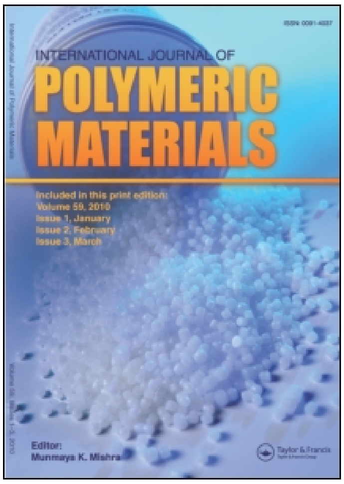

International Journal of Polymeric Materials
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713647664

The Role of Primary Aromatic Amines in the Intensification of Adhesion Interaction in Polyethylene-steel System

I. A. Starostina[a]; O. V. Stoyanov[a]; S. A. Bogdanova[a]; R. Ja Deberdeev[a]; V. V. Kurnosov[a]; G. E. Zaikov[a]
[a] Department of Technology of Polymers and Compositional materials Conversion, Kazan State Technological University, Russia

To cite this Article Starostina, I. A. , Stoyanov, O. V. , Bogdanova, S. A. , Deberdeev, R. Ja , Kurnosov, V. V. and Zaikov, G. E.(1999) 'The Role of Primary Aromatic Amines in the Intensification of Adhesion Interaction in Polyethylene-steel System', International Journal of Polymeric Materials, 44: 1, 35 — 51

To link to this Article: DOI: 10.1080/00914039908012134

URL: http://dx.doi.org/10.1080/00914039908012134

Intern. J. Polymeric Mater., 1999, Vol. 44, pp. 35–51
Reprints available directly from the publisher
Photocopying permitted by license only

Published by license under
the Gordon and Breach Science
Publishers imprint.
Printed in Malaysia.

The Role of Primary Aromatic Amines in the Intensification of Adhesion Interaction in Polyethylene-steel System

I. A. STAROSTINA, O. V. STOYANOV, S. A. BOGDANOVA,
R. JA. DEBERDEEV, V. V. KURNOSOV and G. E. ZAIKOV*

Department of Technology of Polymers and Compositional materials Conversion, Kazan State Technological University, Russia

(Received 5 January 1998; In final form 3 March 1998)

The role of primary aromatic amines (PAA) in promoting the adhesion interaction between steel and coatings prepared from low pressure polyethylene synthesized by gas-phase method ($LPPE_1$) has been investigated. PAA were demonstrated to come into acid-base interaction with steel by a donor-acceptor mechanism. The increase in coatings adhesiveness is realized through bond formation between an adhesive and a substrate with the help of PAA. Free surface energy of the contact to metal side of coatings modified with PAA increases in parallel with the adhesiveness increase. The acid-base interactions have been found to exert primary control over the polyethylene adhesion to steel.

Keywords: Adhesion; polyethylene; steel; acid-base interaction; free surface energy; modification; primary aromatic amines; polyethylene

1. INTRODUCTION

The increase in polymer coating adhesiveness is the major factor in the successful development of corrosion-resisting coatings. The gas-phase low pressure polyethylene is promising for protective coatings because of high physicomechanical and electrical properties. However, the low adhesion of polyethylene to metals requires its modifications. At present

---

* Corresponding author.

no universal approach exists to modificators selection on account of complicated physicomechanical processes proceeding during the coatings formation and the problems associated with predicting the role which modificator functional groups play in the polymer – substrate interphase interaction. Therefore a problem of improvement of polymer coatings adhesion properties by searching for corresponding modificators and finding out their functions in the adhesiveness strengthening is currently central. In previous work by Deberdeev *et al.*, some primary aromatic amines (PAA) have been investigate [1, 2]. It has been found that they are high effective polyfunctional modificators improving working properties and repeatedly enhancing an adhesiveness of coatings. The correlation between structural morphological changes taking place on modificating in the surface, middle, transition and borderline layers and coating properties has been studied. However, the reasons of coating-metal adhesion strengthening remained unclarified.

The solution of this problem will allow carrying out a search for modificating additives and creating the conditions for the realization of the required interaction adhesion level.

Recently it has been proved that acid-base interactions play an important role in adhesive bonds formation, thus in this work we used acid-base approach to clarifying a nature of interphase interactions.

2. EXPERIMENTALS

2.1. Materials

A list of studied polyethylenes is given in Table I.

