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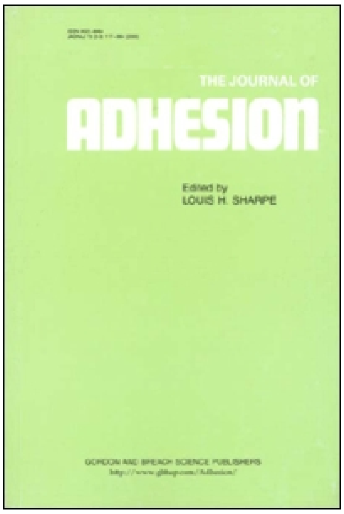

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Kinetics of Adhesion Interaction of Polyolefins with Metals Under Conditions of Contact Thermooxidation

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

III. Effect of Organic Peroxides

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The development of peel strength of adhesive joints between a PE containing organic peroxide (dicumyl peroxide) and steel has been studied. It has been found that the kinetics of this process are controlled by the contact oxidation processes in a thin boundary layer. The peel strength, A, as a function of the contact time, t, is determined by the content of dicumyl peroxide, c_{per}, in the adhesive, contact temperature, T, and the content of oxygen in the contacting environment. The value of A reaches its maximum, $A_{\max}$, at a certain contact time, $t_{A\max}$.

The kinetic characteristics $A_{\max}$ and $t_{A\max}$ as well as the initial growth rate of $A, A^{\bullet}_{t=0} = \lim dA/dt|_{t=0}$, are determined by c_{per} and T. There is a growth of $A_{\max}$ and $A^{\bullet}_{t=0}$ with c_{per} and a decrease of $t_{A\max}$ with T.

The shape of $A(t)$ curves for a peroxide-containing PE, similar to a pure PE, is defined by the competitive influence of two principal tendencies in contact oxidation: oxidative cross-linking inducing the growth of A and oxidative destruction causing the reduction of A. There is a growth of the output of contact oxidation reactions with the increase of c_{per}. The empirical constants of an equation describing the $A(t)$-functions are calculated and the efficiency of the use of peroxides for promoting the PE-adhesion is estimated.

It has been proved that the peel strength at a fixed contact time is determined by the ratio of the gel-fraction in the polymer layer, c_{gel}, which is a measure of the outcome of the oxidative cross-linking, and the content of extractable low-molecular products, c_{lm}, characterizing the effect of oxidative destruction.

Keywords: Polyethylene; steel; organic peroxide; adhesive interaction; contact thermo-oxidation; peel strength; kinetics

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*Corresponding author.

1. INTRODUCTION

In our previous studies we have discussed the kinetics of adhesive interaction processes between a "pure" polyethylene and steel under control of the catalytic contact oxidation [1, 2]. In this paper, we study and analyze generally the same characteristics of a polyethylene containing organic peroxide.

We have proved long ago [3, 4] that the strengthening of adhesive joints between the polyethylene and steel by introducing organic peroxides into polymer is very promising. Then this method became the matter of further investigation [5–9].

Since the reinforcement of the PE-steel adhesive joints is mainly a result of strengthening of the weak boundary layer of PE [10], we can logically suppose that peroxides act as simple cross-linking agents for PE* without any relevance to contact oxidation. However, our studies show that the adhesive ability of a peroxide-containing PE becomes particularly apparent in the case of metal substrates, whose surface compounds catalyze the thermal decomposition of peroxide together with the contact oxidation of PE [7, 8], and slightly depends on the chemical nature of the peroxides [9]** .

The aim of this study is to find out more about the mechanism of adhesive interaction between the PE and steel in the presence of organic peroxide, mainly paying attention to the process kinetics.

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2. EXPERIMENTAL DETAILS

2.1. Materials

Unstabilized low-density polyethylene of trade mark 108-02-20 (obtained from the Novopolotsk Chemical Enterprise) with the following characteristics was used [1, 2]: 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

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*Peroxides are known as efficient cross-linking agents of polyolefins [11].

**The following peroxides were investigated: isopropylbenzene hydroperoxide, bis-*ter*-butyl peroxide, and dicumyl peroxide.

per 100 C atoms of a chain), melting temperature 378 K, temperature of intensive oxidation 488 K (both according to DTA data).

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

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

2.2. Preparation of DCP Containing Adhesive and of Polymeric Films

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

Films of thickness 50 – 700 μm were prepared by hot pressing of mixtures between Teflon films at a temperature of 408 K and under a pressure of 40 KPa for 2.5 min. The hot specimens together with Teflon films were cooled to room temperature between steel plates (the average rate of cooling was about 1°C/sec.), then rinsed with a pure acetone, dried in a warm air flow, and stored in a desiccator.

It was confirmed by DSC and TG tests (with a Mettler TA 4000 scanning calorimeter at a heating rate of 10°C/min) that an intensive thermal decomposition of DCP in the molten PE took place within the temperature region 451 – 455 K and the half-life period of DCP at 403 K was about 100 min. Thus, the time-temperature prehistory of treatment corresponding to the procedures of mixing and subsequent pressing caused neither significant losses of DCP nor premature cross-linking of PE.

2.3. Steel Surface Preparation

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 a current density of 10 A/dm^2 for 2.5 min. as a cathode and then for 0.5 min. as an anode. The steel specimens were rinsed in hot (363 K) distilled water and then dried in a filtered warm air flow (353 K). Further on, the specimens were kept in a desiccator over anhydrous $CaCl_2$ for no more than 24 hours before use. The wetting angle of the prepared steel surface by water was less than 8 – 10°.

