

# Studies on the Surface Properties and the Adhesion to Metal of Polyethylene Coatings Modified with Primary Aromatic Amines

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Received 9 February 1998; accepted 7 May 2000

**ABSTRACT:** The surface free energy and acid–base characteristics of polyethylene coatings formed on steel in the presence of primary aromatic amines (PAAs) were investigated. PAAs were shown to interact with steel by a donor–acceptor mechanism. An increase in the coating adhesion is realized through chemical and physical bond formation between an adhesive and a substrate with the help of the PAA. The free surface energy of the contact-to-metal side of these coatings modified with PAA was shown to grow in parallel with the increase in adhesion. The results correlate with the data on polyethylene surface wetting with nonionic surfactants. Acid–base interactions were found to exert primary control over polyethylene's adhesion to steel. © 2001 John Wiley & Sons, Inc. *J Appl Polym Sci* 79: 388–397, 2001

**Key words:** acid–base interaction; free surface energy; modification; primary aromatic amines; polyethylene

## INTRODUCTION

Increasing the adhesion of polymer coatings is a major factor in the successful development of corrosion-resisting technology. Gas-phase high-density polyethylene (HDPE) shows promise for protective coatings because of its good physicomechanical and electrical properties. However, the weak adhesive bond of polyethylene to metals requires that it be modified. At present, no universal approach to modification exists, due to the complicated physicomechanical processes pro-

ceeding during coating formation and because of the problems associated with predicting the role that modifier functional groups play in polymer–substrate interphase interaction. Therefore, the problem of improving coating adhesion by searching for corresponding modifiers and finding their role in adhesion strengthening is currently central. In previous work by Deberdeev et al., certain primary aromatic amines (PAAs) were investigated.<sup>1,2</sup> It was found that they are highly effective polyfunctional modifiers, improving the working properties and repeatedly enhancing the adhesion of the coatings. The correlation between the structural morphological changes taking place on modification of the surface, middle, transition, and borderline layers and the coating properties

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*Journal of Applied Polymer Science*, Vol. 79, 388–397 (2001)  
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**Table I** Properties of Polyethylene Used

Properties	HDPE <sub>1</sub> <sup>a</sup>	HDPE <sub>2</sub> <sup>a</sup>	LDPE <sup>a</sup>	HDPE <sub>3</sub> <sup>a</sup>
Density (kg/m <sup>3</sup> )	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
Bonds distribution (%)				
Vinyl	93	36	17	60
Vinylidene	3	26	71	25
<i>trans</i> -Vinylene	4	38	12	15
Melt-flow index (g/10 min)	0.55	17.0–25.0	7.0	1.4
Ultimate tensile strength (MPa)	20.6–28.8	—	11	22–24
Elongation at break (%)	550–780	10–200	450	500
Yield stress (MPa)	22.6–28.4	27.5–31.4	11	—
Time to cracking resistance (h)	500–1000	—	—	50

<sup>a</sup> HDPE<sub>1</sub> is the low-pressure polyethylene synthesized by the gas-phasic method (for extrusion); HDPE<sub>2</sub> is the low-pressure polyethylene synthesized by the gas-phasic method (for molding); HDPE<sub>3</sub> is the low-pressure polyethylene synthesized by liquid-phasic method; and LDPE is the high-pressure polyethylene.

was studied. However, the reasons for the improvement in coating–metal adhesion still remain unclarified. A solution to this problem will lead to a search for improved modifying additives and will create the conditions for achieving the required adhesion level. Recently,<sup>3</sup> it was proved that acid–base interactions play an important role in adhesive bond formation, so in this work, we used an acid–base approach to clarify the nature of the interphase interactions.

## EXPERIMENTAL

### Materials

A list of the polyethylenes studied is given in Table I. The following modifying agents were used: various PAAs (4,4'-diamine-3,3'-dichlorodiphenylmethane, *p*-phenylenediamine, *o*-phenylene diamine, polyamine T, benzidine, and amines containing aromatic derivatives of benzimidazole):

- Phenol compounds (diphenylol propene, pyrocatechol, pyrogallol, dinaphthol etc.);
- Secondary aromatic amines (*N,N'*-diphenylphenylene diamine, neozone D);
- Aminophenoles of various structures;
- Anthraquinones and their derivatives;
- Phosphorated antioxidants;

- Sulfur-bearing antioxidants;
- Functionalized agents.

More than 50 compounds were studied altogether.

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

Polymer compositions for the coatings were prepared by mechanical mixing of the ingredients. Metallic plates made of different types of steel were used as substrates. The following steels were studied: cold-rolled annealed steel without a protective tin coating (SS); low-carbon nonalloyed hot-rolled steel with a carbon content of 0.03% (ST-3); low-carbon nonalloyed hot-rolled steel with a carbon content of 0.2% (ST-20); and alloyed cold-rolled steel with the addition of manganese to 1% and with the carbon content of 6.5% (G-65). The substrate surfaces were cleaned with an emery cloth and degreased with either acetone or butyl acetate.