The following modifying agents were used:

- PAA (4,4′-diamine-3,3′-dichlorodiphenylmethane, *p*-phenilene diamine, *o*-phenilene diamine, polyamine *T*, benzidine, amine containing aromatic derivatives of benzimidazole);
- Phenol compounds (diphenilol-propene, pyrocatechol, pyrogallic acid, dinaphthol *etc.*);
- Secondary aromatic amines (*N*,*N*′-diphenyl-phenilene diamine. neozone *D*);
- Aminophenoles of different structure;

TABLE I A properties of polyethylene used

Properties	*LPPE*$_1$*	*LPPE*$_2$*	*HPPE**	*LPPE*$_3$*
Density, kg/m^3	958	960	920	954
Degree of crystallinity, %	82	87	42	63
Melting temperature, °C	133	129–130	108	121
Content of double bonds $>C=C<$ per 1000 atoms of carbons	0, 93	0, 21	0, 3	0, 3
Melt-flow index, g/10 min	0, 55	17, 0–25, 0	7, 0	1, 4
Ultimate tensile Stress, MPa	20, 6–28, 8	–	11	22–24
Relative elongation at rupture, %	550–780	10–200	450	500
Flow limit at tension, MPa	22, 6–28, 4	27, 5–31, 4	11	–
Cracking resistance, *h*	500–1000	–	–	50

* LPPE$_1$ is the low pressure polyethylene synthesized by gas-phase method (for extrusion), LPPE$_2$ is the low pressure polyethylene synthesized by gas-phase method (for molding), LPPE$_3$ is the low pressure polyethylene synthesized by liquid-phase method and HPPE is the high pressure polyethylene.

- Anthraquinones and their derivatives;
- Phosphorated antioxidantes;
- Sulphur-bearing antioxidantes;
- Functional polymer agents.

More than fifty compounds of different classes were studied.

As the wetting liquids we used twice-distilled water, dimethylformamide, glycerol, phenol (liquified with water to 88%), formamide, aniline. Their characteristics and surface energies are listed in Table II. Here *r* is the surface free energy and indeces *t*, *p* and *d* refer to total, polar and dispersive components respectively.

Polymer compositions for coatings were prepared by mechanical mixing of the ingredients. Metallic plates from the sheet steel (SS) and

TABLE II Characteristics of wetting liquids

Liquid	*Formula*	*Molek. weight*	*Density g/sm*^{3}	T_m*	T_b**	r_1^d	r_1^p	r_1
				°*C*			*mJ/m*^{2}	
Water	H_2O	18,015	1,00	0	100	22	50,2	72,2
Dimethyl-formamide	$HCON(CH_3)_2$	73.1	0.9484	−61	153	32,4	4,9	37,3
Glycerol	$CHOH(CH_2OH)_2$	92,1	1,2613	18,6	290	33,9	29,8	63,7
Formamide	$HCONH_2$	45,04	1,1334	2,5	111	31,8	25,7	57,5
Aniline	$C_6H_5NH_2$	93,13	1,022	−6	184,4	41,2	2,0	43,2
Phenol	C_6H_5OH	94,11	1,071	41	220	37,8	2,6	40,4

* T_m – melting-point.

** T_b – boiling-point.

ordinary carbon steel (St-3 and St-20) were used as substrates. The substrate surface was cleaned with emery cloth and degreased with either acetone or butyl acetate.

2.2. The Preparation of Polymer Coatings

Polymer coatings were formed by pouring slowly the polymer composition on the substrate, pressing, heating for 20 min at 225 + 1°C and subsequent cooling to room temperature. The thickness of coating was controlled with the help of a frame.

Water resistance was assessed by the time of onset of peeling beginning. The cathodic peeling technique in 0,1N sodium chloride solution was used for the defectless separation of substrate and coating. The cathodic peeling resistance was estimated with the defect diameter after holding the coatings for 8 hours in 0,1N sodium chloride at voltage 6 V. The strength of coating-steel adhesive joint was evaluated by coating separation from the substrate under the angle of 90°C (ASTM D 3167–76 BC 5053).

The separation rate was 10 mm/min at room temperature. The samples for contact angle measurement were peeled under cathodic polarization conditions up to the total separation of coating, washed properly with distilled water and air-dried.

Drops of wetting liquids were placed on the contact sides of each substrate and coating.

2.3. Contact Angles

Contact angles were determined by the sessile drop method using a CM-8 type cathetometer. The height h and foot 1 of the drop was measured and the values of contact angle cosine were calculated using the equation

$$\cos\theta = \frac{(1/2)^2 - h^2}{(1/2)^2 + h^2}$$

About 10 contact angles per liquid were measured for each substrate so the value of $\cos\theta$ was an average of 10 measurements. The experimental error was 5%.

2.4. Acidity Parameters and Surface Free Energy

The degree of acidity was determined for a number of polymer and metal surfaces by E. Berger method [3]. The calculations of the free surface energy and its components were carried out for the contact to metal side of modified polyethylene coatings by the method of geometrical mean approximation.

