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Kinetics of Adhesion Interaction of Polyolefins with Metals Under Conditions of Contact Thermooxidation

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Kinetics of Adhesion Interaction of Polyolefins with Metals Under Conditions of Contact Thermooxidation

IV. Origination of Gradients of Macromolecular Transformations

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The formation of gradients of macromolecular transformations at contact oxidation in the adhesive layer during formation of adhesive joints of pure and peroxide-containing polyolefins with steel was studied. Indirect methods were used, such as measurement of fluidity in adhesive samples, measurement of shear creep and shear modulus of a polymer melt layer for different adhesive thickness, and some others. Effective viscosity, μ, was calculated from the experimental shear creep curves as a function of the thickness, h, of a cross-linking PE melt layer for several levels of contact time. The experimentally-measured values of viscosity were regarded as the complex average values of a certain viscosity gradient. It was found that in the case of catalytically-inactive substrate (Cellophane), there was no gradient. The dependence of the shear modulus on the layer thickness was determined. The measurements of fluidity of adhesive samples scraped at different distances from the interface for various contact times confirmed that the gradient of macromolecular transformations also originated when steel was in adhesion contact with polyethylene and ethylene-vinylacetate copolymer which did not contain peroxide. In the adhesive layers near the adhesive-steel interface, the catalyzed oxidative cross-linking prevailed. Within the adhesive layers located far enough from the interface, the oxidative destruction was dominant. For a catalytically-inert substrate (Teflon), the oxidative destruction prevailed over the whole thickness of the polymer layer.

Keywords: Polyethylene; steel; organic peroxide; adhesion interaction; contact thermo-oxidation; gradient of cross-linking and destruction

1. INTRODUCTION

The kinetics of adhesive interaction processes between polyethylene and steel under the control of catalytic contact oxidation was the main subject discussed in our first papers of this series [1, 2]. The reinforcement of PE-steel adhesive joints is mainly the result of strengthening a weak boundary layer of PE [3]. Two main competitive tendencies in contact oxidation are responsible for the strength characteristics of a PE boundary layer, namely, the oxidative cross-linking causing an increase in strength of the PE boundary layer and the oxidative destruction weakening this layer [1].

Organic peroxides, the acknowledged cross-linking agents of polyolefins, proved to be the PE additives which, under certain contact conditions, provide a great advantage of the first trend [4].

Catalytic contact oxidation processes of PE start at the interface [1], gradually penetrate into the polymer bulk and, consequently, lead to formation of respective gradients. The existence of the gradients of oxidation products containing carbonyl groups and the gradients of iron-containing compounds was observed in Ref. [2].

In this paper, we discuss the formation of gradients of the macromolecular contact-oxidation transformations – scission and cross-linking of macromolecules – during formation of adhesive joints of both pure and peroxide-containing polyolefins with steel.

2. EXPERIMENTAL DETAILS

2.1. Basic Materials

We used unstabilized low-density polyethylene of trademark 108-02-20 (obtained from the Novopolotsk Chemical Enterprise) with the following characteristics: 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 (the number of tertiary-substituted C atoms per 100 C atoms of a chain), melting temperature 378 K, and temperature of intensive oxidation 488 K (both according to DTA data). Unstabilized copolymer of ethylene with vinylacetate (EVAC) of trademark Myraviten D23EA (the content of vinylacetate groups was 11%) with density

$0.931 \, g/cm^3$, average value of molecular weight $M_\eta = 51500$, and melting temperature 363 K was also used.

Bis (1-methyl-1-phenyl ethyl) peroxide, dicumyl peroxide (DCP), supplied by Aldrich, was utilized.

A steel foil 70 µm thick (approximately corresponding to the USA AJS 1010 steel) was used as the substrate.

2.2. Preparation of Adhesive and Polymeric Films

DCP was introduced into a polymer melt by mixing the components in a roll-mixer for 5 min at 403 K.

Films 30–700 µm thick were prepared by hot pressing of mixtures or pure polymers between Teflon films at a temperature of 408 K under a pressure of 40 kPa for 2.5 min. The hot samples together with Teflon films were cooled to room temperature between steel plates (at an average cooling rate of about 1°C/sec), rinsed with a pure acetone, dried in a warm air flow, and stored in a desiccator.

2.3. Preparation of Steel Surface

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

2.4. Preparation of Samples of Adhering Systems

Two types of samples were prepared, namely, metal-polymer-metal and metal-polymer laminates. The polymer films with different thickness were bonded with the substrate by direct hot-pressing at a fixed temperature under a pressure of 40 kPa for a definite time in free air.

2.5. Estimate of the Gradient of Macromolecular Contact-oxidation Transformations of Adhesives

2.5.1. Measurement of Fluidity

Samples of polymer-metal type were debonded by an electrolytic method (a kind of forced cathode delamination). The sample served as a cathode in an aqueous 2% Na_2CO_3 solution with current density $2 \, A/dm^2$. There occurred an interfacial debonding of the polymer film [5]. The obtained adhesive films were cooled to the temperature of liquid nitrogen. Scraps $3-5 \, \mu m$ thick were gradually cut off by a special device at various distances from the adhesive contact surface.

