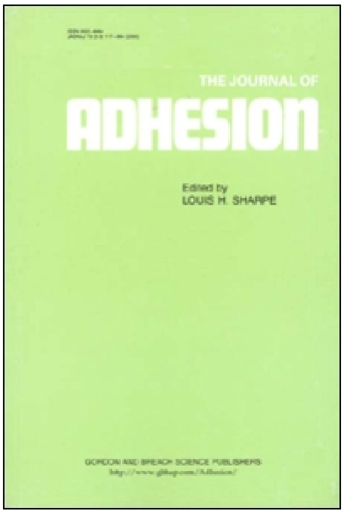

The Journal of Adhesion

Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713453635

Contact Oxidation and Adhesive Interaction of Polyolefins with Metals

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To cite this Article Kalnins, M. M.(1991) 'Contact Oxidation and Adhesive Interaction of Polyolefins with Metals', The Journal of Adhesion, 35: 3, 173 — 180

To link to this Article: DOI: 10.1080/00218469108030446

URL: http://dx.doi.org/10.1080/00218469108030446

J. Adhesion, 1991, Vol. 35, pp. 173–180
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Printed in the United Kingdom

NOTE

Contact Oxidation and Adhesive Interaction of Polyolefins with Metals

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(Received December 6, 1989; in final form November 5, 1990)

KEY WORDS Adhesive interaction; polyolefins; metals; weak boundary layer; contact oxidation; oxidative crosslinking.

Polymer–metal systems: adhesive joints of metals, metal–polymer composites, polymeric coatings on metals etc., are of great practical interest. The polyolefin-based systems (large supply, widespread, cheap polymers, distinguished by high chemical resistance, anticorrosive capacity and other valuable properties) and steel (including steel of the common grades, which are in great need of rust protection) are wisely used. One of the basic requirements, guaranteeing high serviceability of the abovementioned systems, is a strong and durable adhesive interaction between polymer and metal. In this paper, the most essential research results, obtained in our laboratory, in the field of controlling the processes of adhesive interaction between polyolefin melts and steel surfaces, have been generalized (for more detail, see Ref. 1).

There are two determinants in the strategy for selecting effective principles which ensure the necessary adhesion between polyolefins and metal in an adhesive joint.

Firstly, contact between polyolefin melt and metal inevitably leads to the appearance of a cohesively weak, structureless, polymeric boundary layer.[2,3] This is accounted for by enrichment of polymeric boundary zones by low-molecular compounds and impurities, which are pushing toward the interface during crystallization of the polymer†.[4]

Secondly, the adhesive interaction of the polymeric melt with the metal is always connected, to this or that degree, with oxidative transformations in a polymer. This is accounted for by the necessity of maintaining a sufficiently high temperature during contact (considerably higher than the melting temperature of a polymer) and the presence of oxygen. This oxygen can advance to the interface and boundary layer of the polymer melt through the polymer layer, from substrate cavities, and directly from the metal surface (oxygen, physically and chemically adsorbed by metal oxide, see Fig. 1).[9]

Polyolefin oxidation, occurring upon contact with the metal, involves a complicated set of transformations, associated with profound changes in the chemical composition of the chain skeleton.[10,11] Both the surface metal compounds and metal compounds which, in the contact process, go into the polymer phase[12] exert a catalytic effect upon these transformations. It is resonable to call similar oxidative transformations the contact oxidation.

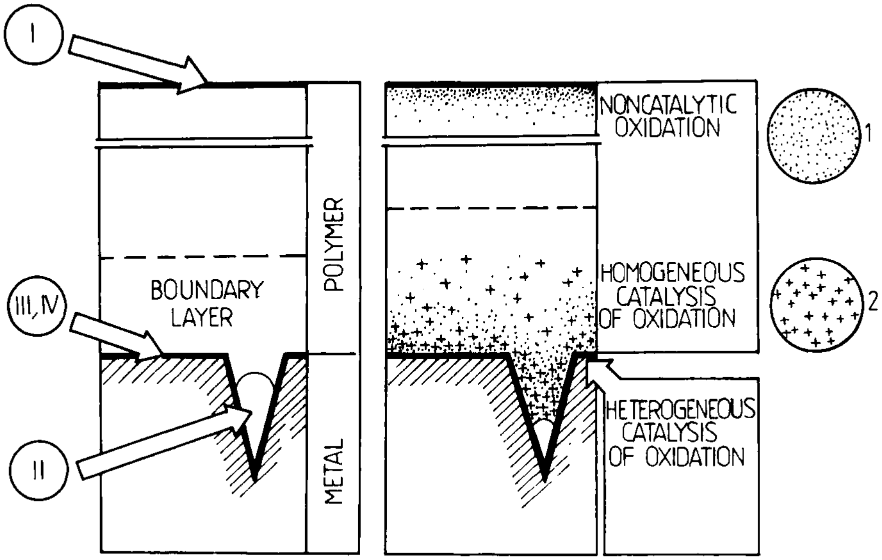

FIGURE 1 General scheme of oxygen sources and localization of the zones of contact oxidative transformations. Oxygen: diffusing through the polymer layer (I), advancing from substrate cavities (II), adsorbed (III) and chemisorbed (IV) by metal oxide. 1—oxidized polymer, 2—products of interaction between oxidized polymer and metal.