2.5. IR-Spectroscopy

Infrared spectra in the region of 400–4000 sm^{-1} were recorded with the spectrophotometers Specord 75-IR, M-80 and IFS-113 Bruker in the transmission and internal reflection variations. A 300–400 μm thick films obtained by means of defectless separation from the substrate as well as; pure modifiers, heat treated ones and a similar containing finely dispersed iron were investigated. The samples for infra-red spectra measurements were prepared in a form of suspension with vaseline oil.

The NH_2-groups were identified by the absorption bands of the N—H bond symmetric valent oscillations in the region of 3460 cm^{-1} (ν_{as}) and 3360 cm^{-1} (ν_s) [4].

3. RESULTS AND DISCUSSION

3.1. The Effect of Different Additives on Polyethylene-steel Adhesive Interaction

Our study revealed that classes of substances such as secondary aromatic amines, phenoles, aminophenoles *etc*., in general do not promote adhesion to steel. Some of them only slightly increase water resistance and cathodic peeling resistance without providing adequate adhesion properties of the coatings. An increased coating adhesiveness estimated by the water resistance and cathodic peeling resistance is observed only for the $LPPE_1$ modified with polyamine-T (PAA) (Figs. 1a and b).

From Figure 1b we see that the water resistance of coatings modified with PAA increases up to 35 days as compared with 1 day for unmodifired coatings. In this case the separation strength increases five

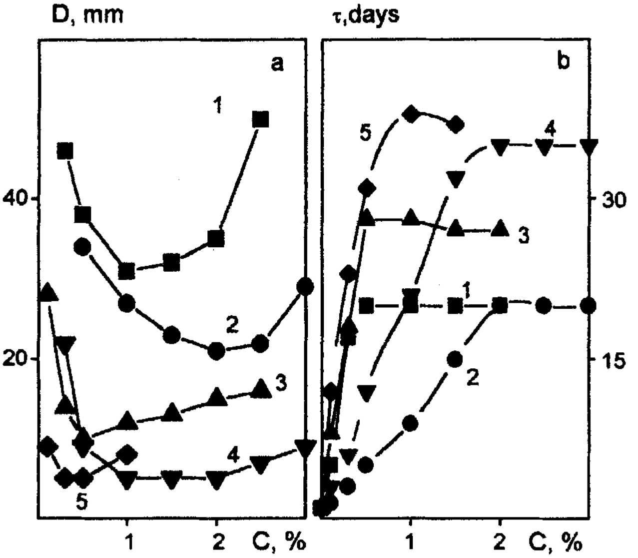

FIGURE 1 Cathodic peeling resistance (a) and water resistance (b) of modifired coatings; the x-axis is the content of modifire 1 – LPPE$_1$ + pyrocatechol, 2 – LPPE$_1$ + diphenilol-propene, 3 – LPPE$_1$ + p-phenilene diamine, 4 – LPPE$_1$ + 4,4′-diamine-3, 3′dichloroidiphenylmethane, 5 – LPPE$_1$ + polyamine *T*.

times. For example, on injecting 4, 4′-diamino-3, 3′-dichlorodiphenylmethane to the composition in amounts of 2% the separation strength increases to 22 kN/m as compared with 5,2 kH/m for unmodifired coating. The results of thermophysical studies of PAA modifired compositions shows that modifiers used offer stabilizing properties. It should be, however, noted that this stabilizing action is weaker than in the case of traditionally used stabilizers such as Irganox 1010, characterized by thermo-oxidative period of several hours at the concentration of 0, 1 – 0, 2%.

All additives being considered are related to polar substances and contain functional active groups which are capable of interphase interaction strengthening in modifired LPPE-metal systems. However, only some of them work as adhesion promotors, namely PAA.

To identify the causes of interphase interactions strengthening in the system steel-modifiered LPPE$_1$ we need to clarify the nature of PAA interactions with metal and polymer in the process of coating formation.

3.2. The Free Surface Energy of Modifired Polyethylene and a Substrate

To explain the advantages of PAA over other investigated additives we must find the adhesive-sensitive parameter of material. This parameter must also serve as the physicochemical equivalent of the adhesive joints resistance to outer exposure, represent the response function of the adhesive joint formation conditions, and be conceptually compatible with adhesive joints physical parameters. The free surface energy is one of the most fundamental parameters of this kind [5].