The scraps were pressed into small cylindrical samples (1 mm in height and 1.5 mm in diameter) at 403 K under a pressure of 40 kPa for 1 min. The fluidity was determined by measuring the base diameter of a droplet of the molten sample (by a long-focus microscope) at a temperature of 30°C above the melting point of the adhesive in a special oven in a stream of purified nitrogen to avoid oxidation (see scheme in Fig. 1). The time function of the fluidity coefficient, $\rho(t) = d(t)/d_0$ (with $d(t)$ as the current diameter of the droplet base, d_0 the initial diameter, and t the time) was determined. The equilibrium value of the fluidity coefficient, $\rho^* = \lim \rho(t)|_{d\rho/dt \to 0}$, was calculated. This may serve as an indirect measure of viscosity of the polymer, which itself is a function of the average molecular weight of the polymer. Standard deviation of the measurements was less than 10%.
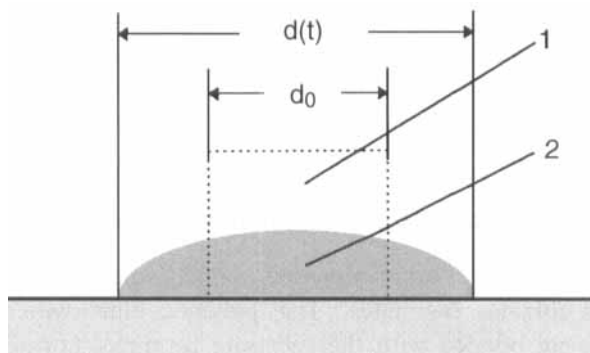
FIGURE 1 Determination of fluidity of the adhesive melt: 1 – the initial shape of a cylindrical sample and 2 – the shape of a melted droplet. Explanations in the text.

2.5.2. *Determination of Rheological Characteristics of a Cross-linking Adhesive Layer*

The shear creep of a polymer melt layer with different thickness ($b = 30 - 700\,\mu m$) directly in the process of cross-linking was studied on the basis of lap-shear substrate-polymer-substrate samples (10 mm wide and 120 mm long, length of overlap 10 mm) at a constant load P (which provided a fixed shear stress $\tau = (2.0 - 3.0) \cdot 10^2$ Pa) and a fixed temperature (see Fig. 2a). The absolute shear deformation, Δl, was measured by a long-focus microscope. From the creep-time curves of the relative shear deformation, $\gamma(t)$ ($\gamma = 1/2(\Delta l/b)$), the effective viscosity was calculated: $\mu_e(t) = \tau/\gamma^\bullet(t)$; $\gamma^\bullet = d\gamma/dt$.

The change in shear deformation of a cross-linked polymer melt layer with contact time (after termination of creep) was measured on the same samples by a gradual increase of the load, P. The initial linear region of the $\gamma(\tau)$ curves was used for calculating the shear modulus, G.

Standard deviation of the measurements for both characteristics was less than 7%.

A simplified version of capillary viscometry was also used. The time dependence of the force, P, necessary to squeeze the cross-linking polymer melt with thin substrate particles through a capillary at a steady shear rate (see Fig. 2b where $D = 9.5$ mm, $H = 13.0$ mm, $l = 15$ mm, and $d = 2$ mm) and a fixed temperature was found. The ratio $P_t/P_{t=0}$ was determined as a function of the particle content (with average diameter $7\,\mu m$); P_t denoted the force at a certain time, and $P_{t=0}$ was the initial force. Standard deviation of the measurements was about 12%.

2.6. Determination of the Average Thickness of an Adhesive Layer on the Steel Surface After Peeling

Samples of adhesive metal-polymer joints (10 mm wide and 100 mm long) were delaminated by peeling in a ZT-20 tensile testing machine at a cross-head speed of 0.8 mm/s at room temperature. A sample with a precisely-measured area (about $1\,cm^2$) was subjected to flash heating (923 K for 30 s) in the pyrolysis chamber of a Yanagimoto GCG-5DH gas cromatograph. The products of pyrolysis were detected as a cumulative peak by an ion-flame detector.
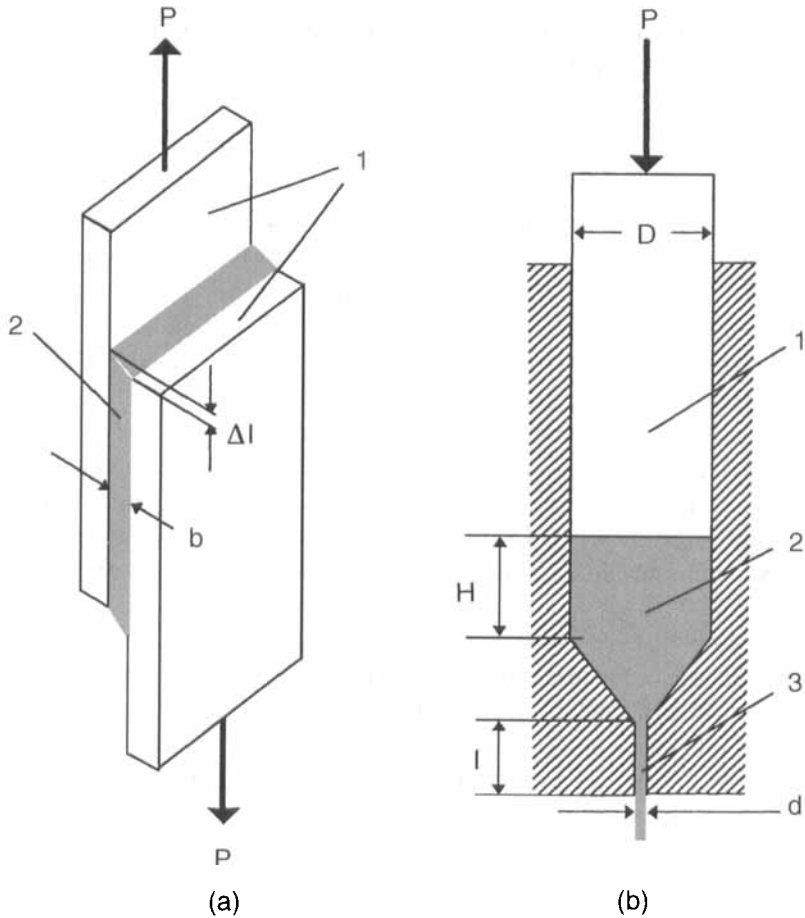
FIGURE 2   Measurement of shear creep of a polymer melt layer (a): 1 – sheets of substrate and 2 – adhesive layer, and the scheme of a capillary viscometer (b): 1 – piston, 2 – polymer melt containing thin substrate particles, and 3 – capillary. Explanations in the text.

