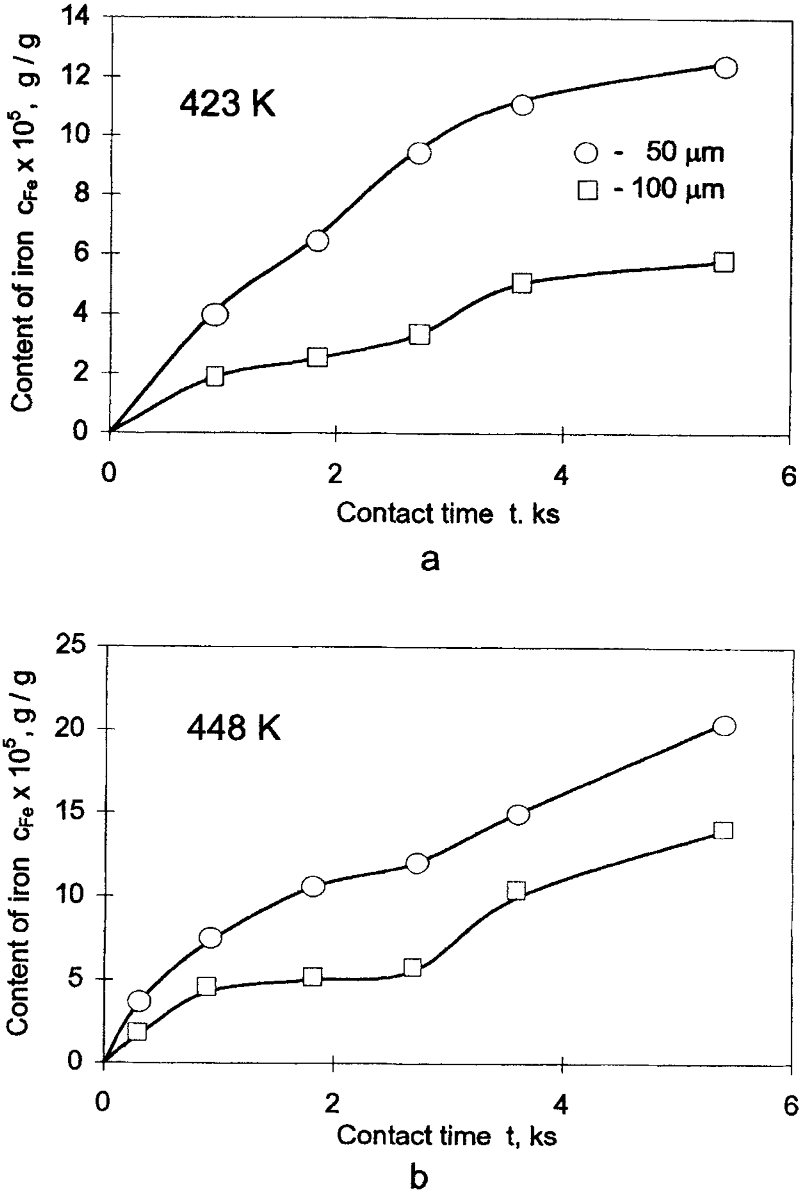

FIGURE 1 Variation of iron content, c_{Fe}, transferred into polymer with contact time, t, in conditions of free access of air through the layer at various contact temperatures (a) 423 K, (b) 448 K, (c) 473 K) for two levels of thicknesses of the polymer layer (50 and 100 μm), determined by XSFA method.

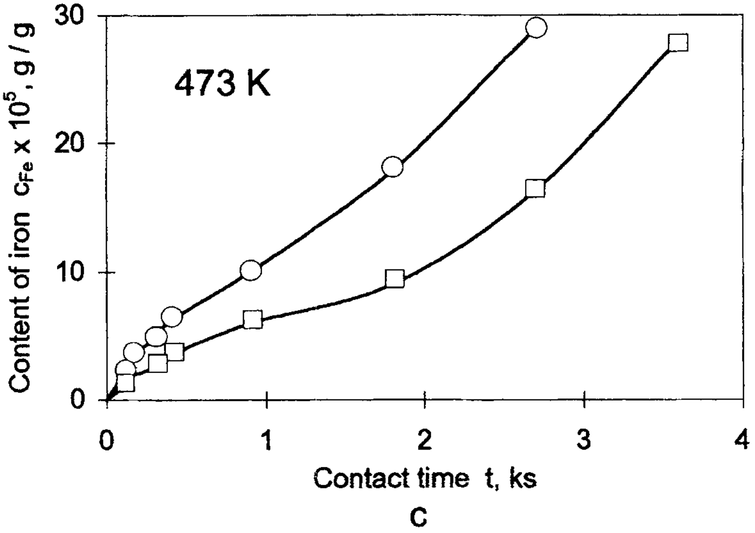

FIGURE 1 (Continued).