We found that the modification with PAA results in extreme change of r_s for the surface contacting the steel. The component r_s^d remains constant whereas the concentration dependence of r_s^p has a maximum (Figs. 2–4). The correlation between r_s and the adhesion characteristics of modified coatings can be followed. The curves for r_s pass through the maximum in the range of PAA concentration conforming

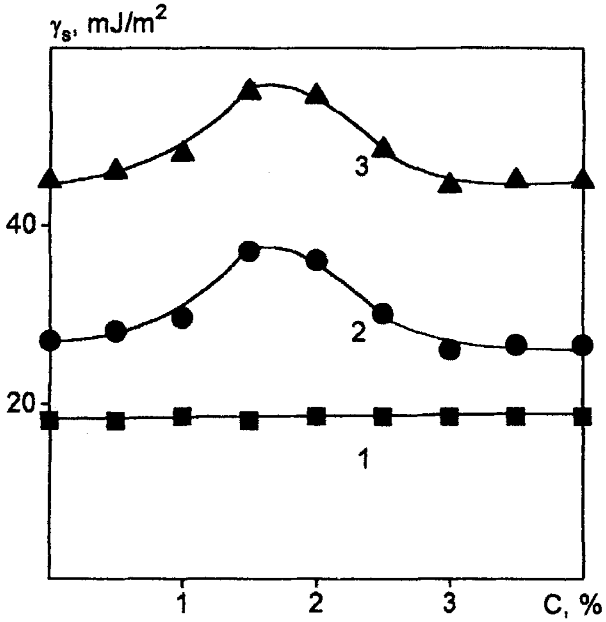

FIGURE 2 Free surface energy of coatings modifired with 4,4′-diamine-3,3′dichlorodiphenylmethane plotted against the modifire concentration. 1 – the dispersive component, 2 – the polar component, 3 – the total free surface energy of coating.

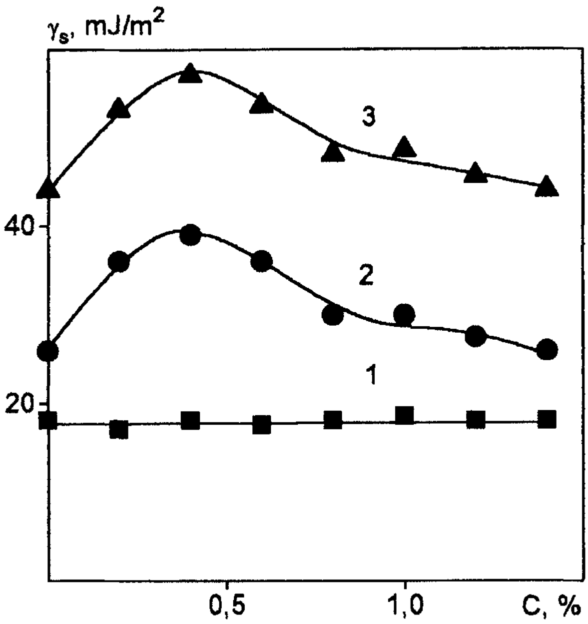

FIGURE 3 Free surface energy of coatings modifired with *p*-phenilene diamine plotted against the modifire concentration. 1 – the dispersive component 2 – the polar component 3 – the total free surface energy of coating.

to the maximum of cathodic peeling resistance of modified coatings (Fig. 1a). In this case the dispersive component remains constant and equals that of unmodifired $LPPE_1$. The polar component, however, shows an extreme.

It is necessary to note that for all investigated secondary amines the similar dependence of r_s is not observed (Fig. 5). The values of r_s^d, r_s^p and r_s in the entire range of investigated concentrations oscillate about the average values corresponding to the unmodifired $LPPE_1$. The secondary aromatic amines incorporated into the polymer do not increase the cathodic peeling resistance of polyethylene coatings. Their adhesiveness is at low level.

As noticed above the PAA modification leads to the reinforcement of peeling strength for coatings from $LPPE_1$. The fracture of adhesive joint in process of peeling strength determination bear the pronounced cohesive character. A thicker layer of polymer remains on the

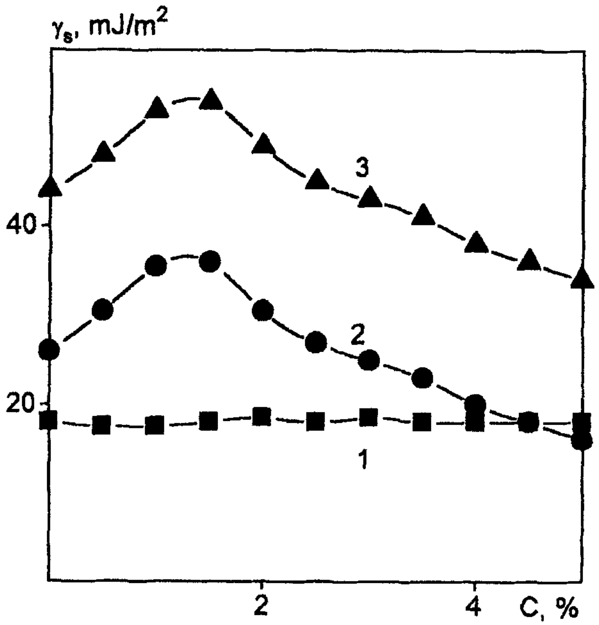

FIGURE 4 Free surface energy of coatings modifired with benzidine plotted against the modifire concentration. 1 – the dispersive component 2 – the polar component 3 – the total free surface energy of coating.

surface of substrate than in the case of coatings from the starting $LPPE_1$ [6].