To determine absolute values of the average thickness of the polymer, standard samples with the known polymer thickness were used. These samples were prepared by evaporating dilute solutions $(10^{-4} – 10^{-2}\%)$ of PE in toluene. The average thickness was calculated from the amount of solution on the sample surface and the area of this surface. Standard deviation of the measurements was about 20%.

The size of the experimental points in the figures corresponds approximately to the respective error bars.

3. RESULTS AND DISCUSSION

To obtain information on the influence of contact oxidation on the kinetics of peroxide-induced cross-linking of PE, the behavior of shear deformation of a thin PE layer locked between two parallel substrate surfaces was studied directly in the process of cross-linking.

The relative shear deformation, γ, as a function of time, t, is shown in Figure 3.

The dotted line corresponds to the PE melt layer without a cross-linking agent. The straight line of the function $\gamma(t)$ means that the shear rate $\gamma^{\bullet} = d\gamma/dt$ = constant and, consequently, the viscosity of the melt $\mu = \tau/\gamma^{\bullet}$ = constant. This evidences that contact oxidation does not lead to any marked changes in the molecular weight of the PE.
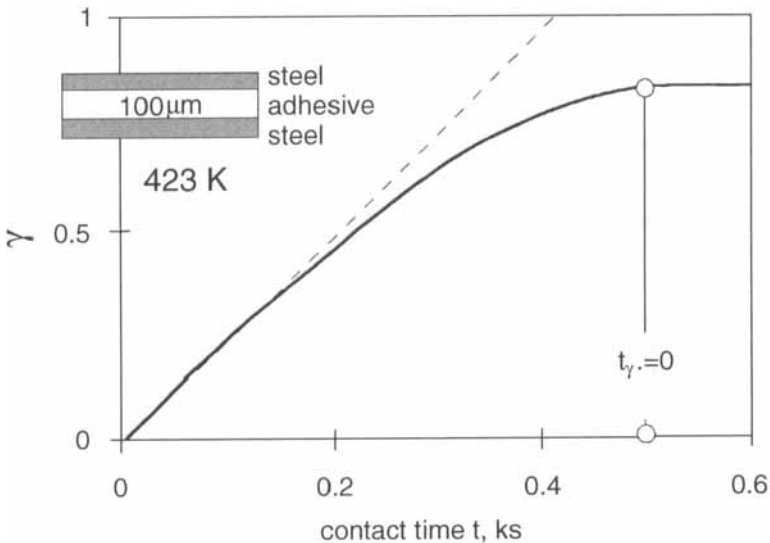

FIGURE 3   Shear creep curve of a thin polyethylene melt layer. The relative shear deformation, γ, *versus* time, t, for a pure PE (dotted line) and for a PE containing 0.5% of DCP (continuous line) with shear stress $\tau = 2.3 \times 10^2$ Pa.

The continuous $\gamma(t)$ line shows the creep behavior of a PE layer containing the cross-linking agent. It is clear from Figure 3 that $\gamma^* = d\gamma/dt$ decreases noticeably with contact time, whereas the calculated effective viscosity $\mu(t) = \tau/\gamma^*(t)$ increases, which can be explained by the cross-linking of the polymer. It can be assumed that the observed reduction in shear deformation rate of a cross-linked layer of the polymer melt is not only the result of increasing molecular weight of the polymer (by branching of macromolecules at early stages of cross-linking) and growing sizes of microgels. Actually, it also depends on the increasing density of cross-links within the network (it seems that at advanced stages of cross-linking the rupture of a continuous but poorly cross-linked network also takes place in our shear conditions).

At a certain value of contact time $(t_{\gamma^*=0})$, γ^* reaches zero (μ tends to ∞). Apparently, this is just the moment when a rather dense and resistant network begins to form.

The effective viscosity, μ (calculated from the $\gamma(t)$ experiments), as a function of the thickness b, of the cross-linking PE melt layer for several values of the contact time (Fig. 4a) shows that, starting from a sufficiently high thickness ($b^* \approx 400\,\mu m$ and more), the viscosity does not depend on b (let us designate this viscosity by μ_{b^*}). For $b < b^*$, the melt viscosity grows with decreasing thickness of the layer. The effect produced by the steel surface on the cross-linking of PE is self-evident. Even if we assume that there is neither appreciable formation of iron compounds nor diffusion of these compounds into the bulk of the polymer melt (which is typical of contact oxidation under conditions of restricted oxygen sources [2]), the catalytic effect of the substrate can manifest itself through the acceleration of peroxide decomposition and the thermal-oxidative generation of free macroradicals directly at the steel-polymer interface. The originated radicals may take part in chain-transfer reactions. The above processes can probably be responsible for the formation of the gradient of cross-linking degree and the respective melt viscosity. The experimentally-measured viscosity may be regarded as the complex average value of a certain viscosity gradient (see Fig. 5). The growth of μ with decreased thickness of the layer clearly demonstrates the existence of such a gradient.

In the case of catalytically inactive substrate (Cellophane), there is no change in viscosity with an increase in the layer thickness (Fig. 4b).

The respective values of viscosity are equal to those for the PE cross-linking far from the interface with the steel surface ($\mu_{b'}$, $b > b^*$).

The function $\mu(b)$ for $b < b^*$, in the case of the steel substrate, can be roughly approximated by straight lines (see Fig. 4a). Therefore, we can evaluate the viscosity of the cross-linking melt in the boundary layer by extrapolating the $\mu(b)$ function to $b = 0$. Let us designate this viscosity by $\mu_{b-0} \lim \mu(b)|_{b \to 0}$ (see also Fig. 5).