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2.4. Preparation of Samples of Adhering Systems

Most of the samples were metal-polymer-metal laminates. The polymer films of 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, mostly in the air. Oxygen and argon were also used as environments. A specially-designed, membrane-type reactor was used for this purpose [12].

2.5. Studies of Chemical Transformations of Adhesives

The laminated specimens were debonded by an electrolytic method (a kind of forced cathode delamination). The specimen served as a cathode in aqueous Na_2CO_3 solution (2%) with a current density of 2 A/dm^2. There occurred an interfacial debonding of the polymer film [13]. The adhesive films obtained were used for analysis.

The IR spectra (spectrophotomer Specord IR-75) for the adhesive films were obtained. The ratio, D^*_{cg}, between the optical density of the carbonyl group absorption in the region 1710–1740 cm^{-1} and that in the region 4350 cm^{-1} (internal standard) was determined. Standard deviation of the measurements was less than 10%.

Gel-fraction (c_{gel}) was determined by extraction of samples by boiling toluene (in a stream of nitrogen). The content of a low-molecular part of the polymer (c_{lam}) was determined by a mild extraction of samples by boiling hexane. Standard deviation was about 10–15%

2.6. Evaluation of Peel Strength of Adhesive Joints

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

In most cases, a visual adhesive failure was observed. In fact, a cohesive mode of failure (fracture in the weak boundary layer of a

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polymer) actually took place. The thickness of the residual polymer layer on the metal surface determined by reactive (pyrolytic) gas chromatography [14] was no less than 10 – 50 nm, on the average.

The size of the experimental points in the figures corresponds approximately to the respective error bars (where the error bars are not shown specifically).

3. RESULTS AND DISCUSSION

Variations of the peel strength, A, of the PE-steel joints with the contact time, t, for various DCP-contents, c_{per}, in the adhesive and different contact temperatures are presented in Figure 1. The value of A reaches its maximum, $A_{\max}$, at a certain contact time, $t_{A\max}$. The kinetics characteristics, $A_{\max}$ and $t_{A\max}$, as well as the initial growth

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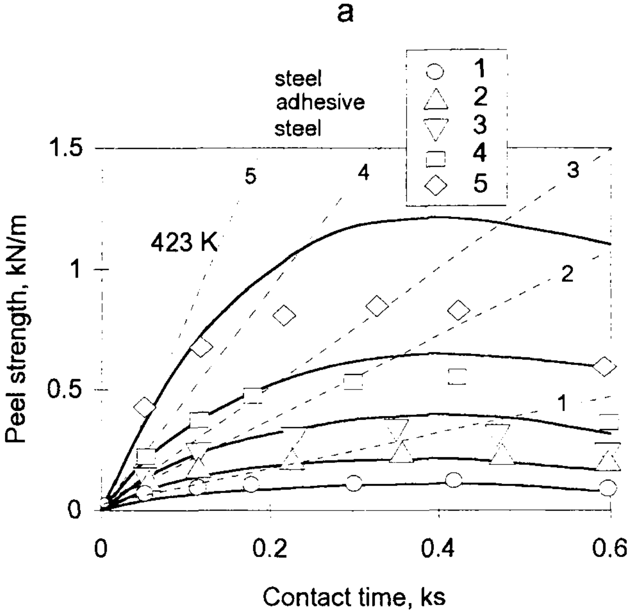

FIGURE 1 Peel strength, A, of adhesive PE-steel joints *versus* contact time, t, for different contact temperatures: $T = 423$ (a), 453 (b) and 483 K (c). The content of DCP in the adhesive, $c_{\text{per}} = 0$ (1); 0.2 (2); 0.5 (3); 1.0 (4) and 2.0% (5). The symbols denote experimental points, while continuous lines correspond to the calculated $A(t)$ curves. The slope of dotted lines shows the initial growth rate of A: $A^{\bullet}_{t=0} = \lim dA/dt|_{t=0}$.

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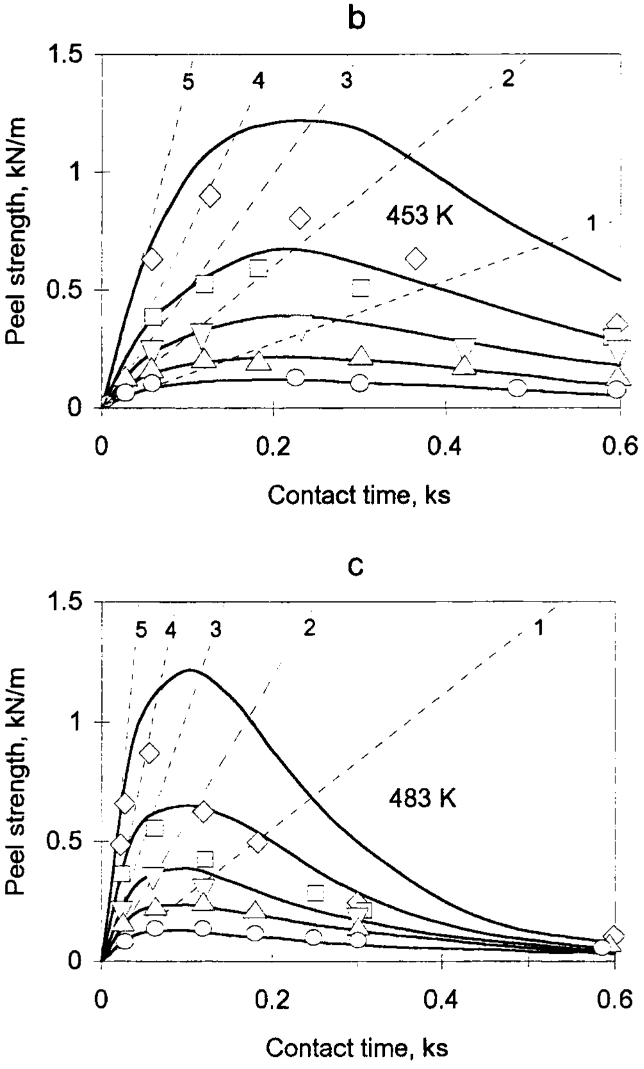