In this connection the measurement of metal substrate surface energetics after cathodic peeling of the coatings containing different amount of PAA is of immediate interest (Fig. 6). The smooth fall of r_s with increase in 4,4′-diamino-3,3′-dichlorodiphenylmethane content in a coating indicates a mixed instead of merely adhesive character of cathodic peeling [7]. As the modifier concentration increases thicker polymer layers remain on the metal surface. As a result of this phenomenon, the substrate free energy appears to decrease to the values close to those of $LPPE_1$.

As for phenols, the surface energetics investigation of modifired coatings fails to reveal detectable changes in the character of free surface energy. The greatest increase (in order of 5 kD/m^2) r_s^p and r_s is observed only for diphenilol-propene (Fig. 7).

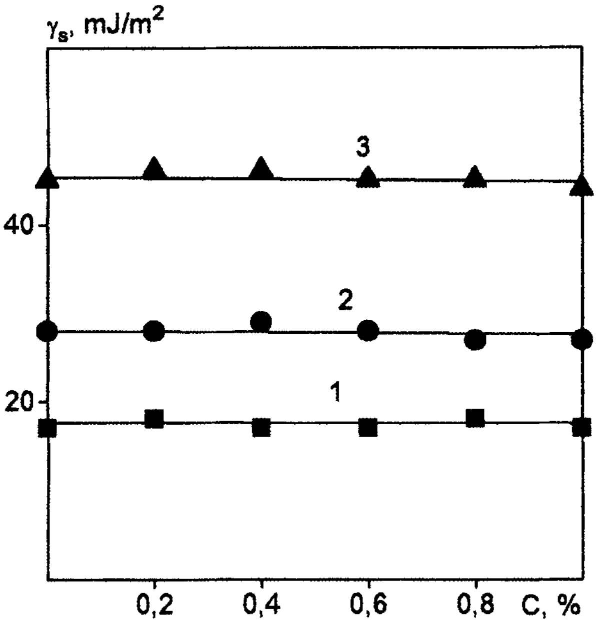

FIGURE 5 Free surface energy of coatings modifired with N,N'-diphenyl-phenilene diamine plotted against the modifire concentration. 1 – the dispersive component 2 – the polar component 3 – the total free surface energy of coating.

Hence it follows that the correlation between the adhesive and surface energy characteristics of the coatings modified with PAA revealed by our studies is valid. Thus, the chemical modification of LPPE_1, leading to the presence of surface polar amine groups which cause the increase in r_s and W_a for modifired LPPE_1 are responsible for the increase in adhesiveness of a given composition.

Based on the strength of data the question cannot be answered why other modifiers containing active functional groups are not effective as anticipated from the proposed r_s and adhesion correlation. It is apparent that the nature of functional groups has a role. The resolution of the issue is possible on the basis of an acid-base theory, since the acidity and basicity of polar molecules in the composition of condensed phases are primarily responsible for the process of wetting and polymer adhesion to solids [8].

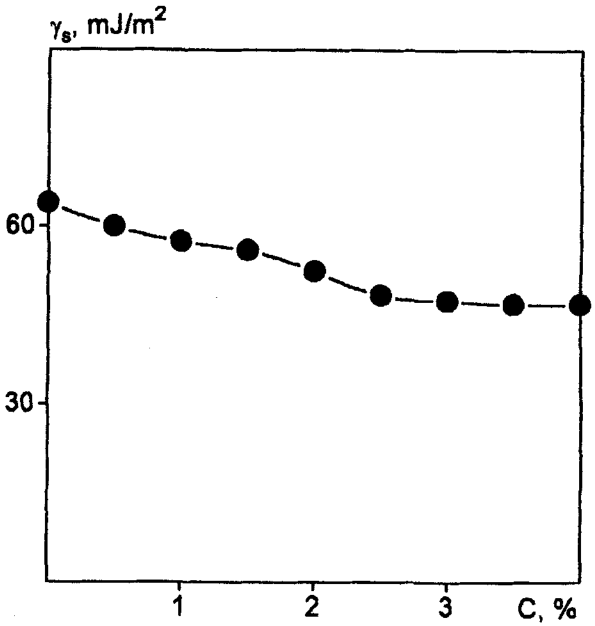

FIGURE 6 Free surface energy of the substrate SS after cathodic peeling the coatings modifired with 4,4′-diamine-3,3′-dichlorodiphenylmethane, the *x*-axis is the modifire concentration.