It should be noted that μ_{b-0} is quite a conventional characteristic, since the function $\mu(b)$ for $b < 30\,\mu m$ (30 μm is the smallest thickness of the layer which can be surely obtained in the creep experiment) may be different from linear, as shown in Figure 6. Figure 6a shows that the ratio $P_t/P_{t=0}$ for the cross-linking polymer melt containing a thin-particulate substrate (see Section 2.6) increases with increased content
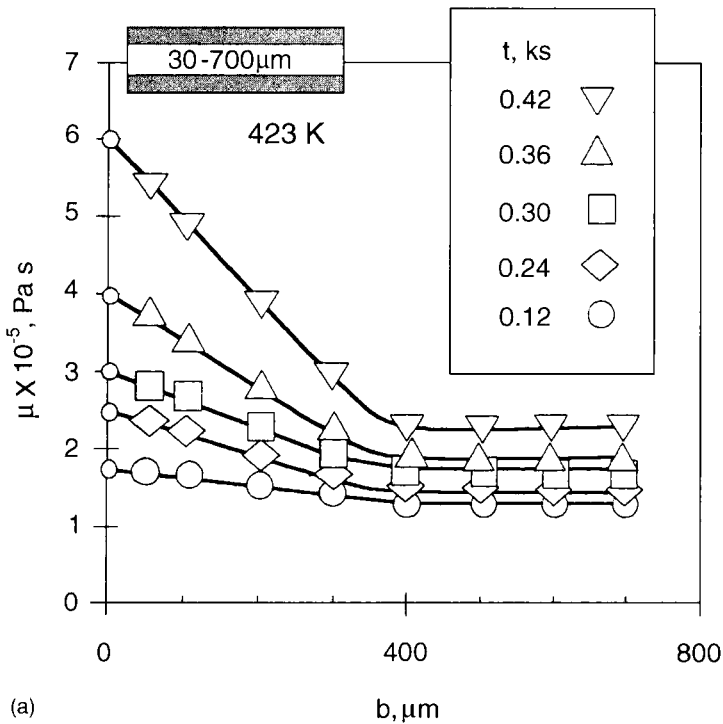

FIGURE 4 Variation of the effective viscosity, μ, with the thickness, b, of a cross-linking PE layer containing 0.5% of DCP for different contact times, t, at 423 K in contact with steel (a) and Cellophane (b).
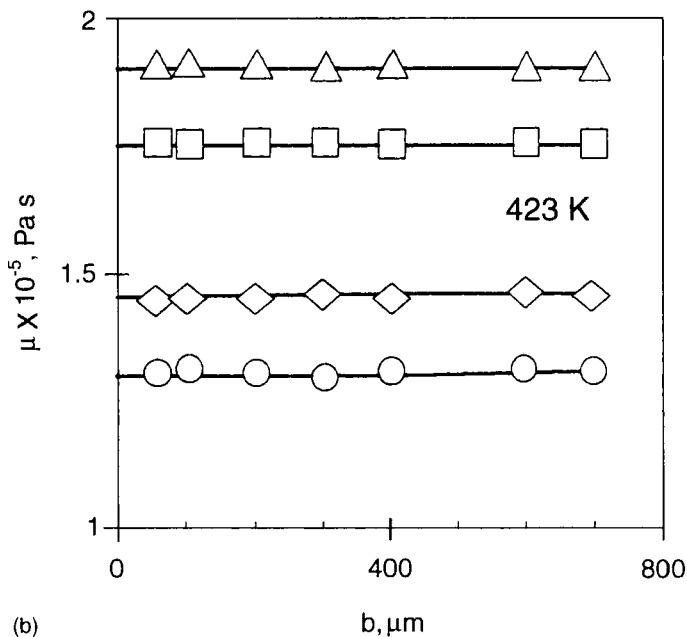
(b)

FIGURE 4   (Continued).

of the substrate only in the case of iron particles, *i.e.*, when we deal with a catalytically-active substrate[1]. In Figure 6b, based on the data of Figure 6a, the equivalent calculated average thickness, b_e, of a polymer layer between the particles was used instead of the content of iron particles. For $b_e > 6 \mu m$, the function of viscosity[1] *versus* thickness of the layer has a linear character (see Fig. 4a for comparison). For $b_e < 6\mu m$, there is a growth in viscosity with decreasing thickness of the layer. This means that the real values of viscosity in the boundary layer may be higher than the respective values $\mu_{b} = 0$ obtained by extrapolation. Nevertheless, since the extrapolation procedure was performed identically in all cases, the value of μ_b may be used as the general characteristic of catalytic cross-linking in the boundary layer.

It follows from Figure 7 that the viscosity in the boundary layer $(\mu_{b=0})$ for a certain contact duration is several times higher than that in the adhesive layer located far from the interface with the iron

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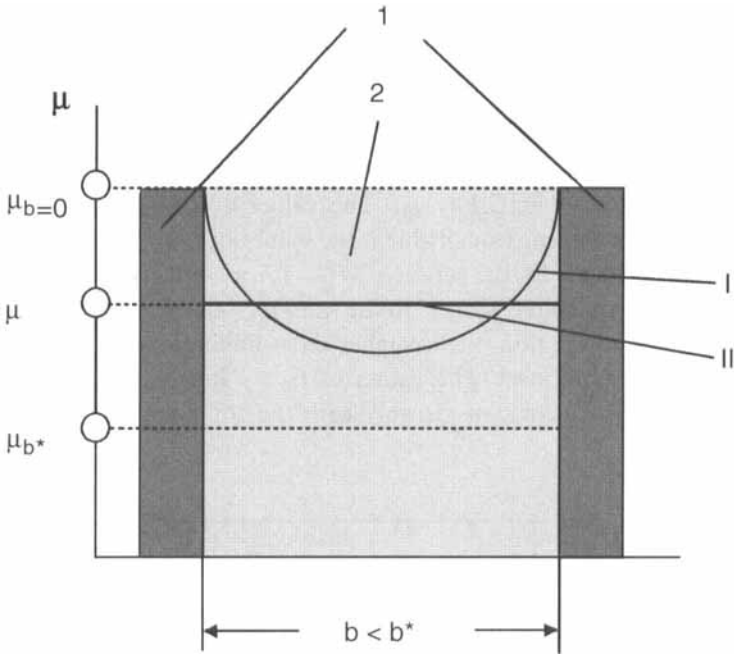[1]The ratio $P_t/P_{t=0}$ can be roughly considered to be proportional to viscosity.