FIGURE 1 (Continued).

rate of A, $A^{\bullet}_{t=0} = \lim dA/dt|_{t=0}$, are determined by c_{per} and the contact temperature, T. Figure 1 shows the increase of $A_{\max}$ and $A^{\bullet}_{t=0}$ with c_{per} and the decrease of $t_{A\max}$ with T.

$A_{\max}$ and $A^{\bullet}_{t=0}$ increase significantly with growing oxygen content in different contact media (Fig. 2).

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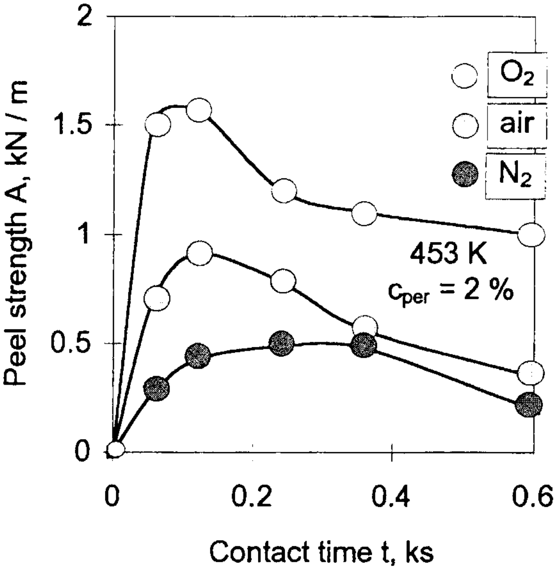

FIGURE 2 Peel strength, *A*, of adhesive joints between a peroxide containing PE and steel *versus* contact time, *t*, in contact media with different content of oxygen.

The process of accumulation of carbonyl groups in the PE layer during oxidation on the steel surface (catalytically-active substrate) and on the surface of SiO_2-coated steel (inactive substrate) is faster for the polymer with peroxide (Fig. 3).

As seen from Figure 4, if the adhesive with peroxide is thermally treated prior to contact, we observe a sharp drop in the peel strength. Most probably, it is due to consumption of peroxide in the cross-linking reactions of the PE itself (compare curves 1 and 2). The subsequent extraction of the soluble residues leads to a further decrease of the peel strength *A* (curve 3). Introducing some fresh DCP by diffusion, we can restore the adhesiveness of the adhesive (curve 4), despite a decrease in fluidity of the cross-linked polymer melt. This Figure shows that only direct participation of the peroxide in the formation of adhesive joints during the contact oxidation yields a significant increase in the joint strength.

The gel-fraction, c_{gel}, in the polymer layer after its contact with metal is used as a measure of the outcome of oxidative cross-linking. The content of extractable low-molecular products, c_{lm}, characterizes

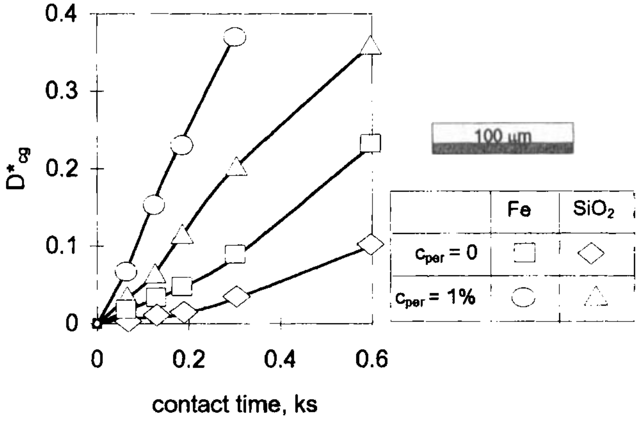

FIGURE 3 Ratio, D^*_{cg}, of the optical densities of absorption of carbonyl groups and in the region 4350 cm^{-1} (internal standard) for the PE layer *versus* contact time on the steel surface (Fe) and the quartz coated steel (SiO$_2$).