3.3. Acid-base Interaction in the Polymer-steel System

In terms of acid-base properties the initial polyethylene is considered to be the most neutral polymer. Consequently, the strength and longevity of the adhesive joints on its base are insignificant.

The ability of polymer to form high strength adhesive joints strength may increase with imparting acid or base properties by means of incorporating of compounds with active functional groups into the composition. Evidently a modifier must be selected in terms of the substrate functionality for realization of optimal acid-base interaction.

Therefore, we need to know whether the steel posesses acid or base properties. The currently available data concerning this question are inadequate and contradictionary, suggesting that the chemical constitution is different for a variety of steel types. Fowkes reasoned [9] that ferric oxide have both acid and base groups on its surface.

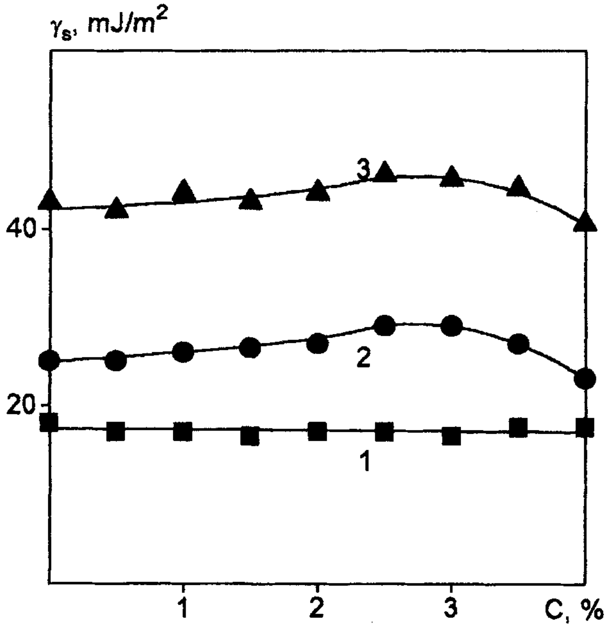

FIGURE 7 Free surface energy of coatings modifired with diphenilol-propene plotted against the modifire concentration 1 – the dispersive component 2 – the polar component 3 – the total free surface energy of coating.

This does not mean that steel surface is neutral as a whole, in contrast, it can play the role of strong acid (as SiO_2) and of a strong base (as hydrated Al_2O_3).

Thus, steel functionality is determined by many factors including the chemical formulation, the mode of surface treatment, technological conditions of adhesive joint formation. According to a method [3], we can estimate the acidity D′ of any solid smooth surface, the acidity of three types of steel used in this work and contact sides of coatings modified with aromatic amines and phenols has been determined. The results obtained are listed in Table III. As it may be seen from the data values of D′ vary from 2, 21 for St-3; 2, 58 for St-20 to 4, 56 for sheet steel. The acidity of material tends to increase with increase in the value of D′. In our case the signs of D′ for all three types of steel are positive, indicating acidity which is highest for sheet steel. The values of D′ for steel and unmodifired $LPPE_1$ are comparable. In the context of this approach it means the absence of detectable acid-base

TABLE III Data of D′ of the adhesion joint components

Surface	*SS*	*St*-3	*St*-20	*LPPE*$_1$	*LPPE*$_1$ + 2%*DX**	*LPPE*$_1$ + 3%*DPhP***
D′, $(mJ/m^2)^{1/2}$	4,56	2,21	2,58	3,59	−0,62	7,61

* DX-4, 4′-diamino-3, 3′-dichlorodiphenylmethane.
** DPhP-diphenilol-propene.

interaction, that is in line with low cathodic peeling strength and water resistance for unmodifired LPPE$_1$ coatings. The value D′ for coatings, modifired with 4, 4′-diamine-3, 3′-dichlorodiphenylmethane suggests that this coating has more basic character as compared with metal. This is expected since amines are Lewis bases. All the above testifies that the capacity of acid-base interactions on the interface can increase and the system considered has a high adhesive properties. An important point is that the increasing acidity of substrate correlates with the adhesiveness for the LPPE$_1$-coatings modified with PAA (Figs. 8, 9).