FIGURE 5 Schematic representation of a hypothetical viscosity gradient (I) and the respective complex average viscosity (II) for the thickness of the adhesive layer, $b < b^*$. (1 – adherends and 2 – adhesive). Explanations in the text.

substrate (μ_{b^*}). The value of $\mu_{b=0}$ also continues to grow at a considerably higher rate.

Another evidence of a more rapid cross-linking at the interface with steel is the decrease in contact time which corresponds to a ceasing of creep $(t_{\gamma^*=0})$ with a decrease in the thickness of the adhesive layer (Fig. 8).

The end of creep does not yet mean the termination of cross-linking. This only indicates the formation of a strong continuous network of the cross-linking polymer. In order to obtain information on the possible subsequent cross-linking after the end of creep $(t > t_{\gamma^*=0})$, the shear modulus, G, of the polymer layer was calculated as a function of contact time. We failed to detect any increase of the modulus with increasing contact time; the experimentally-measured values of G did not change up to 0.6 ks of the extra contact time. It is most probable that the density of cross-links is not high enough to impose sufficient restrictions on the segmental mobility of the PE chains.

The variation of these equilibrium values of G with the polymer layer thickness, b, is shown in Figure 9. The general character of the $G(b)$ curves is similar to that of $\mu(b)$ (see Fig. 4a). Both quantities grow with decreasing b (at $b < b^*$). The only difference is that G changes more sharply. Thus, we used $\ln G$ for determining the extrapolated modulus $(G_{b=0} = \lim G(b)|_{b \to 0})$. The values of G_{b^*} are presented in Table I. As is evident from Table I, the values of $G_{b=0}$ are higher than those of G_{b^*}; whereas the ratio $G_{b=0}/G_{b^*}$ for a contact temperature of 423 K is approximately similar to the ratio $\mu_{b=0}/\mu_{b^*}$ (see Fig. 7). This is another demonstration of the higher cross-linking degree of PE near the interface with steel. The values of $G_{b=0}$ and G_{b^*}, as well as the ratio $G_{b=0}/G_{b^*}$, grow considerably with the contact temperature (see Tab. I).
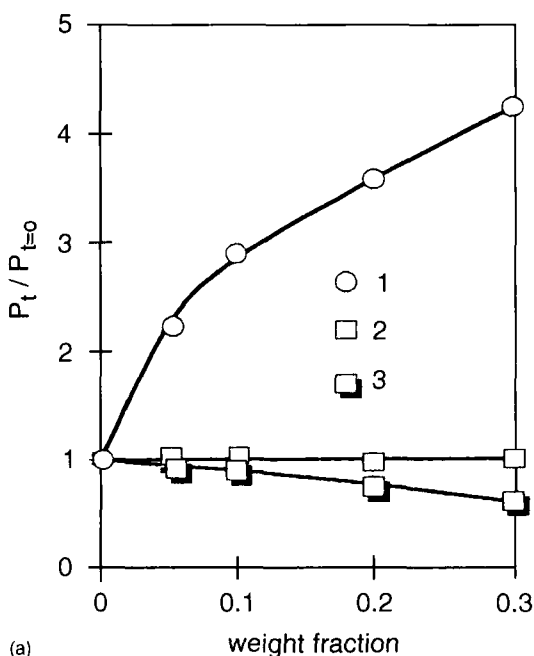

(a)

FIGURE 6   Variation of the ratio $P_t/P_{t=0}$ for the cross-linking polymer melt with a content of thin-particulate substrate: 1 – iron, 2 – silicate glass, and 3 – quartz; at a content of DCP 0.5%, premature contact time 60 s, and a contact temperature of 423 K (a). The ratio of $P_t/P_{t=0}$ for the PE-iron system as a function of the equivalent calculated average thickness of a polymer layer between particles, b_c (b). The level of the dotted line corresponds to the ratio for a pure PE ($b_c \to 0$).
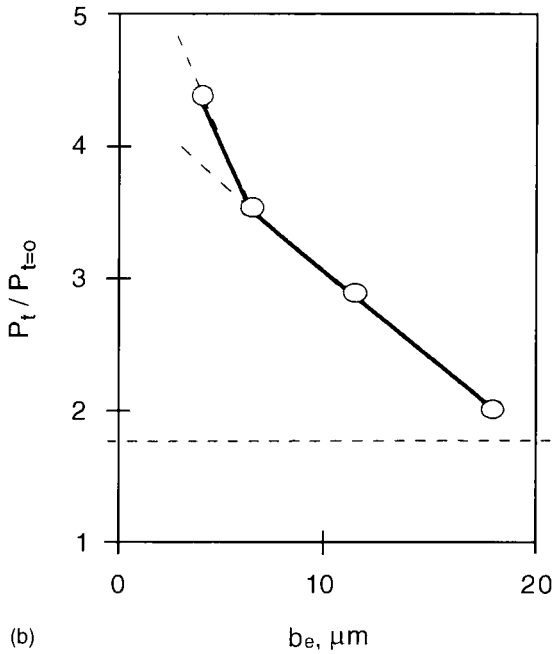
(b) b_e, μm

FIGURE 6   (Continued).

TABLE I   Shear modulus, G, of the cross-linking PE layer in contact with steel at various contact temperatures (the content of DCP is 0.5%)

T, K	G, $MPa \cdot 10^4$		
	G_b.	G_{b-0}	$G_{b=0}/G_b$.
423	8 (1.0)[a]	30 (1.0)	3.8
453	11 (1.4)	90 (3.0)	8.2
483	14 (1.8)	164 (5.5)	11.7

[a] In brackets: the ratio to the value of G at 423 K.