### Preparation of Polymer Coatings

Polymer coatings were formed by a powdering of the polymer compositions onto the substrates followed by pressing, heating for 20 min at 225

**Table II Characteristics of Wetting Liquids**

Liquid	Formula	Molecular Weight	Density (g/cm <sup>3</sup> )	$T_m^a$	$T_b^b$	$\gamma_1^d$	$\gamma_1^p$	$\gamma_1^t$
				(°C)		(mJ/m <sup>2</sup> )		
Water	H <sub>2</sub> O	18.015	1.00	0	100	22	50.2	72.2
Dimethylformamide	HCON(CH <sub>3</sub> ) <sub>2</sub>	73.1	0.9484	-61	153	32.4	4.9	37.3
Glycerol	CHOH(CH <sub>2</sub> OH) <sub>2</sub>	92.1	1.2613	18.6	290	33.9	29.8	63.7
Formamide	HCONH <sub>2</sub>	45.04	1.1334	2.5	111	31.8	25.7	57.5
Aniline	C <sub>6</sub> H <sub>5</sub> NH <sub>2</sub>	93.13	1.022	-6	184.4	41.2	2.0	43.2
Phenol	C <sub>6</sub> H <sub>5</sub> OH	94.11	1.071	41	220	37.8	2.6	40.4

<sup>a</sup>  $T_m$ , melting point.<sup>b</sup>  $T_b$ , boiling point.

± 1°C, and subsequent cooling to room temperature. The thickness of the coatings was predetermined using a patternframe.

Water resistance was assessed from the start-peeling time after holding in water at room temperature. The greater this time, the greater is the coating adhesion to the metal. The cathodic peeling technique in a sodium chloride solution was used for the separation of the substrate and the coating.

According to this method, the initial defect of a 5-mm diameter was made in the coating. In the process of holding the coatings at a voltage, the defect diameter increased with decreasing adhesion interaction. At the end of the test, the defect diameter characterized the square of the peeled coating and, hence, its size can indicate the coating adhesion to metal. The cathodic peeling resistance was estimated from the defect diameter after holding the coatings for 8 h in 0.1 M sodium chloride at a voltage of 6 V. The strength of the coating-steel adhesive joint was evaluated by separating the coating from the substrate at an angle of 90° (ASTM D 3167-76 BC 5053).

The separation rate was 10 mm/min at room temperature. Samples for contact angle measurement were peeled under cathodic polarization conditions until totally separated, washed properly with distilled water, and air-dried. Drops of the wetting liquids were placed on the contact sides of each substrate and of the coating.

### Contact Angles

Contact angles were determined by the sessile drop method using a CM-8 type cathetometer. The height  $h$  and base  $L$  of the drop were mea-

sured and the contact angles ( $\Theta$ ) were calculated using the equation

$$\cos \Theta = \frac{(L/2)^2 - h^2}{(L/2)^2 + h^2}$$

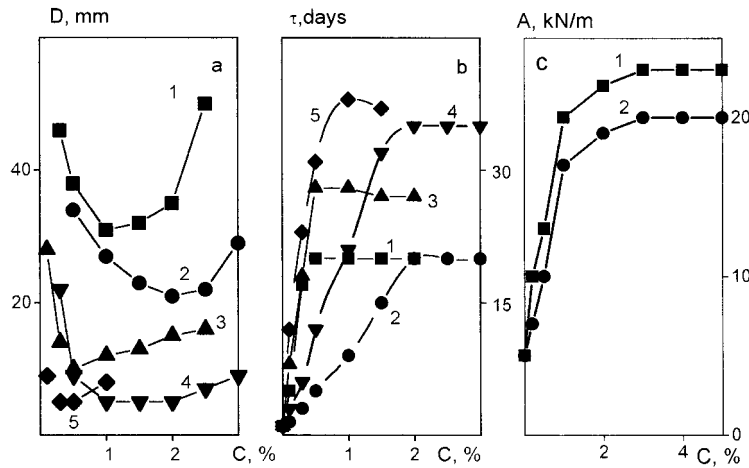
About 10 contact angles per liquid were measured for each substrate. The experimental error was established using an interval evaluation of an average of 10 measurements with a confidence probability of 0.95. It was 5%.

### Acidity Parameters and Surface Free Energy

The degree of acidity was determined for a number of polymer and metal surfaces by the Berger method.<sup>4</sup> The calculations of the free surface energy and its components were carried out for the contact-to-metal side of the modified polyethylene coatings by the method of geometrical mean approximation.