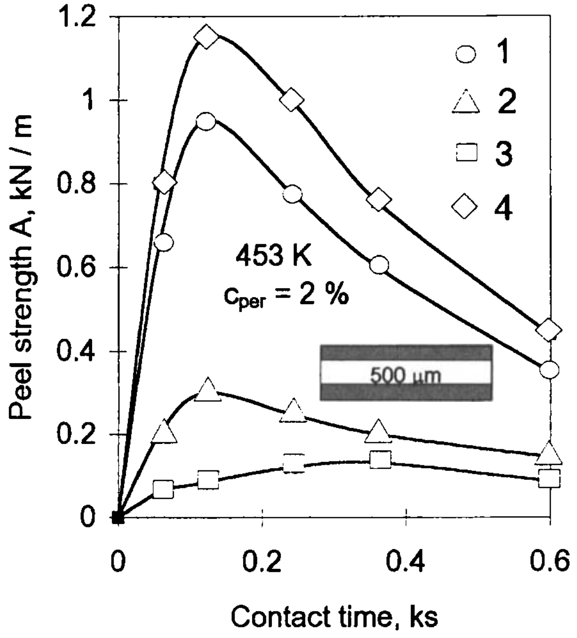

FIGURE 4 Peel strength – contact time curves of adhesive PE-steel joints for various manipulations with the adhesive prior to contact: no manipulations, adhesive contains 2% of DCP (1); adhesive containing 2% of DCP was kept for 1.2 ks at 423 K (2); the same as in (2) with a subsequent extraction of soluble DCP residues (3); the same as in (3) with a subsequent introduction of 0.7% of DCP through diffusion from solution.

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the effect of oxidative destruction. Figure 5 indicates that both these values, c_{gel} and c_{lm}, increase with the contact time and the content of peroxide.

It is important to note that, unlike the $A(t)$ curves (see Fig. 1), $D^*_{\text{cg}}(t)$ curves (see Fig. 3) as well as $c_{\text{gel}}(t)$ and $c_{\text{lm}}(t)$ curves (see Fig. 5) have no maximum. As we have reported earlier [1], taking into account the actual cohesive mode of fracture within the thin boundary layer of adhesive, the shape of $A(t)$-curves for the adhesive joints between a pure PE and steel is defined by the competitive effect of two main trends of the contact oxidation, namely, the oxidative cross-linking causing the increase in A and the oxidative destruction causing the decrease in A. The appearance of a maximum on the $A(t)$ curves suggests that the process of oxidative cross-linking prevails only at the beginning of the contact course (until the maximum is reached).

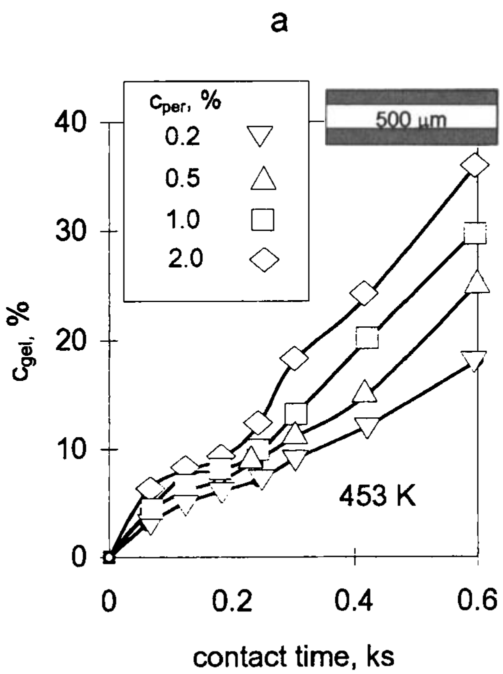

FIGURE 5 Gel fraction, c_{gel}, (a) and content of low-molecular compounds, c_{lm}, (b) after contact with steel in a peroxide-containing adhesive layer *versus* contact time.

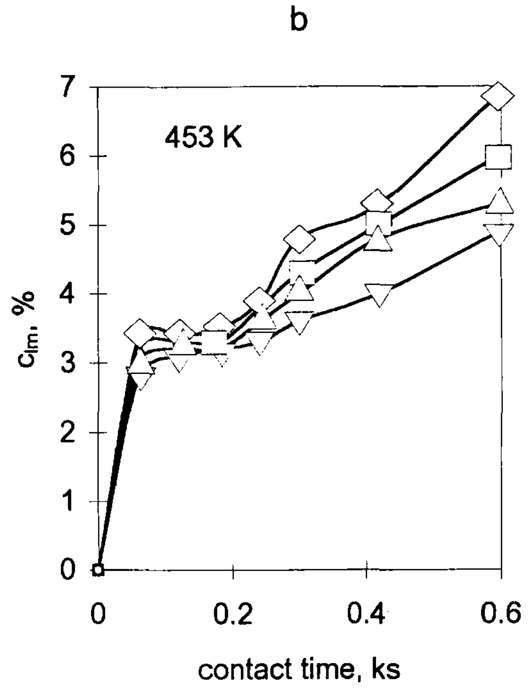

FIGURE 5 (Continued).

Consequently, a certain A-value should be determined by the respective ratio $c_{\text{gel}}/c_{\text{lm}}$. Indeed, as is evident from Figure 6, the experimental data satisfy the expression

$$A = Kc_{\text{gel}}/c_{\text{lm}}^{\alpha} \tag{1}$$

where K and α are empirical constants.

The content of low-molecular products of the contact oxidation, c_{lm} ($\alpha \approx 3.6$), affects the peel strength, A, more seriously than the gel-fraction, c_{gel}. The constant K increases with the content of peroxide in the adhesive (Fig. 7).