It was of special interest to look for certain evidence of the existence of a gradient of contact oxidation transformations (scission or cross-linking) of macromolecules also for an adhesive without peroxide. Our attempts to do this by using the shear creep method failed. Apparently, the contribution of nonactivated contact oxidation to the closed adhering system (metal-adhesive-metal) with a restricted source of
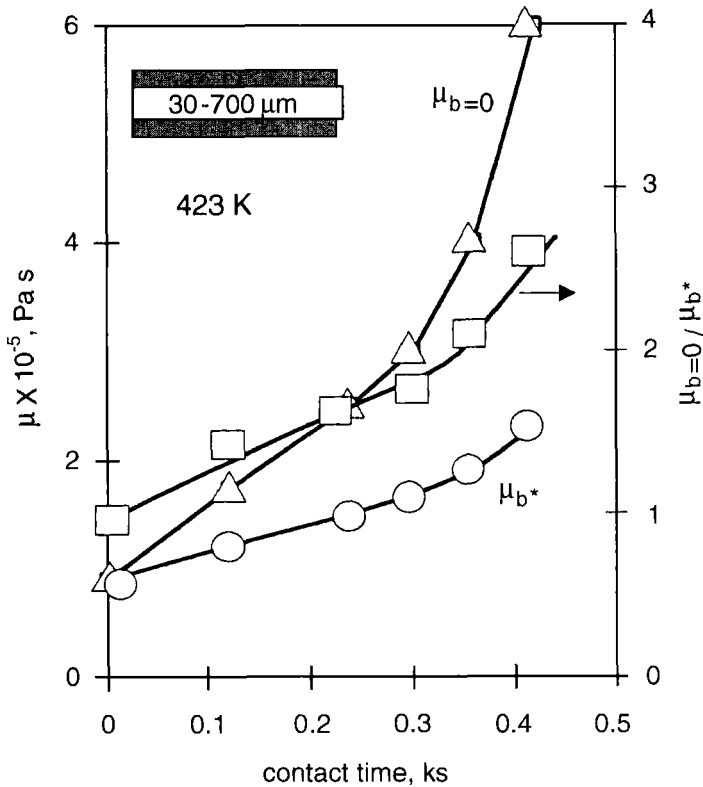
FIGURE 7   Effective viscosity, $\mu_{b'}$, and $\mu_{b=0}$ and the ratio, $\mu_{b=0}/\mu_{b'}$, as a function of contact time (from the data of Fig. 4).

oxygen[2] is quite negligible. We expected the formation of gradients for the open adhering system (polymer-metal) with free access of oxygen through the polymer melt layer [1].

The shear creep technique was not acceptable for this type of adhering system. Therefore, we used the equilibrium fluidity coefficient, ρ^* (for thin adhesive layers scraped at a certain distance from the interface), as an indirect attribute, which can characterize the general trend of macromolecular transformations. The growth of ρ^* in

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[2]For such systems, only the oxygen captured at the interface during initial contact stages and the oxygen which is adsorbed or chemisorbed by the oxide of the metal surface can take part in the contact oxidation processes [3].
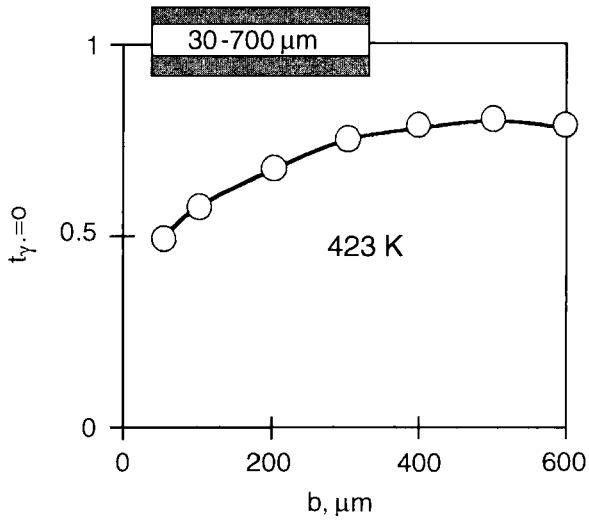
FIGURE 8 Variation of $t_{\gamma^\bullet=0}$ with the thickness of a cross-linking PE layer.
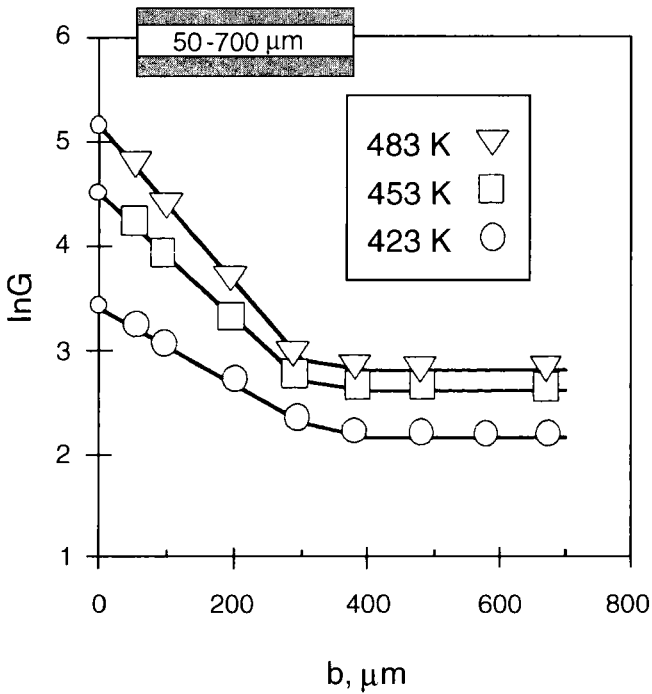

FIGURE 9 Variation of the shear modulus, G, with the thickness, b, of a cross-linking PE layer containing 0.5% of DCP at 423 K in contact with steel (contact time 1.0 ks).

comparison with its initial value shows that the destructive scission of macromolecules prevails, while the decrease in ρ^* indicates that the cross-linking is predominant. The permanence of ρ^* most probably evidences the absence of any macromolecular changes.