### IR Spectroscopy

Infrared spectra in the region of 400–4000 cm<sup>-1</sup> were recorded with the spectrophotometers Specord 75-IR, M-80, and IFS-113 Bruker, both in the transmission and internal reflection modes. Films, 300–400- $\mu$ m thick, were obtained using defectless separations from the substrate as well as spectra of pure modifiers, heat-treated samples, and a similar one containing finely dispersed iron. The samples for infrared spectra measurement were prepared as a suspension in vaseline oil. The NH<sub>2</sub> groups were identified by the absorption bands of the N—H bond's symmetric valent oscillations in the region of 3460 cm<sup>-1</sup> ( $V_{as}$ ) and 3360 cm<sup>-1</sup> ( $V_s$ ).<sup>5</sup>



**Figure 1** (a) Cathodic peeling resistance and (b) water resistance of modified coatings; the  $x$ -axis is the modifier content: (1) HDPE<sub>1</sub> + pyrocatechol; (2) HDPE<sub>1</sub> + diphenyl propene; (3) HDPE<sub>1</sub> + *p*-phenylenediamine; (4) HDPE<sub>1</sub> + 4,4'-diamine-3,3'-dichlordiphenylmethane; (5) HDPE<sub>1</sub> + polyamine T. (c) Strength of the coating-steel adhesive joint plotted against the modifier concentration: (1) HDPE<sub>1</sub> + 4,4'-diamine-3,3'-dichlordiphenylmethane; (2) HDPE<sub>1</sub> + *p*-phenylenediamine.

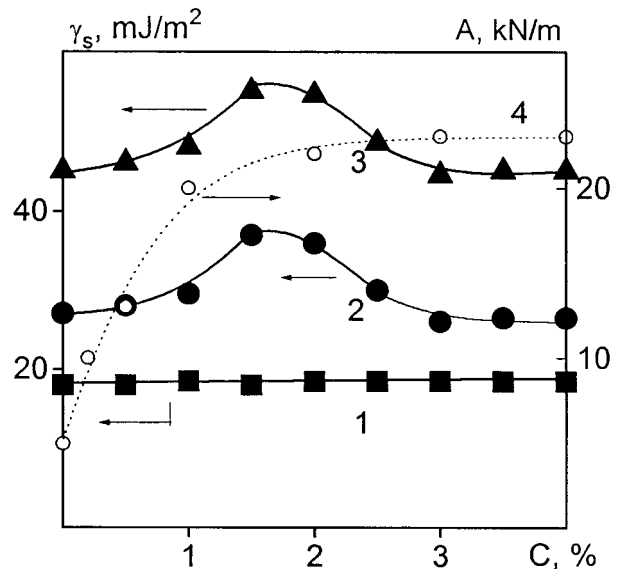
## RESULTS AND DISCUSSION

### Effect of Additives on the Adhesion of Polyethylene to Steel

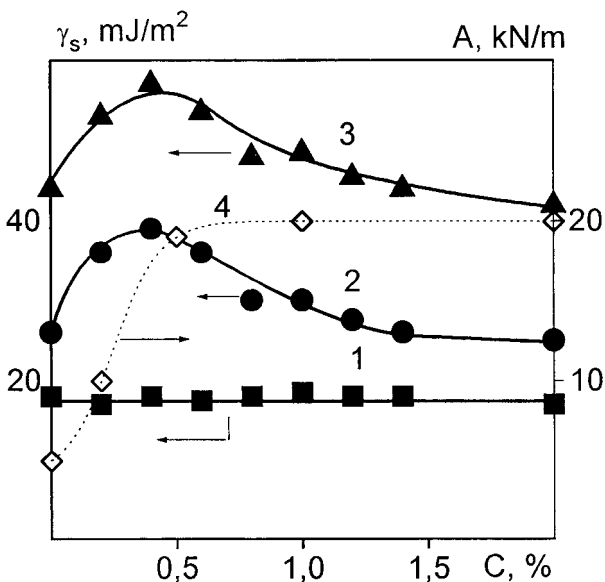
Our study revealed that substances such as secondary aromatic amines, phenols, and aminophenols do not show themselves as adhesion-to-steel promoters whatever the type of modified polyethylene. Some of them only slightly increase the water resistance and cathodic peeling resistance and fail to provide adequate adhesion. Positive evidence of repeatedly increased coating adhesion (estimated by water resistance and cathodic peeling resistance) is observed only for the HDPE<sub>1</sub> modified with PAA [Fig. 1(a,b)].

The dependence of the cathodic peeling resistance on the modifier concentration passes through a minimum for all compositions investigated. As can be seen from Figure 1(b), the water resistance of the coatings modified with PAA increases up to 35 days, compared with only 1 day for the unmodified coatings. In this case, the bond strength increases fivefold. For example, injecting 4,4'-diamino-3,3'-dichlordiphenylmethane into the composition in amounts of 2% causes the bond strength to increase to 22 kN/m as compared with 5.2 kN/m for the unmodified coatings [Fig. 1(c)]. The results of thermophysical studies of the PAA-modified compositions testify that the modifiers used do have stabilizing properties. However, it should be noted that this stabilizing action is weaker than it would be in

the case of the traditionally used stabilizers such as Irganox 1010, characterized by a thermooxidative period of several hours at a concentration of 0.1–0.2%.