All the above observations show that the competitive effect of oxidative cross-linking and destruction that determine most seriously the kinetics of formation of the strength of adhesive joints between a pure PE and steel [1] is valid also for the case of PE with peroxide. It is

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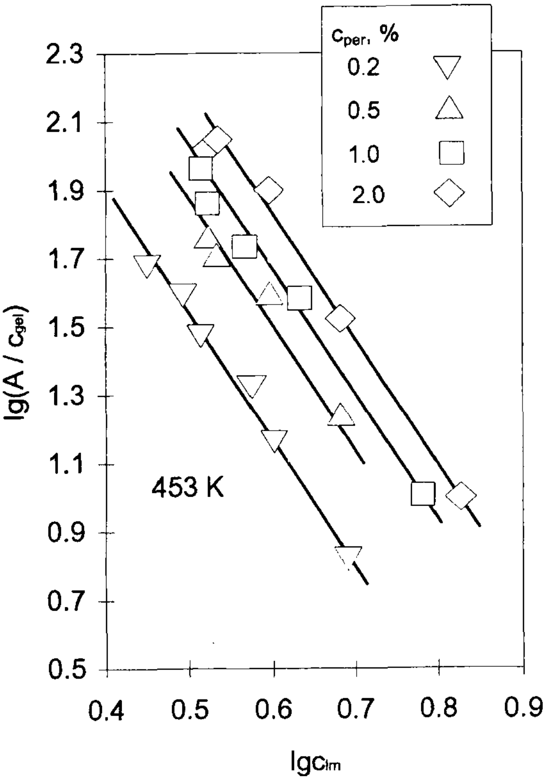

FIGURE 6 Correlation between experimental values of A, c_{gel} and c_{lm}.

a substantial reason for applying the same dogmas to the description of the kinetic curves $A(t)$.

Here we can use the following equation [1]:

$$A(t) = A_\infty [\exp(-k_2 t) - \exp(-k_1 t)] \qquad (2)$$

where k_1 and k_2 are the rate constants of the change in A-values resulting from the oxidative cross-linking (process I) and oxidative destruction (process II), respectively, while A_∞ is a constant equal to the value of A at the completion of each process.

Taking into account Eq. (2), we introduce several particular characteristics [1]: A_{max} is the peel strength at its maximum; $t_{A\max}$ is the contact time necessary to reach A_{max} and $A^\bullet_{t=0} = \lim dA/dt\,|_{t=0}$ is

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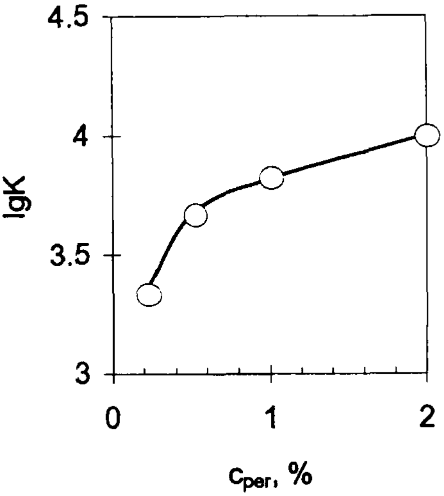

FIGURE 7 Dependence of K (see Eq. (1)) on c_{per}.

the initial growth rate of A. According to Eq. (2), these characteristics are correlated as follows: $A^{\bullet}_{t=0} = \Delta k A_{\infty}$, where $\Delta k = k_1 - k_2$; $t_{A\max} = \ln \chi_k / \Delta k$ (where $\chi_k = k_1/k_2$) and $A^{\bullet}_{t=0} = A_{\infty} \ln \chi_k / t_{A\max}$.

Since we can approximate the experimental points $A^{\bullet}_{t=0} = (t_{A\max})$ by straight lines (Figs. 8 and 9), we can speak here about the compliance with the expression $A^{\bullet}_{t=0} = A_{\infty} \ln \chi_k / t_{A\max}$.

The linear shape of the contact temperature functions $A^{\bullet}_{t=0}$ (Fig. 10) shows that, according to $A^{\bullet}_{t=0} = \Delta k A_{\infty}$, the temperature function of $\Delta k = k_1 - k_2$ can be characterized by the efficient activation energy, $E = 38 \pm 2$ kJ/mol, for all of the studied range of peroxide content, c_{per}, in the adhesive.

The experimental points of $A^{\bullet}_{t=0}$ (c_{per}) also can be approximated by straight lines (Fig. 11). This approximation is given by

$$A^{\bullet}_{t=0} = A^{*\bullet}_{t=0}\,(1 + \beta c_{\mathrm{per}}) \tag{3}$$

where β is an empirical constant (here and below, the parameters corresponding to $c_{\mathrm{per}} = 0$ are designated by *).

The analysis of the $(A)t$-curves carried out earlier [1] shows that $\chi_k = (k_1/k_2) = \mathrm{const}$ for all of the range of contact temperature, T, while $\Delta k = k_1 - k_2$ is constant only for a certain fixed T. Let us assume

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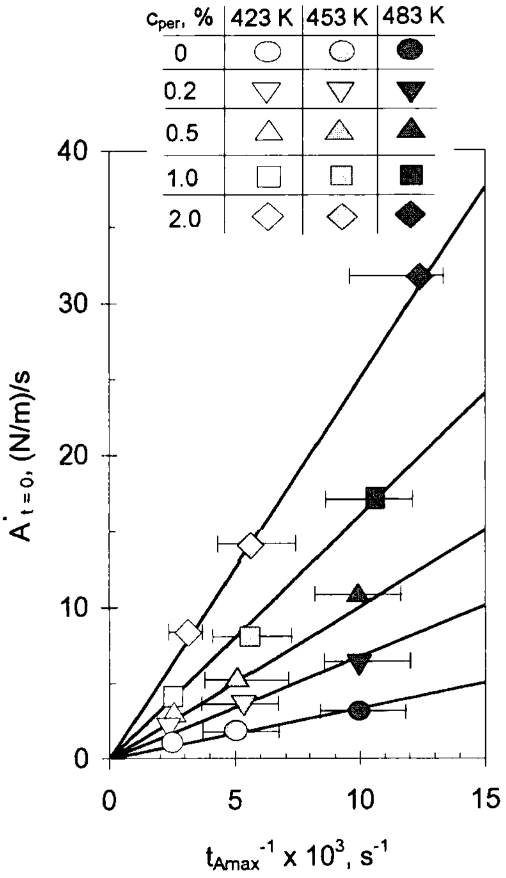