It is seen from Figures 10–12 that under conditions of contact oxidation a peculiar gradient of macromolecular transformation arises. Within the adhesive layers located far enough from the interface, we observe the increase of ρ^* with an increase in the contact
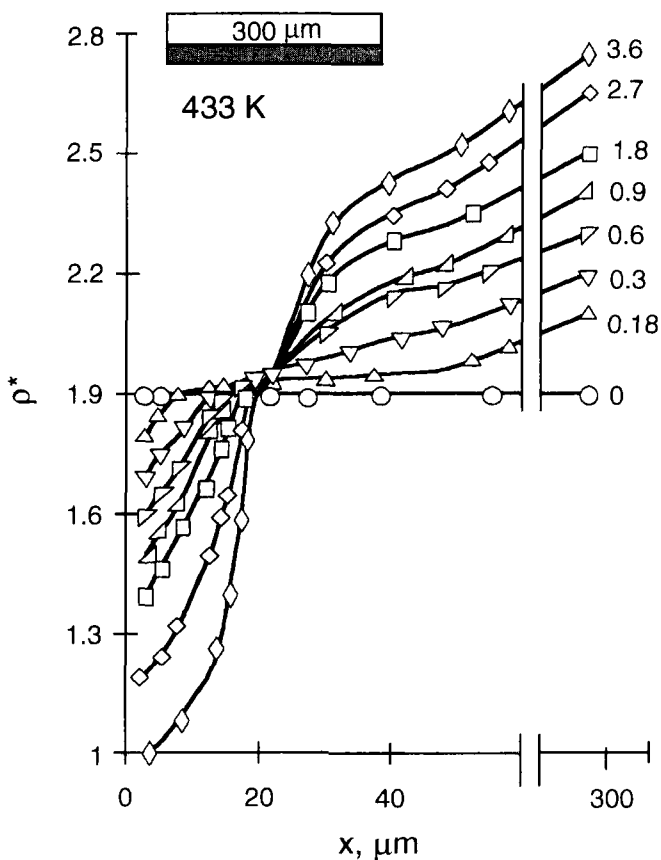

FIGURE 10   Fluidity coefficient, ρ, of EVAC in contact with steel (figures by the curves denote contact time, ks) as a function of the distance, x, from the interface.
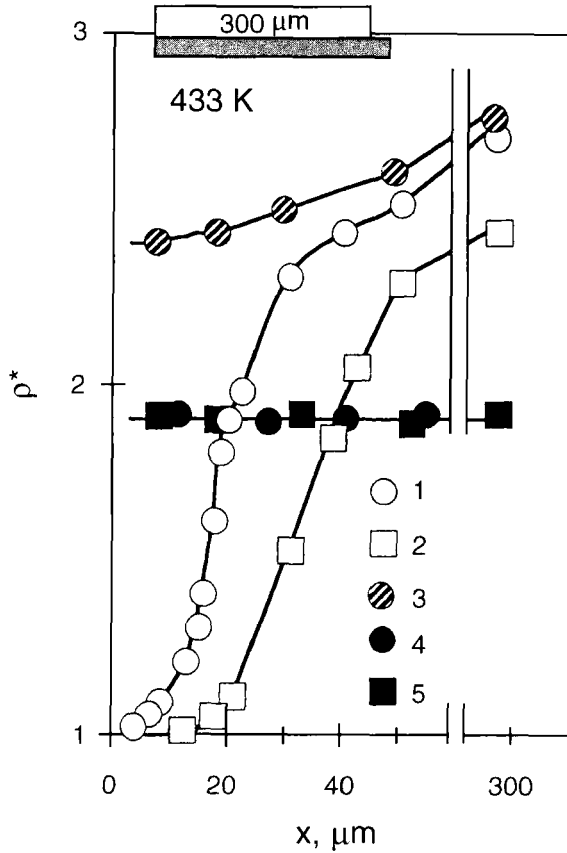
FIGURE 11   Variation of the fluidity coefficient, ρ, of EVAC (1, 3 and 4) and PE (2 and 5) in contact with steel (contact time 3.6 ks – 1, 2 and 3; no contact – 4 and 5) as a function of the distance, x, from the interface.