**Figure 2** Free surface energy of coatings modified with 4,4'-diamine-3,3'-dichlordiphenylmethane plotted against the modifier concentration: (1) the dispersive component; (2) the polar component; (3) the total free surface energy of coating; (4) strength of the coating-steel adhesive joint plotted against the modifier concentration (HDPE<sub>1</sub> + 4,4'-diamine-3,3'-dichlordiphenylmethane).



**Figure 3** Free surface energy of coatings modified with *p*-phenylenediamine plotted against the modifier concentration: (1) the dispersive component; (2) the polar component; (3) the total free surface energy of coating; (4) strength of the coating–steel adhesive joint plotted against the modifier content (HDPE<sub>1</sub> + *p*-phenylene diamine).

All the additives considered here are polar and they contain functional active groups which are capable of strengthening interphase interaction in modified HDPE–metal systems. However, only a few of them work as adhesion promoters, the chief example being PAA. That is why it is necessary to clarify the nature of PAA interactions with metal and the polymer during coating formation and, hence, to understand the reasons why interphase interactions are strengthened in steel-modified HDPE<sub>1</sub>.

#### Free Surface Energy of Modified Polyethylene and a Substrate

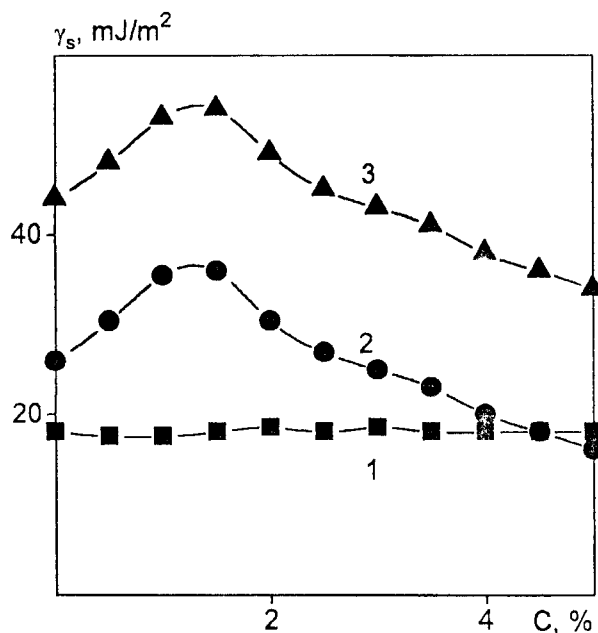
After establishing the advantages of PAA over other additives, the question arises as to what is the most adhesive-sensitive parameter of the material. The free surface energy is one of the most fundamental parameters of this kind since it helps to estimate and predict the adhesion interaction.<sup>6</sup>

It was revealed in our work that modification with PAA causes an extreme change in  $\gamma_s$  for the surface contacting steel, to an extent dependent on the additive concentration. The component  $\gamma_s^d$  remains constant, whereas the concentration de-

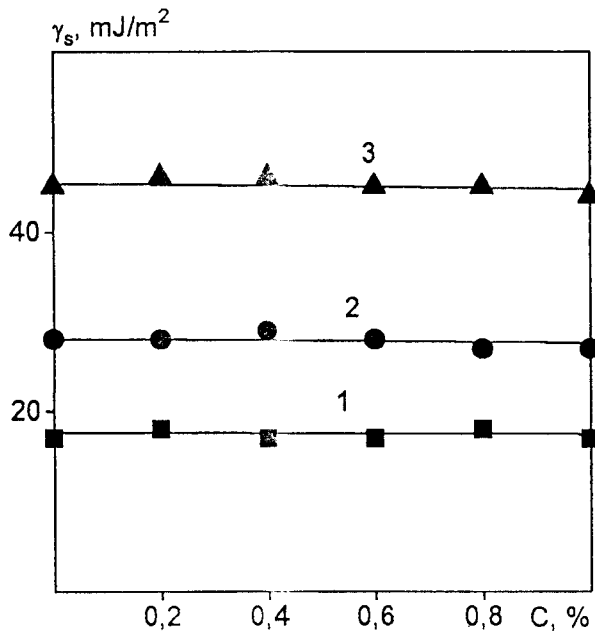
pendence of  $\gamma_s^p$  shows a maximum (Figs. 2–4). A correlation can be observed between  $\gamma_s$  and the adhesion characteristics of modified coatings. The curves for  $\gamma_s$  pass through a maximum in the range of a PAA concentration conforming to the maximum cathodic peeling resistance of the modified coatings [Fig. 1(a)]. In this case, the dispersive component remains constant and equal to the one for unmodified HDPE<sub>1</sub> and the extreme limit is observed for the polar component.

It is necessary to note here that the secondary amines investigated show other dependence of  $\gamma_s$  (Fig. 5). The values of  $\gamma_s^d$ ,  $\gamma_s^p$ , and  $\gamma_s$  in the whole range of concentrations investigated oscillate about the average values corresponding to the unmodified HDPE<sub>1</sub>. The secondary aromatic amines inserted into the composition do not increase the cathodic peeling resistance of the polyethylene coatings. Their adhesion is poor.