FIGURE 8 Correlation between $A^{\bullet}_{t=0}$ and $t_{A\max}$ (contact in air).

that the presence of peroxide does not affect essentially the main features of the kinetics and that the growth of c_{per} causes only some increase in the output of the contact oxidation reactions, which sequentially determines the growth of A_{∞}.

Thus, according to the above expression $A^{\bullet}_{t=0} = \Delta k A_{\infty}$, we have

$$A^{\bullet}_{t=0} = \Delta k A_{\infty}(c_{\text{per}}) \tag{4}$$

$$A^{*\bullet}_{t=0} = \Delta k A^{*}_{\infty} \tag{5}$$

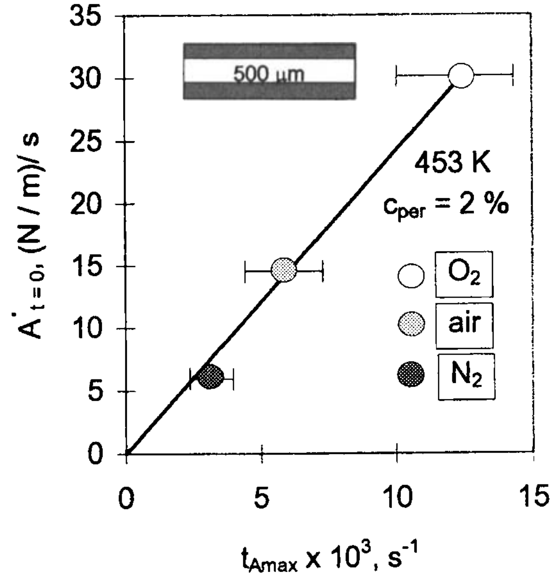

FIGURE 9 Correlation between $A^{\bullet}_{t=0}$ and t_{Amax} (contact in oxygen, air and nitrogen).

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Combining Eqs. (3), (4) and (5), we obtain

$$A_{\infty} = A^{*}_{\infty}\,(1 + \beta\, c_{\text{per}}). \tag{6}$$

There are several possibilities to find the constant, β, necessary for calculation of $A_{\infty}(c_{\text{per}})$.

First of all, it can be determined from Eq. (3) as

$$A^{\bullet}_{t=0}\,/A^{*\bullet}_{t=0} = (1 + \beta c_{\text{per}}) \tag{3}$$

The respective values of the ratio $A^{\bullet}_{t=0}/A^{*\bullet}_{t=0}$ for various c_{per} can be seen in Table I.

Besides, we can find β by the following equation [1]:

$$A^{\bullet}_{t=0} = A_{\infty} \ln \chi_k/t_{A\max} \tag{7}$$

Substituting Eq. (3) into Eq. (7) we have

$$A^{\bullet}_{t=0} = A^{*}_{\infty}(1 + \beta c_{\text{per}}) \ln \chi_k/t_{A\max} \tag{8}$$

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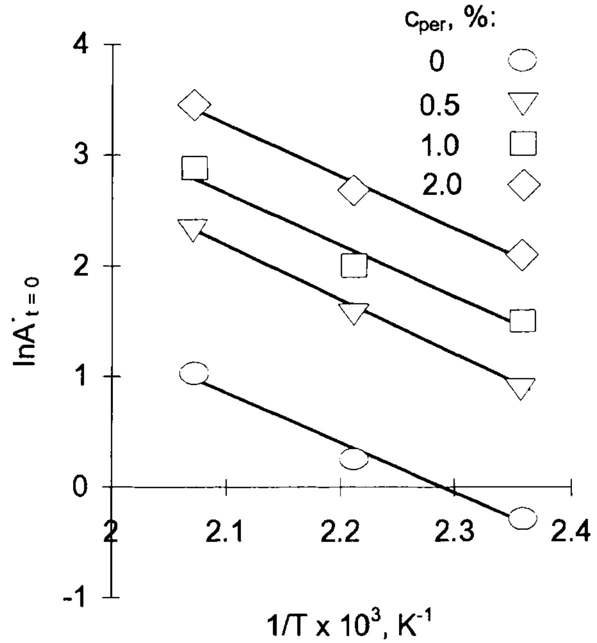

FIGURE 10 Variation of $A^\bullet_{t=0}$ with the contact temperature, T.