time, which means that the destruction is predominant here. However, there is a decrease in ρ^* with contact time in the adhesive layers which are close to the interface. This results from the fact that the steel surface compounds [1] and the iron compounds, which diffuse into the bulk of the polymer [2], catalytically affect the oxidative cross-linking of the adhesive. In the adhesive layers located very close to the interface ($x \approx 5\,\mu m$) $\rho^* = 1$, which indicates that the adhesive totally loses its fluidity due to formation of a continuous network of cross-links.
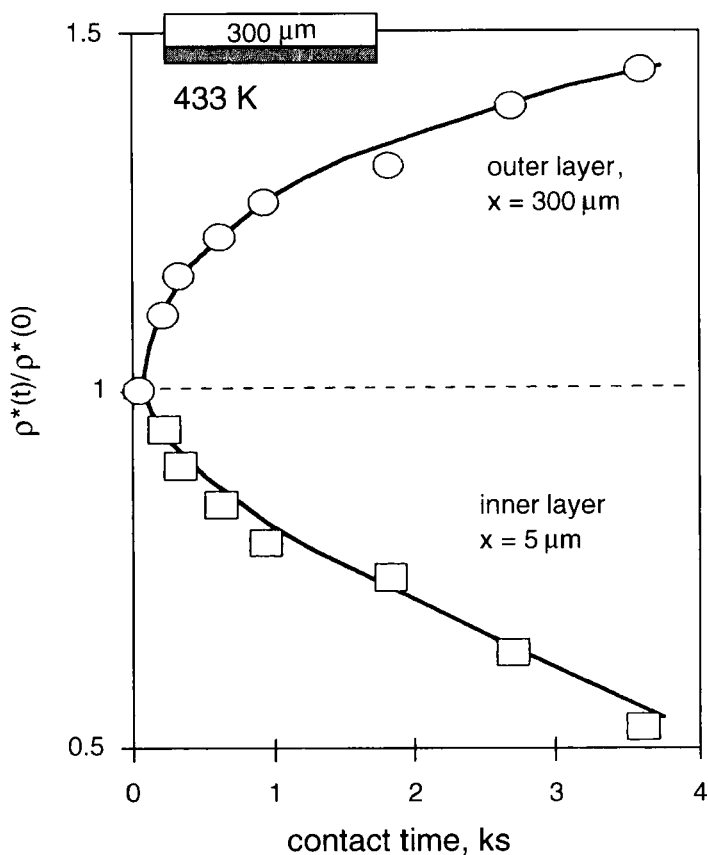
FIGURE 12   Ratio of fluidity coefficients, $\rho^*(t)/\rho^*(0)$, as a function of contact time at 433 K for the outer (at a distance from the interface, x, of about 300 μm) and the inner (a distance from the interface, x, about 5 μm) layers. $\rho^*(t)$ is the fluidity coefficient at a certain fixed contact time and $\rho^*(0)$ is the initial value of the fluidity coefficient (data from Fig. 10).

In the case of the catalytically-inactive substrate Teflon, the oxidative destruction prevails over the whole thickness of the PE layer (see curve 3 in Fig. 11).

From the data in Figure 11 we determine the value of the x_0 coordinate at which the curve $\rho^*(x)|_{t=\text{const}}$ crosses the curve $\rho^*(x)|_{t=0}$; whereas x_0 is equal to the thickness of the adhesive layer, which is located near the interface and where the cross-linking predominates. As is evident from Figure 13, there is a certain growth of x_0 with an

increase in the contact time. The average value of the thickness, h, of the adhesive layer remaining on the steel surface after peeling also grows with the contact time (Fig. 13).

The ratio x_0/h decreases considerably with t. However, even for a large contact time, the values of x_0 are still higher than h. From this it follows that the front of cohesive fracture in the adhesive runs far from the x_0 coordinate in the cross-linked part of the adhesive.
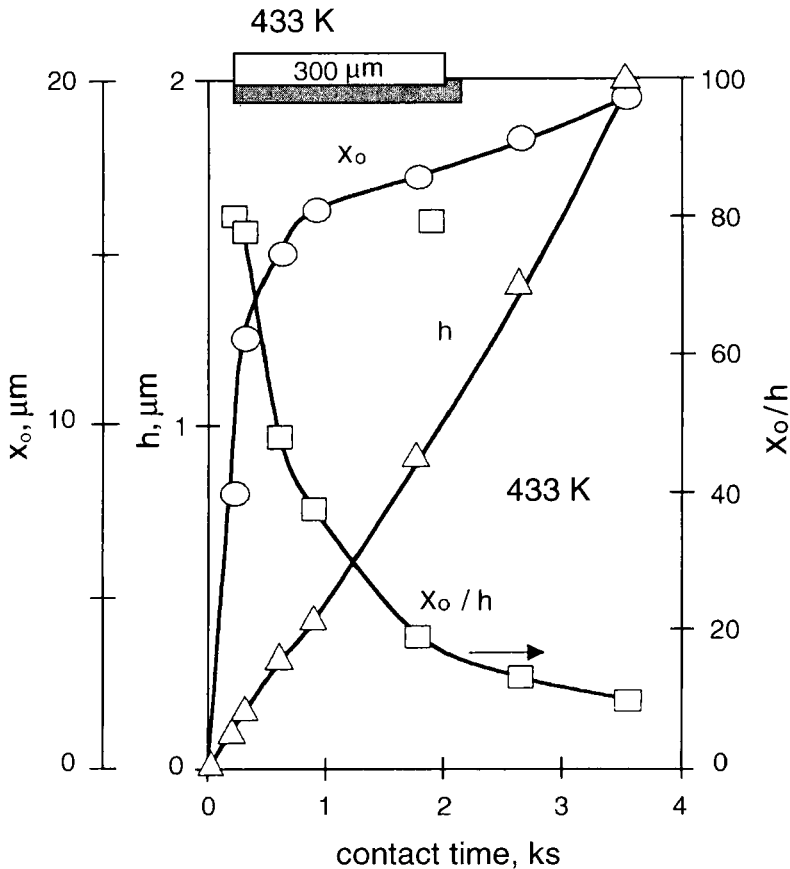

FIGURE 13   Values of x_0 (the distance between the interface and a layer in which $\rho^*(t) = \rho^*(0)$), h (the average thickness of a cohesively-fractured layer of the adhesive remaining on the metal surface), and the ratio, x_0/h, *versus* contact time, t, with EVAC as the adhesive, steel as the substrate, and a contact temperature of 433 K.

4. CONCLUSIONS

A gradient of cross-linking degree develops during adhesive interaction between the organic peroxide-containing polyethylene melt and steel, which results from the catalytic effect produced by the steel surface on the peroxide-induced cross-linking of polymers in the conditions of contact oxidation.

In the case of catalytically-inactive substrate (Cellophane), there is no gradient at all.

A gradient of macromolecular transformations originates also upon adhesive contact with steel of polyethylene and ethylene-vinylacetate copolymer which do not contain peroxide. In the adhesive layers located near the adhesive interface with the steel substrate, catalyzed oxidative cross-linking prevails. Within the adhesive layers located far enough from the interface, oxidative destruction is dominant.

For a catalytically inert substrate, Teflon, the oxidative destruction prevails over the whole thickness of the polymer layer.

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