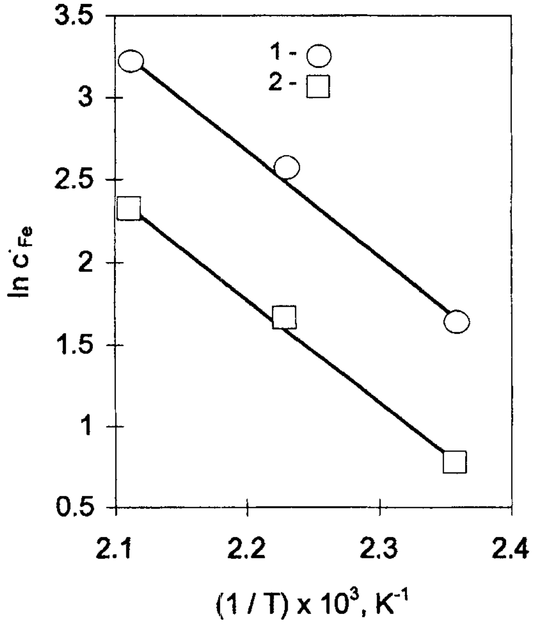

FIGURE 2 Values of $\dot{c}_{Fe}$ *versus* contact temperature T (Arrhenius plots) for two thicknesses of the polymer layer (1–50 μm and 2–100 μm).

TABLE I Kinetic characteristics of adhesive joint strength: initial growth rate of peel strength $\dot{A}$, $(N/m)s^{-1}$ at contact temperature T and average iron content in a polymer layer $C_{Fe} \times 10^5$ g/g. (3.6 ks at 453 K); thickness of polymer layer 300 μm (Roman numerals-sources of oxygen)

	Media of primary contact and their designation (italic)														
Media of subsequent contact and their designation	*OXYGEN* *OX*			*AIR* *AI*			*ARGON** *AR*			*VACUUM** *V*			*HIGH VACUUM*** *HV*		
	$\dot{A}$			$\dot{A}$			$\dot{A}$			$\dot{A}$			$\dot{A}$		
	T, K		C_{Fe}	*T, K*		C_{Fe}	*T, K*		C_{Fe}	*T, K*		C_{Fe}	*T, K*		C_{Fe}
	423	*453*		*423*	*453*		*423*	*453*		*423*	*453*		*423*	*453*	
	Closed adhesion system: *metal-polymer-metal*														
Closed adhesion system				II, III, IV						III, IV			absence of oxygen		
cl	–			1.4	3.3	**6.7**	–			0.2	0.8	–	0	0	**1.7**
designation of adhes. joint				*AI*, ***cl***						*V*, ***cl***			*HV*, ***cl***		

TABLE I Continued

		Open adhesion system: *polymer-metal*			
oxygen ***ox*** designation of adhes. joint	I, II, III, IV 3.3 9.0 – *OX*, ***ox***	–	–	–	–
air ***ai*** designation of adhes. joint	— –	I, II, III, IV 2.6 **4.4** **16** *AI*, ***ai***	–	–	–
argon ***ar*** designation of adhes. joint	–	–	III, IV 1.1 2.4 **6.3** *AR*, ***ar***	–	–
vacuum ***v*** designation of adhes. joint	–	–	–	III, IV 1.0 2.5 – *V*, ***v***	–

Notes: *-vacuum (1.3 dPa), membrane type reactor; **-high vacuum (1.3 mPa) with reduction in hydrogen (tubular reactor)

TABLE II Comparison of contribution of different kinds of oxygen to kinetic characteristics (from experimental data of Tab. I)