The changes in the character of  $\gamma_s$  for HDPE<sub>1</sub> in the presence of PAA is confirmed by the determination of wettability of the HDPE<sub>1</sub> surface. The nonionic surfactants, oxyethylated alkylphenols with various degrees of oxyethylation, were used as wetting liquids. Our study revealed the extreme character of wetting (Fig. 6). The value of the contact angle depends upon the free surface energy  $\gamma_s$ . Wetting of the nonmodified HDPE<sub>1</sub>



**Figure 4** Free surface energy of coatings modified with benzidine plotted against the modifier concentration: (1) the dispersive component; (2) the polar component; (3) the total free surface energy of the coating.



**Figure 5** Free surface energy of coatings modified with *N,N'*-diphenylphenylenediamine plotted against the modifier concentration: (1) the dispersive component; (2) the polar component; (3) the total free surface energy of coating.

surface is the greatest for the surfactant with the lowest degree of oxyethylation. The same order of data is obtained for high DX content. At the point of a maximum of  $\gamma_s$  and its polar component  $\gamma_s^p$ , a maximum of wetting is observed for the surfactant with a greater content of polar ( $-\text{CH}_2-\text{CH}_2-\text{O}-$ ) groups responsible for polar interactions, and vice versa, the surfactant with a low content of polar groups shows lesser wetting at the point of a maximum of  $\gamma_s$  and  $\gamma_s^p$ .

As noticed above, PAA modification leads to an increase in the coatings' peel strength from HDPE<sub>1</sub>. The fracture surfaces of adhesive joints from peel strength determinations show the pronounced cohesive character of the failure. Thicker layers of the polymer remain at the surface of the substrate than in the case of coatings from the untreated HDPE<sub>1</sub>.<sup>7</sup>

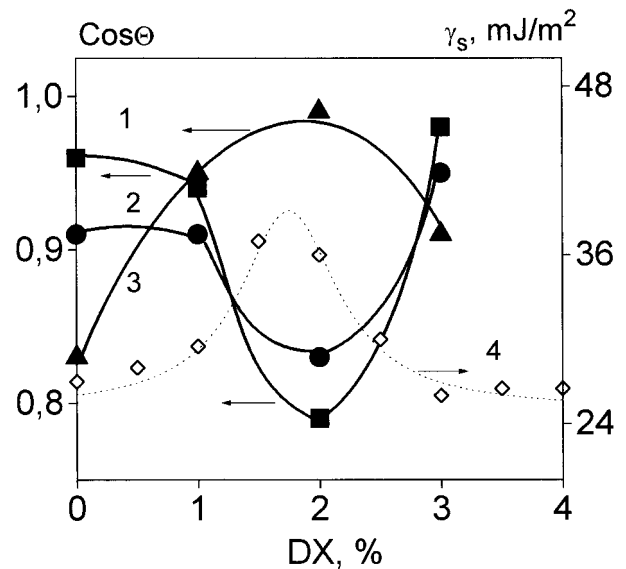
In this connection, the measurement of metal substrate surface energetics after cathodic peeling of the coatings containing different amounts of PAA is of immediate interest (Fig. 7). The smooth fall of  $\gamma_s$  with increase in the 4,4'-diamino-3,3'-dichlorodiphenylmethane content in a coating supports the idea of a more complicated process, rather than a merely adhesive type of cathodic peeling. It was shown by Povstugar et

al.<sup>8</sup> that traces of the polymer coating may remain at the metal surface during the cathodic peeling. In our case, the higher the modifier concentration, the more evident are these traces. That is why the free surface energy of metal substrates reduces the values toward those for modified HDPE<sub>1</sub>.

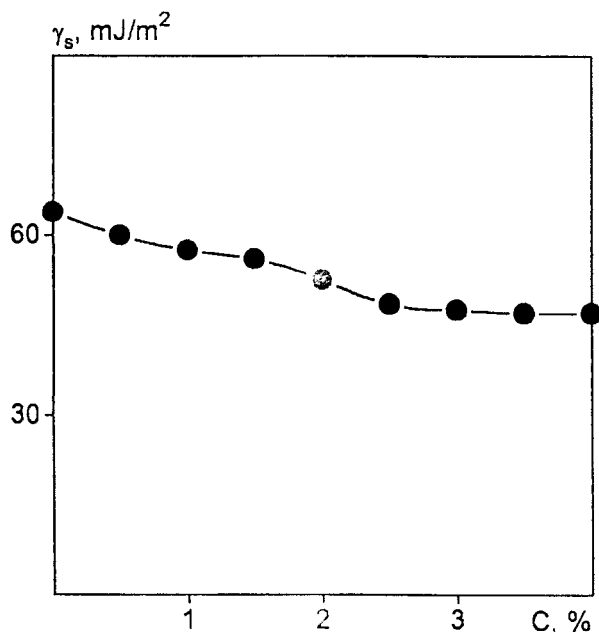
As for phenols, the surface energetics investigation of the modified coatings failed to reveal any changes in the character of the free surface energy. The greatest increase (of the order of 5 kJ/m<sup>2</sup>) in  $\gamma_s^p$  and  $\gamma_s$  was observed only for diphenylpropene (Fig. 8).