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† The concept of a "weak boundary layer" was put forward by Bikerman, on the basis of the behavior of adhesive joints of polyethylene with metals,[5] who considered its appearance to be the result of impurities advancing toward the interface. However, we have shown[4] that, in contrast to Bikerman's opinion,[6,7] removal of the additives from the polymer adhesive prior to contact formation by reprecipitation and extraction methods is insufficient to reduce the tendency for a weak boundary layer to form. Polyolefin–metal adhesive joints, regardless of their formation history, fail in a weak boundary layer.[2] The interfacial failure of adhesive joints under the prolonged effect of water is an exception.[8]

TABLE I
Definitions and symbols of some characteristics of adhesive, boundary layer and adhesive joint

Characteristics of:		
Macromolecules of adhesive	Adhesive in boundary layer	Interface of adhesive joint
L_M—length of chains	m—common number[1] of intermolecular bonds	β—specific surface of molecular contact
n_b—number[1] of branches	m_l—the same, related to one chain	a—common number[2] of interfacial bonds
n_c—number[1] of crosslinks	m^*—number[1] of strong intermolecular bonds	C_H—content[2] of gaseous inclusions
n_{ox}—number[1] of oxygen-containing groups	m_l^*—the same, related to one chain	σ_{ad}—strength
n_{eg}—number[1] of end groups	α—degree of order of arrangement of chains	
R—configurational regularity	C_H—content of heterogeneous gaseous inclusions	
M – segmental mobility	μ—melt viscosity	
	σ_B—strength	

[1] related to unit length of chain.
[2] related to unit of interface area.

The ultimate goal in the formation of adhesive joints is ensuring contact conditions that lead to sufficiently high values of interface interaction strength (σ_{ad}) and strength of the adhesive boundary layer (σ_B). Considering a limited series of characteristics of adhesive macromolecules, of the boundary layer and of the interface (Table I), we can present a general scheme of changes in σ_{ad} and σ_B based on these characteristics (Fig. 2, Table II). As it is seen from the scheme, the increase in strength values can be attained through respective variation of the characteristics which are directly accounted for by the process of contact oxidation. The variation of these characteristics can be associated with the principal trends of the process of contact thermooxidation (Table II).

The schemes under consideration reflect merely the qualitative aspects of the link between these characteristics. However, this is sufficient for specifying the strategy required to govern the contact oxidation. It becomes clear that the oxidative destruction, contributing to the increase in a and β (strengthening of interfacial interaction), should at the same time cause an essential decrease in cohesive characteristics of the adhesive (thereby causing a trend toward formation of a weak boundary layer). The accumulation of gaseous products of contact oxidative destruction as heterogeneous inclusions, both in the boundary layer and on the interface,† may be particularly dangerous.

The increase in the polar functional group content does not affect the values of σ_{ad} and σ_B in a simple manner and it cannot be considered (as in Ref. 14) as the main trend in contact thermooxidation, ensuring high strength of polyolefin–

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† There are rather convincing proofs of the fact that the presence of gaseous inclusions at the interface contricutes to dissipation of fracture energy[13] and causes the increase in peel strength of adhesive joints. At the same time, these inclusions appear to have been the source of failure in adhesive joints during long-time service, particularly under the effect of liquid media.