Kinds of Oxygen source	*Designation and expression for calculation of respective kinetic characteristic (see Tab. I)*	*Kinetic characteristic*		
		$\dot{A}$, *(N/m)*s^{-1}*(%)*		$C_{Fe} \times 10^5, g/g$
		Contact temperature, K		
		423	*453*	*453*
Sum of all sources I, II, III, IV	$(AI, \mathbf{ai})$	**2.6** (100%)	**4.4** (100%)	**16** (100%)
I	$[(AI, \mathbf{ai})$-$(AI, \mathbf{cl})]$	2.6–1.4 = **1.2** (46%)	4.4–3.3 = **1.1** (25%)	16–6.7 = **9.3** (58%)
II	$[(AI, \mathbf{cl})$-$(AR, \mathbf{ar})]$	1.4–1.1 = **0.3** (12%)	3.3–2.4 = **0.9** (20%)	6.7–6.3 = **0.4** (2%)
III, IV	$[(AR, \mathbf{ar})$-$(HV, \mathbf{cl})]$	**1.1** (42%)	**2.4** (55%)	6.3–1.7 = **4.6** (29%)
Absence of oxygen	$(HV, \mathbf{cl})$	**0** (0%)	**0** (0%)	**1.7** (11%)

oxygen sources involved in the contact oxidation: oxygen which *diffuses through* the polymeric film (source I, only for an opened adhesion system: polymer-metal), oxygen which is *captured at the interface* in the initial stage of contact (source II), and oxygen which is *absorbed* and *chemisorbed* by the metal surface oxide (sources III and IV, respectively) [14].

The values of peel strength, A, of the adhesive joints and iron content, c_{Fe}, at fixed values of contact time, t, and initial variation of peel force $(\dot{A} = \lim(dA/dt)|_{t \to 0})$ decrease with decreasing oxygen content in the contact medium (Fig. 3, Tab. I). This means that dissolution of iron into the polymer is indeed determined by contact oxidation. As can be seen from the Table II, oxygen which is *absorbed* and *chemisorbed* by the surface metal oxide (sources III and IV, respectively) plays an important role in this process. Significant dissolution of iron takes place also in the absence of oxygen.

The curves of Figure 1 show only the average iron content. It was of interest to evaluate the distribution of iron within the layer. The depth profil of iron in the polymer layer (Fig. 4), even in the case of prolonged contact (up to 3.6 ks), was at a distance less than 15 μm

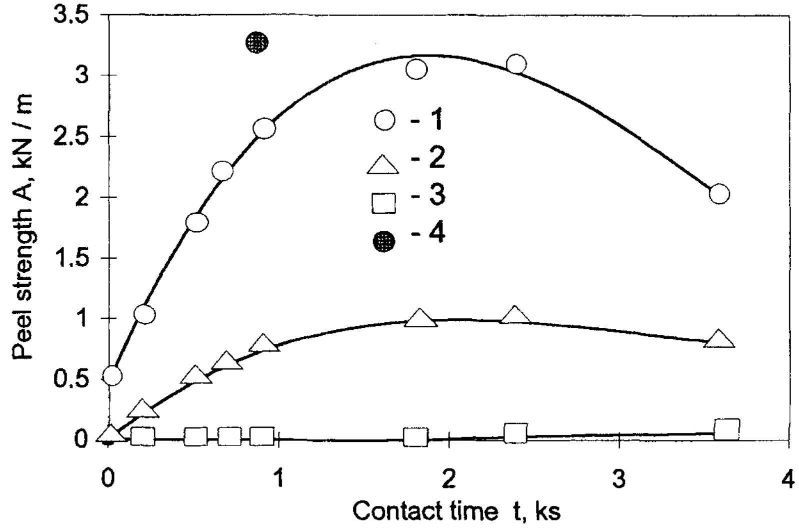

FIGURE 3 Variation of peel strength, A, with contact time, t, of adhesive joints polymer-metal (an open system) under different contact conditions: 1-contact in air medium, 2-in vacuum, 3-in high vacuum with preliminary reduction of oxide in hydrogen, 4-the same as in 3 with a subsequent air inlet.

from the contact surface with the metal (y is a coordinate in the direction of the diffusion of the iron compounds). This constitutes only about 10–15% of the whole thickness of the layer. Thus, the average iron content in the area of the gradient (c^*_{Fe}) is 7–10 times greater than the respective average values of c_{Fe}.

The profile curves were used for evaluating the effective coefficient of diffusion, D, of iron compounds into the polymer.