Hence, it follows that the correlation between the adhesion and the surface energy characteristics of the coatings modified with PAA revealed by our studies is logical. The chemical modification of HDPE<sub>1</sub> leads to the emergence of polar amine groups in its constitution and causes an increase in  $\gamma_s$  and  $W_a$  for modified HDPE<sub>1</sub> with, consequently, better adhesion.

It follows that  $\gamma_s$  is a characteristic which is responsive to the adhesion activity of additives incorporated in polyethylene. However, the question cannot be answered as to why other modifiers, also containing active functional groups, are not effective from the point of view of a  $\gamma_s$  increase and improved adhesion. It is clear that the nature of the



**Figure 6** Effect of the modifier concentration and the free surface energy on the contact angle to oxyethylated alkylphenols of polyethylene coatings. The degree of oxyethylating  $n$  (the number of oxyethylated groups): (1)  $n = 6$ ; (2)  $n = 9$ ; (3)  $n = 12$ ; (4) free surface energy of coatings modified with *N,N'*-diphenylphenylenediamine plotted against the modifier concentration.



**Figure 7** Free surface energy of the substrate SS after cathodic peeling of the coatings modified with 4,4'-diamine-3,3'-dichlorodiphenylmethane. The x-axis is the modifier content.

functional groups is significant. In addition, good results have been found by PAA modification of the polyethylenes with a high double-bond content.

The nature of the PAA interaction with metal during the coating formation needed to be ascertained. The resolution of the issue is possible by means of an acid–base theory, since the acidity and basicity of polar molecules in the condensed phases are primarily responsible for the interaction of one liquid with another and with the solids in the process of wetting and of polymer adhesion to the solids.<sup>9,10</sup>

#### Acid–Base Interaction in the Polymer–Steel System

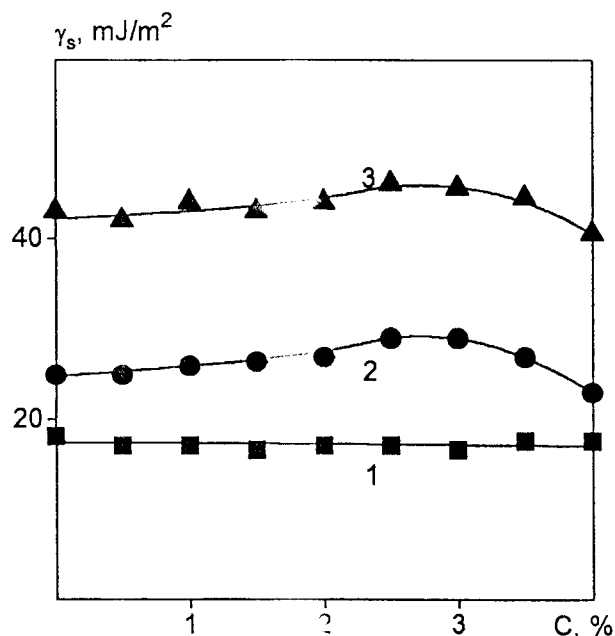
In terms of acid–base properties, the virgin polyethylene is considered to be the most neutral of all polymers. Consequently, the bond strength and durability of its adhesive joints are insignificant.

The ability of a polymer to interact and the resulting adhesive joint strength may increase as a result of imparting acid or base properties during thermochemical modification by inserting compounds with active functional groups into its composition. Evidently, a modifier must be selected in terms of the substrate functionality to realize the optimum acid–base interaction.

So, it needs to be ascertained whether the steel possesses acid or base properties. The currently available data concerning this question are inadequate and contradictory, suggesting that the chemical constitution is different for different steel types. This, in turn, causes a difference in surface functionality for chemically distinct oxidizing steel. Fowkes<sup>3</sup> reasoned that ferric oxides have both acid and base groups on their surface. This does not mean that the steel surface is neutral as a whole. On the contrary, it can play the role of a strong acid (such as SiO<sub>2</sub>) and a strong base (such as hydrated aluminum oxide). Thus, steel functionality is determined by many factors including its chemical formulation and the mode of surface treatment.

According to one method,<sup>4</sup> allowing us to estimate the acidity  $D'$  of any solid smooth surface, the acidity of three types of steel used in this work and of the contact sides of coatings modified with aromatic amines and phenols was determined.  $D'$  was determined by substrating  $2[\gamma_s^p(\text{probe})^{1/2}]$  for the two acidic probes from  $2[\gamma_s^p(\text{probe})^{1/2}]$  for the two basic probes:

$$D' = 2[\gamma_s^p(\text{aniline})^{1/2} + \gamma_s^p(\text{formamide})^{1/2}] - 2[\gamma_s^p(\text{phenol})^{1/2} + \gamma_s^p(\text{glycerol})^{1/2}]$$



**Figure 8** Free surface energy of coatings modified with diphenylol propene plotted against the modifier concentration: (1) the dispersive component; (2) the polar component; (3) the total free surface energy of coating.