The parameter D′ has been measured by us for the coatings, modifired with diphenilol-propene. These resutls indicate (Tab. III) that the surface of interest has higher acidity than those of investigated

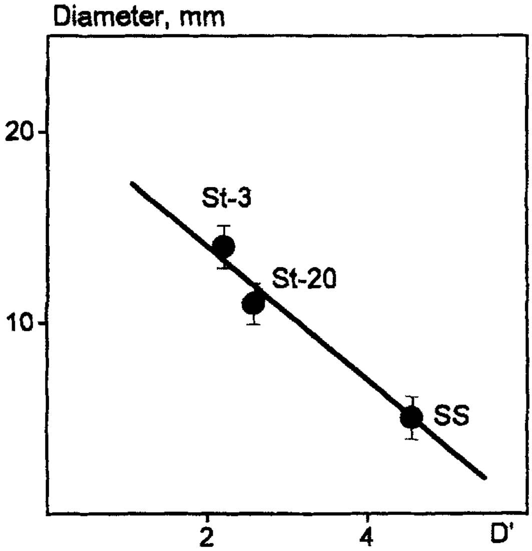

FIGURE 8 Correlation between maximum of cathodic peeling resistance (minimum of the defect diameter) and the acidity parameter of steel.

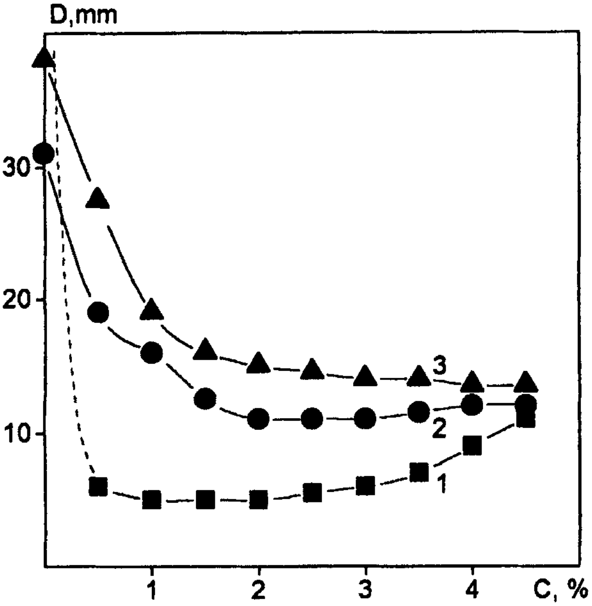

FIGURE 9 Cathodic peeling resistance of modifired coatings formed on the substrate SS (plot 1), St-20 (plot 2), St-3 (plot 3); the x-axis is the content of 4,4′-diamine-3,3′-dichlorodiphenylmethane.

steels. Since the modification of polyethylene with phenols imparts acid properties on the polymer, the acid-base interaction in the systems of this kind is weaker than on addition of PAA.

The results obtained on the basis of acid-base theory are supported by infra-red spectrum data for model systems presenting different modifires and their mixtures with finely dispersed iron, heat treated under the technological conditions of coating formation. IR-spectra of individual substances and their mixtures with iron are virtually identical for ineffective additives like secondary aromatic amines and phenols. IR-spectra of PAA and their mixtures with iron are significantly different. Some of them, as example are listed on Figures 10 and 11. The systems PAA + iron exhibit large band changes in the region of 3300 – 3500 cm^{-1} responsible for valent oscillations of N—H bond of primary amine groups (ν (NH_2)).

These effects involve band broadening with absorption amplification in the region of low frequency, suggesting the realization of

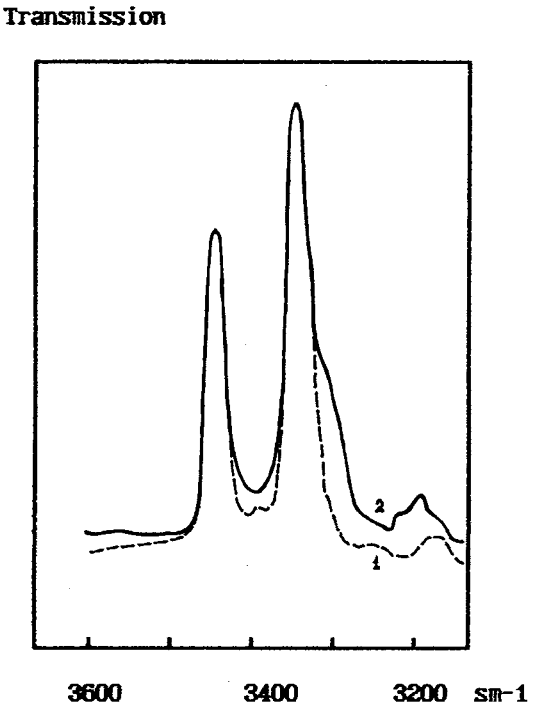

FIGURE 10 IR-transmission spectra: 1 – heat treated 4,4′-diamine-3,3′dichlorodiphenylmethane, 2 – heat treated 4,4′-diamine-3,3′-dichlorodiphenylmethane with fine-dispersed iron. Forming time – 20 min. Forming temperature – 220°C.

donor–acceptor interaction between amine group and functional groups on the metal surface. Thus, the role of acid-base interactions in providing the adhesiveness of LPPE$_1$-coatings is doubtless. However, the results obtained fail to explain low adhesiveness of coatings prepared from PAA-compositions with LPPE$_2$, LPPE$_3$ and HPPE. A special case of LPPE$_1$ appears to be determined by its chemical structure leading to the realization of specific interactions between PAA and polymer macromolecules.