The solution of the equation for Fick's 2nd law for the boundary conditions: $c = c_0$ at $y = 0$, $t > 0$, and $c = 0$ at $y > 0$, $t = 0$ is as follows [15]:

$$c(y) = c_0\{1 - \mathrm{erf}[y/2\,(Dt)^{1/2}]\} \tag{1}$$

where c is the local content of the diffusing matter, and y is the coordinate in the direction of one-dimensional diffusion.

From the gradient curves, the depth of penetration, y^*, can be obtained $(c^y{}_{Fe}) = 0)$. It follows from Eq. (1) that:

$$1 - \mathrm{erf}[y^*/2\,(Dt)^{1/2}] = 0 \tag{2}$$

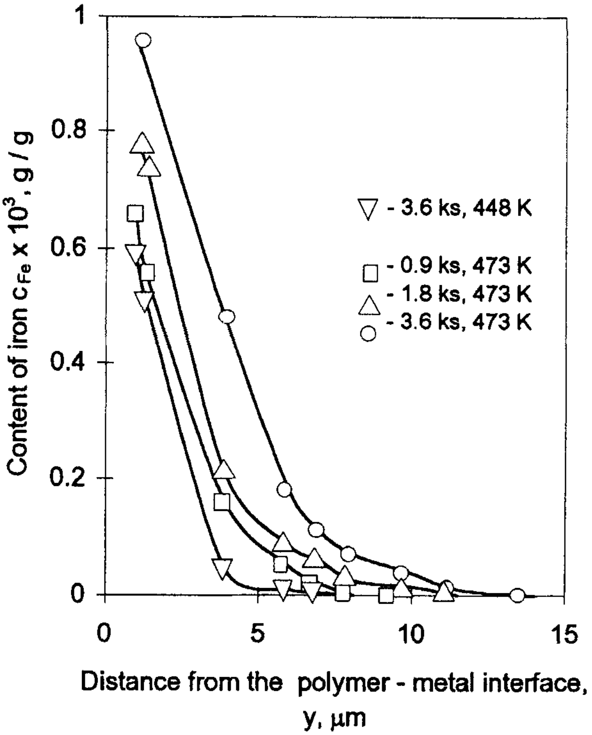

FIGURE 4 Profiles of iron content, c_{Fe}, for different contact time and contact temperature determined by EPMA. Contact of open adhesive joints in air, thickness of the polymer layer is 100 μm.

and from tables [15] that:

$$y^*/2\,(Dt)^{1/2} = 3 \qquad (3)$$

The experimental points lie satisfactorily on a straight line, according to the coordinates of Eq. (3): $y^*(t^{1/2})$ (see Fig. 5). This allows one to calculate the value of D at 473 K. The calculated value is $D = 1.5 \times 10^{-11}$ cm^2/s. This value of D corresponds to a calculated molecular weight, M, of diffusing polyethylene chains of about 1.4×10^4 (calculated using the relationship $D = kM^{-b}$, where $k = 3.0 \times 10^{-3}$ and $b = 2$, see Reference 16). The calculated value of molecular weight, when compared with the molecular weight of the

PE used in this study, indicates that some oxidative degradation has taken place.

This means that the penetration rate (and therefore the shape of the gradient of iron-containing compounds) is diffusion controlled.

The value of activation energy calculated from the temperature dependence of $\dot{c}_{\mathrm{Fe}}$ (Fig. 2) is 52.7 kJ/mol. This value is similar to the value of activation energy of diffusion in nonpolar polymer-polymer systems (40–55 kJ/mol) [15, 18].

It should especially be noted that our attempts to find the constants which would satisfy the dependence of $\dot{c}_{\mathrm{Fe}}$ on contact temperature, T, and thickness of the oxidizing layer, b, according to the equation [1]:

$$\dot{c}_{ox}(b) = \frac{c_{ox}|_{x=0} k \tanh(k^* b)}{k^* b} \tag{4}$$

(where: $c_{ox}|_{x=0}$ is oxygen content at the interface with air; $k^* = (k/D)^{1/2}$, k is the rate constant for oxygen consumption, D is oxygen