**Table III** Data of  $D'$  of the Adhesive Joint Components

Parameter	Surface						
	SS	St-3	St-20	G-65	HDPE <sub>1</sub>	HDPE <sub>1</sub> + 2%DX <sup>a</sup>	HDPE <sub>1</sub> + 3%DPhP <sup>b</sup>
$D'$ (mJ/m <sup>2</sup> ) <sup>1/2</sup>	4.56	2.21	2.58	4.21	3.59	-0.62	7.61

<sup>a</sup> DX, 4,4'-diamino-3,3'-dichlordiphenylmethane.

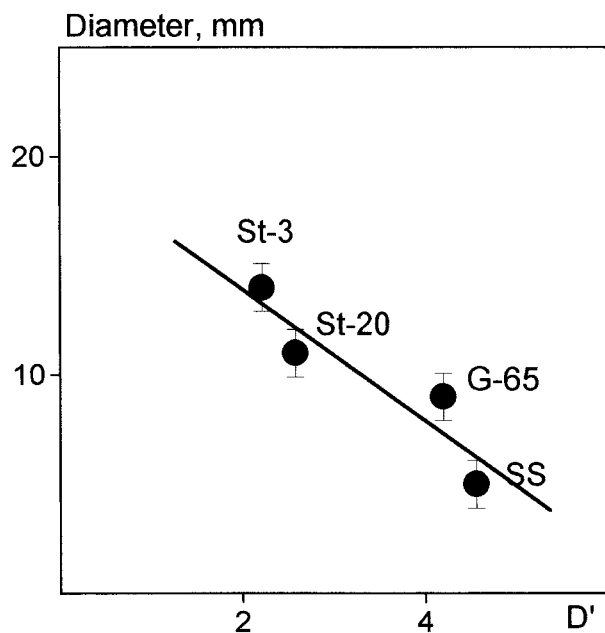
<sup>b</sup> DPhP, diphenylolpropene.

The results obtained are listed in Table III. As can be seen from the data presented,  $D'$  comprises 2.21 for St-3, 2.58 for St-20, 4.21 for G-65, and 4.56 for SS steel. The acidity of the material tends to increase with any increase in the value of  $D'$ . In our case, the signs of  $D'$  for all four types of steel are positive, that is, they are characterized by some acidity, yielding a maximum for SS steel. The values of  $D'$  for steel and unmodified HDPE<sub>1</sub> are sufficiently comparable. In the context of the approach considered, it means a lack of detectable acid-base interaction, which is consistent with low cathodic peeling strength and water resistance for unmodified HDPE<sub>1</sub> coatings. The value of  $D'$  for the coatings, modified with 4,4'-diamino-3,3'-dichlordiphenylmethane, suggests that these coatings have a more base character than that of the metal. This is not surprising since amines are

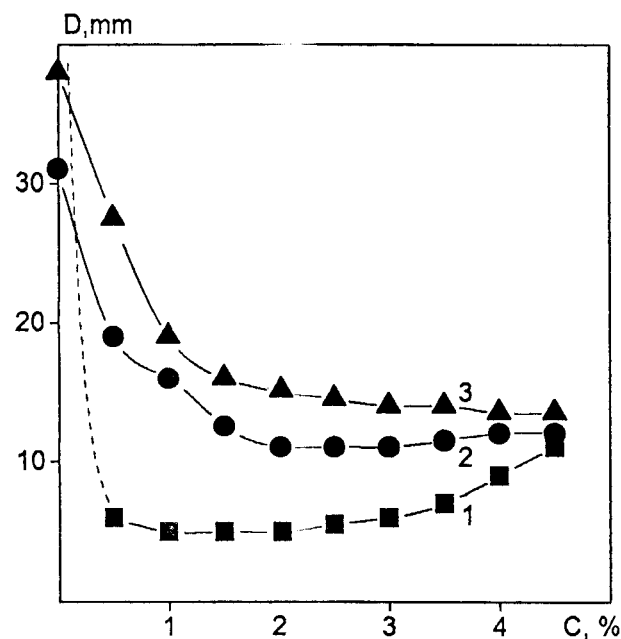
Lewis bases. All the above testifies that the capacity of acid-base interactions on the interface can increase and the system considered has good adhesive properties. An important point is that the increasing acidity of the substrate correlates with the increased adhesion to HDPE<sub>1</sub> coatings modified with PAA (Figs. 9 and 10).

The parameter  $D'$  was measured by us for the coatings, modified with diphenylol propene. These results indicate (Table III) that the surface of interest has more high acidity than that of the one considered for steels, that is, the modification of polyethylene with phenols confers acid properties on the polymer. Because of this, the acid-base interaction in systems of this kind was weaker than after addition of PAA.