According to the results of IR-spectral and quantum-chemical investigation it has been found in our previous work [10] that PAA combine readily with double bonds of polymer at a coating formation temperature. In this process a part of primary amine groups changes to secondary groups. Along with this type of chemical interaction the

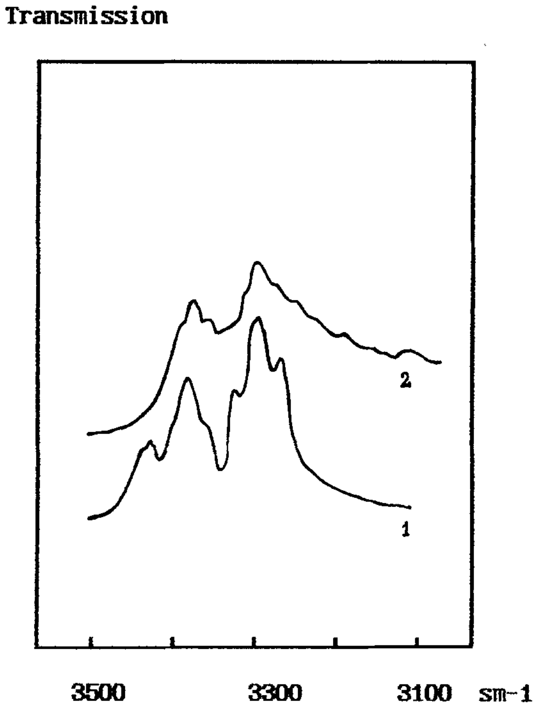

FIGURE 11 IR-transmission spectra: 1 – heat treated benzidine, 2 – heat treated benzidine with fine-dispersed iron. Forming time – 20 min. Forming temperature – 220°C.

physical interaction with formation of H-complexes between oxygen-containing groups of polyethylene and NH_2-groups takes place. Chemical interaction seems to play the most important role.

This is supported by the results of cathodic peeling resistance for the vacuum-formed coatings. The cathodic peeling resistance of coatings in the optimum range of PAA concentration is so high that its character does not change despite the fact that the degree of polymer oxidation in such coatings is vanishingly small and the formation of hydrogen bonds is difficult.

In summary the molecules of PAA diffusing to the polymer-metal interface take part in the interface interaction, therewith one of the modifier functional groups is chemically or physically connected with polymer macromolecules whereas the other group comes into acid-base interaction with steel by a donor–acceptor mechanism.

References

[1] Deberdeev, R. Ja., Stoyanov, O. V., Huzahanov, R. M. and Kurnosov, V. V. (1989). Lakokrasochnie materialy *i* ih primenenie, N2, 52.

[2] Krasovsky, A. N., Kurnosov, V. V., Stoyanov, O. V., Polakov, D. A., Baranov, V. G., Deberdeev, R. Ja. and Aliner, L. B. (1990). *Vysokomolek. soed.*, **32A**, 2174.

[3] Berger, E. J. (1990). *J. Adhes. Sci. and Technol.*, **4**, 373.

[4] Infracrasnaya spectroscopia polimerov. Pod. red. I. Dehanta, Khimiya, Moskva (1976), p. 472.

[5] Vacula, V. L. and Pritykin, L. M. (1984). Phisitceskaja himija adgesii polimerov, Himija Moskva, p. 224.

[6] Starostina, I. A. (1996). Rol' pervichnyh aromaticheskih aminov *v* usilenii adgezionnogo vzaimodejstvija modificirovannogo polietilena so stal'ju-Diss.Kazan', p. 161.

[7] Watts, J. F. (1984). *J. Mater. Sci.*, **19**, 2259.

[8] Kinloch, A. J. (1987). Adhesion and Adhesives. Science and Technology -N. Y.-L.: Univ. Press. p. 441.

[9] Fowkes, F. M. (1990). *J. Adhes. Sci. and Technol.*, **4**, 669.

[10] Starostina, I. A., Stoyanov, O. V., Kurnosov, V. V. and Deberdeev, R. Ja. (1995). In: Kinetika radikalnih dgidkofazhih reakciy, *Tez. dokl.*, *Kazan*, p. 42.