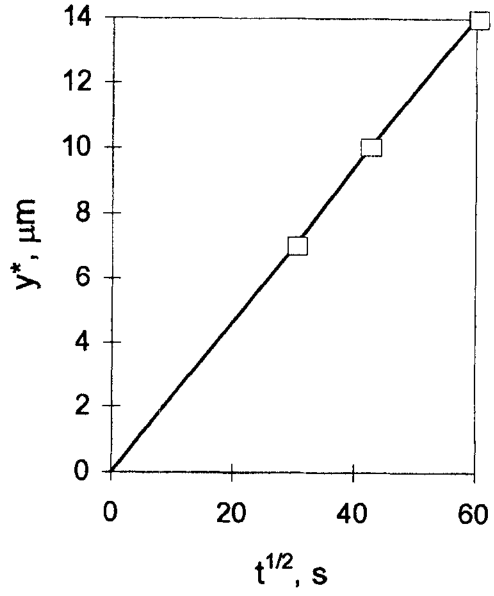

FIGURE 5 Values of y^* *versus* contact time, t, in the coordinates of Eq. (3); contact temperature 473 K.

diffusion coefficient, x is coordinate in the direction of oxygen diffusion) were fruitless. This was probably due to the fact that Eq. (4) describes oxygen consumption as an integral characteristic of the entire thickness of the layer. On the contrary, the formation of iron compounds should be determined by the intensity of oxidation directly on the interface with metal ($x = b$; $y = 0$): $\dot{c}_{ox}|_{x=b} = kc_{ox}|_{x=b}$.

The values of $\dot{c}_{ox}|_{x=b}$ were calculated for different values of T and b; the following expressions were used: $\dot{c}_{ox}|_{x=b} = (\dot{c}_{ox}|_{x=0} \times c_{ox}|_{x=b})/c_{ox}|_{x=0}$; $(c_{ox}|_{x=b}/c_{ox}|_{x=0}) = \tanh(k^*b)/k^*b$, derived from the Eq. (4); $\dot{c}_{ox}|_{x=0}$ values were taken from Table II [1].

As can be seen from the data of Figure 6, there really exists a linear correlation between $\dot{c}_{\mathrm{Fe}}$ values and the corresponding $\dot{c}_{ox}|_{x=b}$ values, but not with A values (because these values are determined by oxidation over the whole layer of adhesive).

It is obvious that iron compounds diffusing into the polymer layer during contact oxidation are iron carboxylates (similarly to copper carboxylates [2,3]). The adsorption region 1570–1620 cm^{-1} appears in scraps (cut close to the interface), along with the absorption region of carbonyl groups (1710–1740 cm^{-1}). The profile of the ratio of the

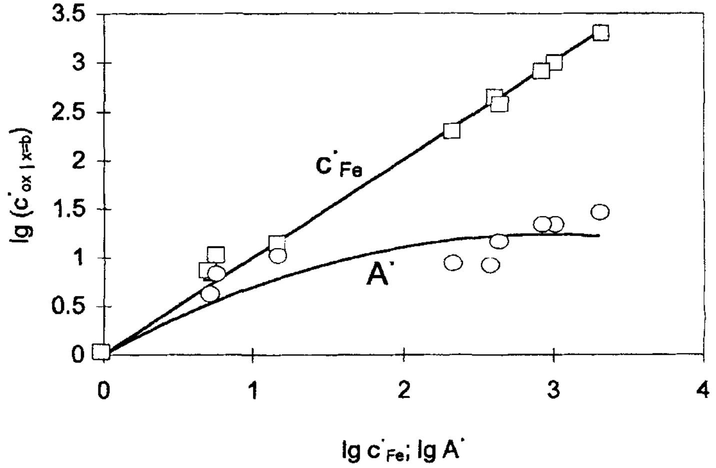

FIGURE 6 Correlation between $\dot{c}_{\mathrm{Fe}}$, $\dot{c}_{ox}|_{x=b}$ and $\dot{A}$ values at contact temperatures (423, 448 and 473 K) and thicknesses of the polymer layer (50, 100 and 300 μm).

corresponding values of optical densities for iron carboxylates (D^*_{Fec}) (Fig. 7) is quite similar to the profile of iron content, determined by the EPMA method (see Fig. 4). The profile of the D^*_{cg} values (carbonyl group content) shows the role of oxygen which has been captured at the interface in the initial stage of contact (source II) and oxygen which has been absorbed and chemisorbed by metal surface oxide (sources III and IV, respectively): there is an obvious increase in the D^*_{cg} value on shifting closer to the interface with the metal.

It is evident from the data of Table III that dissolution of iron into the polymer has been accelerated with the increase in stearic acid content (the model of carboxyl groups containing oxidation products of polyethylene).