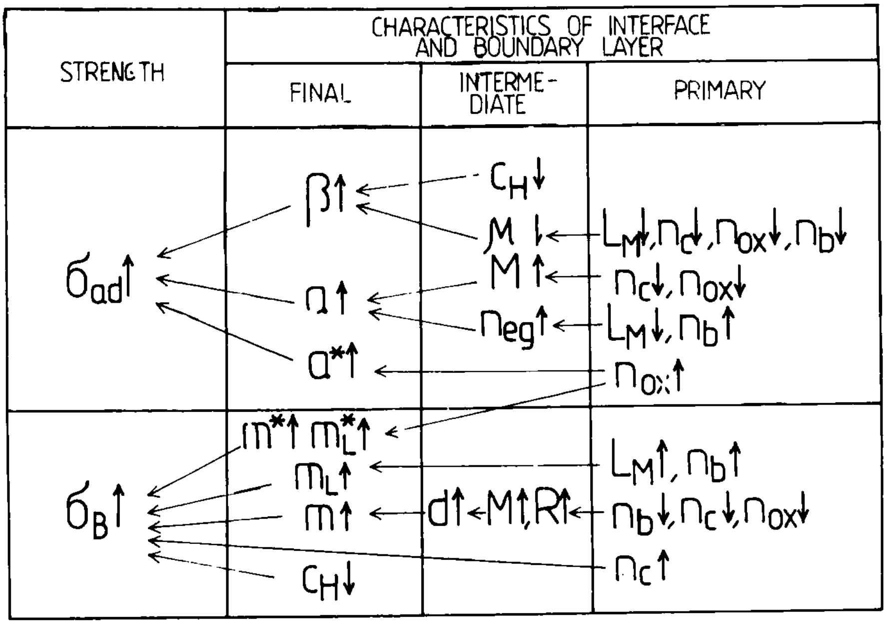

FIGURE 2 The dependence of interfacial interaction (σ_{ad}) and boundary layer (σ_B) strength on the variation of characteristics of the interface and boundary layer.

TABLE II
Influence of main trends of contact oxidation on strength characteristics

Trends of contact oxidation	Influence on strength			
	σ_{ad}		σ_B	
	$\uparrow$	$\downarrow$	$\uparrow$	$\downarrow$
1. Increasing content of oxygen-containing groups: $n_{ox}\uparrow$	$a^*\uparrow$	$\mu\uparrow \rightarrow B\downarrow$ $M\downarrow \rightarrow a\downarrow$	$m^*\uparrow$ $m_L^*\uparrow$	$M\downarrow, R\downarrow \rightarrow d\downarrow$
2. Destruction, shortening of chains: $L_M\downarrow$	$n_{eg}\uparrow \searrow a\uparrow$ $M\uparrow \nearrow$ $\mu\downarrow \rightarrow \beta\uparrow$	—	—	$m_L\downarrow$
3.9*Cross-linking*: Initial stage-branching: $n_b\uparrow$, $L_M\uparrow$	$n_{eg}\uparrow \rightarrow a\uparrow$	$M\downarrow \rightarrow a\downarrow$ $\mu\uparrow \rightarrow \beta\downarrow$	$m_L\uparrow$	$M\downarrow, R\downarrow \rightarrow d\downarrow$
Final stage—Increasing number of cross-links: $n_C\uparrow$, $L_m\uparrow \rightarrow \infty$		$\mu\uparrow \rightarrow \beta\downarrow$ $M\downarrow \rightarrow a\uparrow$	$n_C\uparrow$	$M\downarrow, R\downarrow \rightarrow d\downarrow$
4. Accumulation of volatile products of destruction: $C_H\uparrow$	—	$\beta\downarrow$	—	$C_H\uparrow$

metal adhesive joints. It should be borne in mind that elevated concentration of polar oxygen-containing groups at the interface and in the boundary layer is the cause for decrease in longevity of adhesive joints in polar liquid media, mainly water.[15]

It can be considered as proved that reinforcing of the boundary layer and interfacial interaction in polyolefin–metal systems is attained through stimulation of contact oxidative cross-linking and suppressing of oxidative destruction or, at least, immobilizing its products.[16]

It is natural that all this should take place against a background of moderate increase in concentration of oxygen-containing groups. In this concentration range the chances for guaranteeing water resistance of the adhesive joint increase. It goes without saying that oxidative cross-linking should occur just after interfacial contact has been formed.

The peel strength of adhesive joint A is the work of fracture, related to the unit of delaminated area. So the value A_V (specific work of fracture), related to the volume of conditional boundary layer of the adhesive, can be used as an objective deformational-strength characteristic. In a coarse approximation, $A_V = A/\bar{h}$ (where $\bar{h}$ is the average adhesive layer thickness left on the metal surface after delamination).

It has been shown[17] that the value A_V is defined by the competitive effect of the two basic trends of macromolecular transformations: the oxidative cross-linking and destruction. Quantitatively it is manifested in the following expressions:†

$$A_V(t)/A_{V_0} = k[a(t)]^{\alpha} \tag{1}$$

$$a(t) = [1 + C_{\text{gel}}(t)]\bar{M}(t)/\bar{M}_0 \tag{2}$$

where A_{V_0} is the A_V value corresponding to the minimum contact time t for which it is possible to determine the values of A and $\bar{h}$ with sufficient accuracy, k and α are empirical coefficients, C_{gel} is the fraction of the cross-linked part in the adhesive boundary layer, and $\bar{M}$ and $\bar{M}_0$ are the running and initial value of average molecular weight of adhesive in the boundary layer, respectively.