Let us write the multiplier in the Eq. (8) as

$$B = A^*_\infty(1 + \beta c_{\text{per}}) \ln \chi_k \tag{9}$$

Then Eq. (8) transforms into

$$A^\bullet_{t=0} = B/t_{A\max} \tag{10}$$

and now B can be determined by the slope of the function $A^\bullet_{t=0} = (t^{-1}_{A\max})$. Figure 8 shows that B grows with increasing c_{per} and is independent of the contact temperture, T (see Tab. I). Eq. (9) can be transformed into the following expression:

$$B/B^* = 1 + \beta c_{\text{per}} \tag{11}$$

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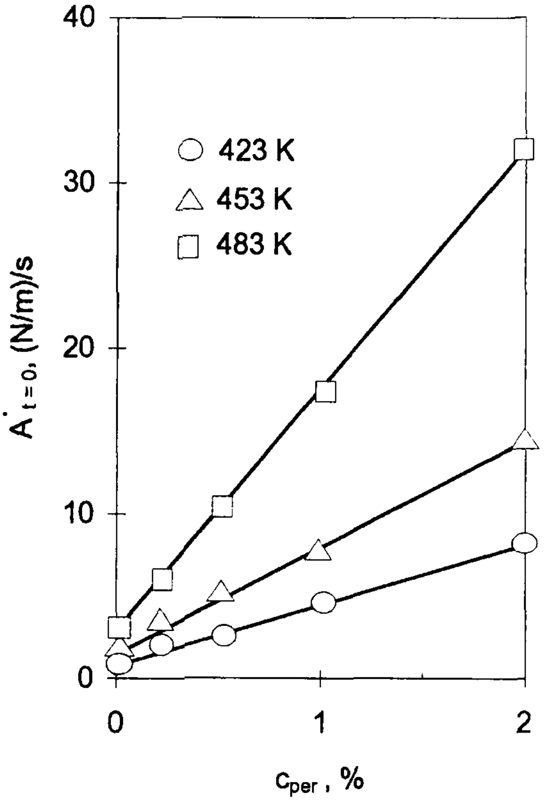

FIGURE 11 Variation of $A^{\bullet}_{t=0}$ with different contact temperatures, T.

TABLE I Comparison of some kinetic parameters of the function $A(t)$ for various contents of peroxide in the adhesive

			c_{per}, %		
Kinetic parameters	0	0.2	0.5	1.0	2.0
$A^{\bullet}_{t=0}$ (423 K)	0.75	1.8	2.5	4.5	8.1
$A^{\bullet}_{t=0}$ (453 K)	1.3	3.0	5.0	7.5	14.5
$A^{\bullet}_{t=0}$ (483 K)	2.8	5.9	10.5	17.5	32.0
$A^{\bullet}_{t=0}/A^{*\bullet}_{t=0}$ (423 K)	1.0	2.4	3.3	6.0	10.8
$A^{\bullet}_{t=0}/A^{*\bullet}_{t=0}$ (453 K)	1.0	2.3	3.8	5.8	11.2
$A^{\bullet}_{t=0}/A^{*\bullet}_{t=0}$ (483 K)	1.0	2.1	3.8	6.3	11.4
$A^{\bullet}_{t=0}/A^{*\bullet}_{t=0}$ (average)	**1.0**	**2.3**	**3.6**	**6.0**	**11.1**
$B\times10^{-2}$, N/m	3.3	6.7	10.0	16.0	25.0
B/B^{*}	**1.0**	**2.0**	**3.0**	**4.8**	**7.6**
A_{max}, kN/m (average)	0.085	0.19	0.33	0.56	0.90
A_{max}/A^{*}_{max},	**1.0**	**2.2**	**3.9**	**6.6**	**10.6**
P/P^{*}(general average)	**1.0**	**2.2**	**3.5**	**5.8**	**9.8**

The parameters corresponding to $c_{per}=0$ are designated by *.

where $B^* = A^*_\infty \ln \chi_k$. The values of B/B^* given in Table I allow us to evaluate β. Finally, according to Eq. (15) [1], we can write

$$A_{\max} = A_\infty f(\chi_k) \tag{12}$$

where $f(\chi_k)$ depends only on χ_k.

Since we have assumed that $\chi_k = \text{const}$, then $f(\chi_k)$ is also constant (*i.e.*, is independent of T and c_{per}). Thus, from Eqs. (6) and (12) it follows that

$$A_{\max}/A^*_{\max} = 1 + \beta c_{\text{per}} \tag{13}$$

This is a third independent way for the estimation of β.

The linearity of the function $A_{\max}/A^*_{\max}(c_{\text{per}})$ (see Tab. I) shows that χ_k indeed is a constant.

As we expected, the experimental values of the ratio of the three kinetic parameters, $A^{*}_{t=0}/A^{**}_{t=0}$, B/B^*, and $A_{\max}/A^*_{\max}$, for a certain c_{per} coincide satisfactorily (see Tab. I). Following the general average of this ratio P/P^* calculated for each c_{per}, the average β from the function $(P/P^*)(c_{\text{per}})$ (Fig. 12) can be estimated: $\beta = 4.5 \times 10^2$, (parts by weight)$^{-1}$.

The constants of Eq. (2) can be estimated taking into account Ref. [1]. Thus, according to Table I, $B^* = A^*_\infty \ln \chi_k = 3.3 \times 10^2$ N/m. From Table VI [1] follows that $A^*_\infty = 2 \times 10^3$ N/m and $\chi_k = 1.18$. A_∞ is calculated from Eq. (6), Δk for each T and c_{per} can be defined from Eq. (5), while $A_{\max}$ can be obtained from Eqs. (12) and (13). The calculated constants are shown in Tables II–IV.

It follows from the above assumption that Δk should not depend on c_{per}. Indeed, the calculated values of Δk for various c_{per} differ very slightly (see Tab. II) and the average value can be calculated (see Tab. III).