Attention must be focused on the fact that, according to our observations, there is a continuous increase in the content of iron-containing compounds in the polymer layer during contact oxidation. Thus, one could expect a corresponding increase in the rate of oxidation due to the homogeneous catalytic effect of iron compounds. At present, there is experimental evidence that the kinetics of oxygen accumulation

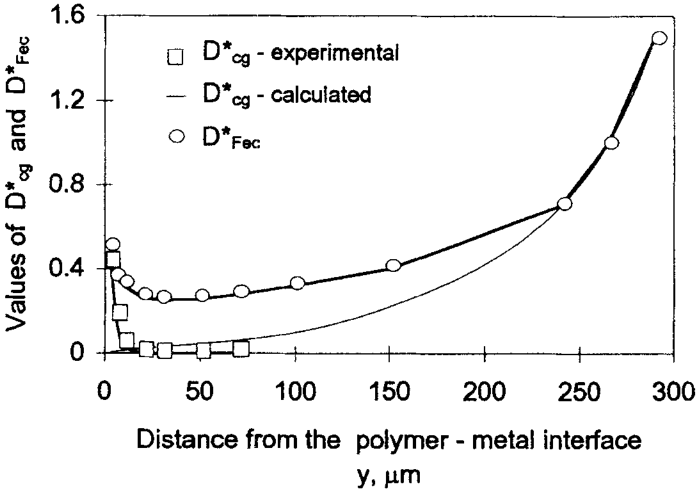

FIGURE 7 Profiles of the ratio of optical densities of IR absorption in the region of iron carboxylates (D^*_{Fec}) and carbonyl groups (D^*_{cg}) of polymer after contact with steel at 473 K for 3.6 ks; an opened adhesive system: polymer-metal. Thin line is the profile of D^*_{cg} calculated according to Eq. (4) for $k^* = 1.5 \times 10^{-2}\ \mu\mathrm{m}^{-1}$.

TABLE III Variation of iron quantity (related to the unit area of contact surface × 10^4, mg/cm^2) which transfers into the bulk of polymer with content of stearic acid and contact time with steel. Thickness of polymer layer-100 μm, contact temperature-473 K; open system (numerator), closed system (denominator)

Contact time, ks	*Content of stearic acid, %*		
	0	*0.5*	*5*
0.9	6.1	5.9	10.0
1.8	9.0	27	29.0
2.7	13/5.5	32	73/17.5

and formation of carbonyl groups is characterized by a period of contant rate [1].

To explain this disrepancy, let us turn to the experimental data of the kinetics of oxidation of polyethylene containing a certain amount of iron stearate (the model of iron compounds when polyethylene is oxidized in contact with steel), see Figure 8. One can see that the content of carbonyl groups increases only in the initial stage of the oxidation process. Later, inhibition takes place instead of catalysis. The inhibition of thermoxidation of polyolefins with a high content of transition metal compounds was observed long ago [19, 20].

Taking into account the existence of the gradient of iron compound content in the polymer regions adjacent to the interface with metal, one can expect the inhibition of contact oxidation, but in more distant regions, the catalysis of oxidation. As a result, this could lead to a peculiar equilibration of oxidation intensity in the regions with different content of iron compounds which would expresses itself as a constant average rate of oxygen uptake.

A progressive decrease in the rate of growth of carbonyl group content in the oxidizing polymer with increasing iron content is presumably accompanied by liberation of volatile oxidation products. The results of DTA and DTG analyses serve as experimental evidence (see Fig. 9 and Tab. IV). The fall of temperature values at the beginning of oxidation (T_b^T and T_b^m), as an effect of catalysis of iron compounds, is accompanied by a significant reduction in the values of peak areas-S^m and S^T.