An increase in $a(t)$ shows that cross-linking prevails, whereas for a decrease destruction prevails.

The antagonism of contact oxidative transformations, associated with cross-linking (processes I) and destruction (processes II) is reflected in the extremal relationships of peel strength to contact duration, $A(t)$. The decrease in A after having attained the maximum magnitude is the result of the dominant role of oxidative destruction. From a position of formal kinetics,[16] the analysis of these relationships resulted in the development of the principles for controlling the process of contact oxidation during adhesive interaction of polyolefins with metals.

It was shown that for a great variety of polyolefin-based adhesives and contact

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† The expression (1) is essentially analogous to an empirical expression of the $P = KM^{\alpha}$ type (where P is a parameter characterizing any of the polymer properties), which has been widely used recently.[18]

conditions the $A(t)$ function can be satisfactorily described by a simple expression.

$$A(t) = A_\infty[\exp(-k_2t) - \exp(-k_1t)] \tag{3}$$

where A_∞ is a constant corresponding to completion of processes I and II, i.e. yield of oxidative transformations, and k_1, k_2 are the effective constants of the growth rate of the value of A occurring as a result of the progression of processes I and II, respectively.

The most significant kinetic parameters and constants of equation (3), defining these parameters, are given in Table III: The desirable trend for the parameters and the constants is indicated by arrows.

It is clear that in order to increase $A'_{t=0}$ and A_{max} and decrease t_{max} it is necessary to develop such adhesive polyolefin–based systems and carry out contact under such conditions that would ensure:

—increase in velocity of oxidative cross-linking processes (increase in k_1),

—increased yield in oxidative transformations (increase in A_∞),

—increased ratio of effective constants for the rate of cross-linking and destruction processes (increase in x).

Table IV gives a generalization of the basic ways in which separate methods affect the kinetics of $A(t)$. Of course, in each separate case there are certain limits for contact temperature variation, modifying additive content, radiation intensity, etc., beyond which the desirable change in kinetic characteristics cannot be realised.

Regardless of whether or not there has been a sufficiently wide spectrum of investigations, the potential for using the process of contact thermooxidation in polyolefin–metal adhesive interaction is beginning to become apparent. To our

TABLE III
Kinetic Parameters Characterising Eq. (3)

Parameter	Constants of Eq. (3), defining this parameter	Expression
Initial growth rate for A: $\uparrow A^\circ_{t=0} = \lim_{t\to 0}[(dA/dt)(t)]$	$\uparrow A_\infty$ $\uparrow K_1$, $\uparrow x$	$A^\circ_{t=0} = \Delta k A_\infty$ $\Delta k = k_1 - k_2 = k_1(1 - x^{-1})$ $x = k_1/k_2$
Maximum value of A: $\uparrow A_{max}$	$\uparrow A_\infty$, $\uparrow x$	$A_{max} = A_\infty\left[\exp\left(-\frac{\ln x}{x-1}\right) - \exp\left(-\frac{\ln x'}{1-x^{-1}}\right)\right]$
t-value, corresponding to A_{max}: $\downarrow t_{max}$	$\uparrow k_1$, $\uparrow x$	$t_{max} = \ln x/\Delta k$

TABLE IV
Methods of controlling the process of contact oxidation during adhesive interaction between polyolefins and steel

Method	Effect on kinetic characteristics of $A(t)$ relation
1. Reduction in adhesive layer thickness b (in the case of free access of oxygen through the layer) and contact temperature T increase[16]	$\uparrow k_1(\uparrow T, \downarrow b)$
2. Increase in oxidative cross-linking agent content c_r: organic peroxides[19,20] silane derivatives[21,22] compounds containing isocyanate groups *[23] in adhesive	$\uparrow A_\infty(\uparrow c_r)$
3. Increase in content of disperse particles ϕ_f which are adsorbents of low-molecular compounds resulting from oxidative destruction in adhesive[24]	$\downarrow k_2(\uparrow \phi_f)$ $\uparrow \Delta k$, $\uparrow x(\downarrow k_2)$
4. Rise in intensity I of UV[25] and γ-radiation[26] in the contact process	$\uparrow A_\infty$, $\uparrow k_1$, $\uparrow x(\uparrow I)$

* In the two latter cases specific interaction of the silane and isocyanate groups of cross-linking agents with surface centres of the metals occurs.

mind, the most promising is the trend based on contact oxidation of the adhesive in the presence of oligomer or polymer additives containing a set of active functional groups. Those groups should ensure addition of a modifier to polymer chains (at the expense of interaction with oxygen-containing groups which are products of contact oxidation), efficiently cross-linking the polymer and, simultaneously, providing strong interaction with the metal surface.

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