TABLE II Variation of $\Delta k \times 10^3$, s^{-1} with c_{per} and contact temperature, T

$c_{per} \times 10^2$	*Contact temperature T, K*		
parts by weight	423	453	483
0	0.35	0.70	1.50
0.2	0.47	0.79	1.63
0.5	0.40	0.77	1.69
1.0	0.41	0.77	1.64
2.0	0.40	0.70	1.65

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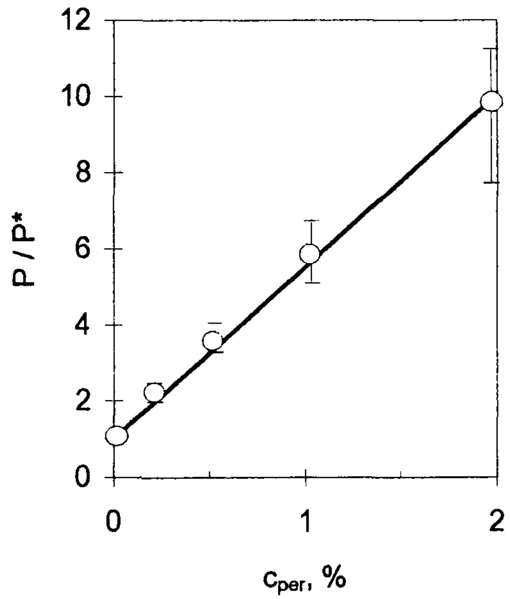

FIGURE 12 Variation of the general average of all parameters (see Tab. I) with the content of peroxide, c_{per}.

TABLE III Calculated values of constants independent of c_{per}

Constants	*Contact temperature T, K*		
	423	453	483
Δk, s^{-1} **	0.41	0.76	1.66
k_1, s^{-1}	2.69	4.98	10.66
k_2, s^{-1}	2.28	4.22	9.00
$t_{A\,\mathrm{max}}$, s	402	217	101

** - average values (see Tab. II).

TABLE IV Calculated values of constants independent of T

Constants	*$c_{per} \times 10^2$, parts by weight*				
	0	0.2	0.5	1.0	2.0
A_{∞}, kN/m	2.0	3.8	6.5	11.0	20.0
A_{max}, kN/m (calculated)	0.12	0.23	0.39	0.67	1.22
A_{max}, kN/m (experimental)	0.085	0.19	0.33	0.56	0.90
A_{max}, calc. /A_{max}, exper.	1.41	1.21	1.18	1.20	1.36

Figure 1 shows the $A(t)$ calculated for various c_{per} and T. The calculated values of A_{max} are about 1.3 times higher than the experimental ones (see Tab. IV). This is most probably due to

TABLE V Parameters characterizing the $A(t)$ kinetics of adhesive interaction between PE and steel in the presence of organic peroxide

Parameters	*Constants determining the parameter*	*Equation describing the parameter*
$\uparrow A^{\bullet}_{t=0}$	$\uparrow (\uparrow c_{\text{per}})$ $\uparrow(\uparrow T)$	$A^{\bullet}_{t=0} = \Delta k A_{\infty}$
$\downarrow t_{A\max}$	$\chi_k =$ const $\uparrow \Delta k(\uparrow T)$	$t_{A\max} = \ln \chi_k/\Delta k$
$\uparrow A_{\max}$	$\uparrow A_{\infty}(\uparrow c_{\text{per}})$ $\chi_k =$ const	$A_{\max} = A_{\infty} f(\chi_k)$

accumulation of gaseous products of the contact oxidation in the boundary layer of the adhesives, which leads to weakening of the boundary by formation of bubbles (defects).

Now we can estimate the potentials of the peroxides used to promote the PE adhesion (Tab. V). A_{∞} is the only constant in Eq. (2) determined by c_{per}, (see Eq. (6)). As seen from Table V, the growth of $A^{\bullet}_{t=0}$ and $A_{\max}$ can be reached by increasing c_{per}. The value of $t_{A\max}$ can be decreased only by raising the contact temperature, T.

The described regularities, of course, are valid only in certain limits of c_{per} and T. At $c_{\text{per}} > 0.03$ of parts by weight and $T > 500\,\text{K}$, the influence of defects in the boundary layer dominates. These values are the limits also from technological considerations.

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CONCLUSIONS

The kinetics of the development of strength of the adhesive joints between a PE containing organic peroxide and steel is controlled by the contact oxidation processes. The peel strength, A, as a function of the contact time, t, is determined by the content of peroxide, c_{per}, in the adhesive, the contact temperature, T, and the content of oxygen in the contacting environment. The peel strength, A, reaches its maximum, $A_{\max}$, at a certain contact time, $t_{A\max}$. The kinetic characteristics, $A_{\max}$ and $t_{A\max}$, as well as the initial growth rate of $A, A^{\bullet}_{t=0} = \lim dA/dt|_{t=0}$, are determined by c_{per} and T. There is a growth in $A_{\max}$ and $A^{\bullet}_{t=0}$ with c_{per}, and a decrease in $t_{A\max}$ with T.

Similar to a pure PE, the shape of the $A(t)$-curves for the formation of adhesive bonds between the steel and peroxide-containing PE is defined by two main conflicting trends of contact oxidation, namely, the oxidative cross-linking causing the increase in A and oxidative destruction causing the reduction in A. With growing c_{per}, an increase of the output of contact oxidation reactions takes place.

The peel strength, A, is determined by the ratio of the gel-fraction, c_{gel}, in the polymer layer after its contact with metal (a measure of the outcome of oxidative cross-linking) and the respective content of extractable low-molecular products, c_{lm} (a characteristic of the effect of oxidative destruction).

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