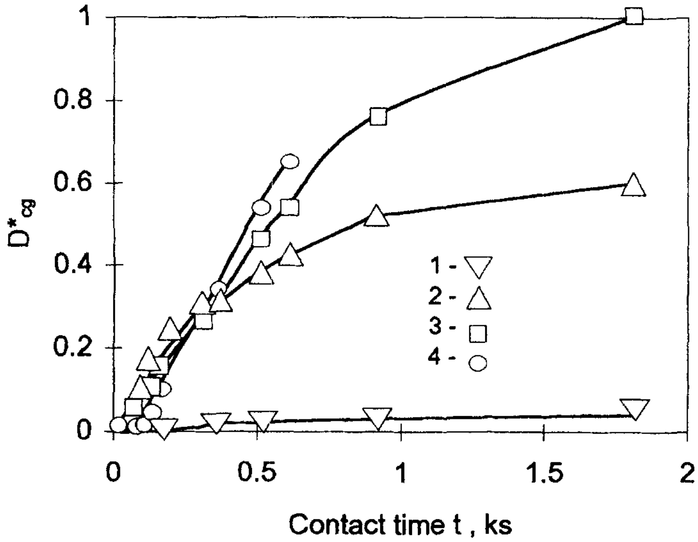

FIGURE 8 Variation D^*_{cg} values (content of carbonyl groups) with time of oxidation, *t*, of the polymer layer (thickness-50 μm) on the surface of Teflon (1,2,3; noncatalytic substrate) and steel (4). Polymer contains iron stearate (recalculated for Fe content, g/g of polymer): 1 and 4: 0; 2: 5×10^{-4}; $3{:}10^{-3}$.

CONCLUSIONS

Iron compounds have been formed, dissolved and penetrated into the bulk of a polymer layer in the process of contact oxidation during adhesion interaction of polyethylene melt with steel. Oxygen, having been captured at the interface in the initial stages of contact, and also oxygen absorbed and chemisorbed by the metal surface oxide, play a significant role in the process of iron dissolution, just as in the process of formation of the strength of adhesive joints. A small amount of iron compounds dissolve under the contact conditions in the absence of oxygen.

The depth of penetration of iron compounds does not exceed 15 μm, even during prolonged (up to 3.6 ks) contact oxidation.

The value of the effective coefficient of diffusion calculated from the iron content profile shows that the process of transfer of iron compounds is diffusion controlled.

The value of the activation energy of formation of iron compounds in a little bit lower than the activation energy of oxygen uptake reactions.

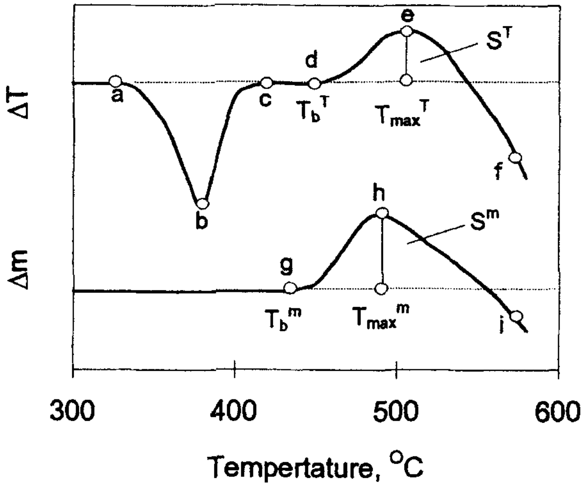

FIGURE 9 A schematic diagram of DTA (ΔT) curve: a b c-endothermic melting peak; d e f-exothermic peak of oxidation, and DTG (Δm) curve: g h i-exothermic peak of oxidation. In the regions d e or g h oxygen uptake prevails; in the regions e f or h i destruction with the release of volatile oxidation products predominates.

TABLE IV Influence of iron stearate content (evaluated for $c_{Fe} \times 10^3$, g/g) on the characteristics of reaction heat ΔT (DTA) and weight change Δm (DTG) during oxidation; 300 μm thick layer supported by Teflon film (non-catalytic substrate); (see also Fig. 9)

$c_{Fe} \times 10^3, g/g$	ΔT *characteristics*			Δm *characteristics*		
	T_b^T, K	T_{max}^T, K	S^T *relative units/g*	T_b^m, *K*	T_{max}^m, K	S^m *relative units/g*
0	452	508	22.3	440	487	1.8
1	430	456	6.6	418	454	1.4
5	417	445	5.5	403	437	0.6

The most probably reaction for generation of iron compounds is the formation of soluble iron carboxylates due to interaction of iron oxide with carboxyl-group-containing products of polyethylene contact oxidation.

Small amounts of dissolved iron compounds accelerate the contact oxidation. The catalysis passes into inhibition with increasing content of iron compounds. This tendency (due to the presence of a gradient of iron compound content) determines the kinetics of contact oxidation during formation of adhesive bonds between polyethylene and steel.

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