The results obtained on the basis of the acid-base theory are supported by infrared spectrum



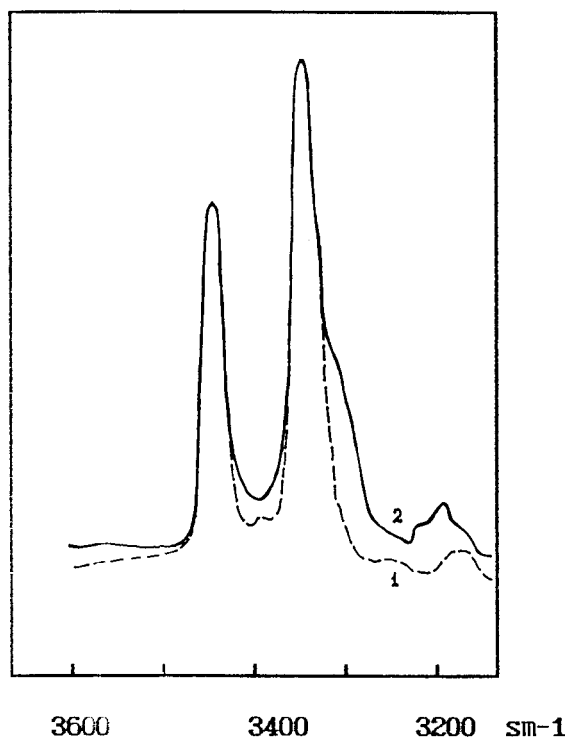
**Figure 9** Correlation between maximum of cathodic peeling resistance (minimum of the defect diameter) and the acidity parameter of steel.



**Figure 10** Cathodic peeling resistance of modified coatings formed on the substrate (plot 1) SS, (plot 2) St-20, and (plot 3) St-3. The x-axis is the content of 4,4'-diamine-3,3'-dichlordiphenylmethane.



## Transmission



**Figure 11** IR transmission spectra: (1) heat-treated 4,4'-diamine-3,3'-dichlorodiphenylmethane; (2) heat-treated 4,4'-diamine-3,3'-dichlorodiphenylmethane with finely-dispersed iron. Forming time, 20 min. Forming temperature, 220°C.

data for model systems consisting of different modifiers and their mixtures with finely dispersed iron, heat-treated under the technological conditions of the 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 mixes with iron are significantly different. Some of them are listed in Figures 11 and 12. The systems PAA + iron observe the band changes in the region of 3300–3500  $\text{cm}^{-1}$  responsible for valent oscillations of the N—H bond in primary amine groups.

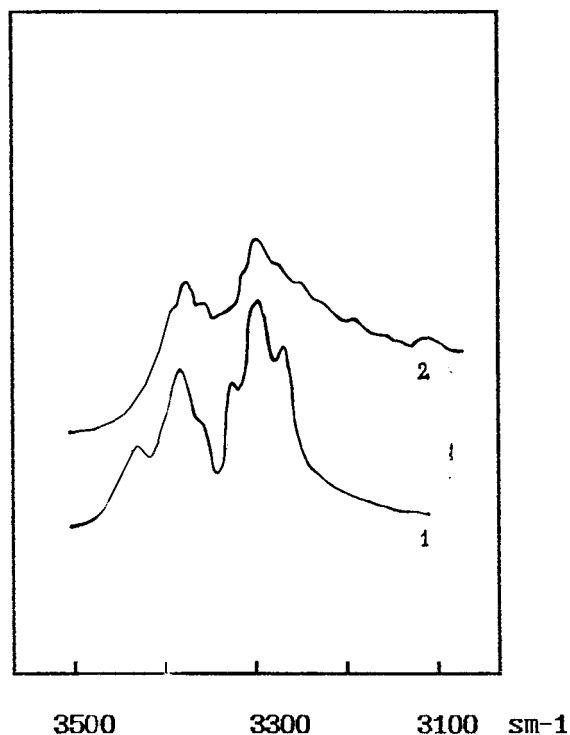
The band widening of valent oscillations in primary amine groups and the band shift to the region of low frequency are observed. Such changes may be thought of as the result of the donor–acceptor interaction between amine groups of the adhesive and hydroxyl groups of the substrate surface. So, the role of acid–base interactions in providing the adhesion of HDPE<sub>1</sub> coatings is established. However, the results obtained fail to explain the poor adhesion of the coatings prepared from PAA compositions with other kinds of polyethylene. The special

nature of HDPE<sub>1</sub> appears to be determined by its chemical structure peculiarities, leading to the specific interactions between PAA and polymer macromolecules.

According to the results of IR spectral and quantum-chemical investigations, it was found in our previous work<sup>11,12</sup> that PAA combines readily with the double bonds of the polymer at the coating formation temperature. In doing so, some of the primary amine groups change to secondary groups. Along with this type of chemical interaction, the physical interaction takes place with formation of H complexes between oxygen-containing groups of polyethylene and NH<sub>2</sub> groups. Chemical interaction seems to play the most important role.

This is supported by the results from determinations of the cathodic peeling resistance of vacuum-formed coatings. The cathodic peeling resistance of coatings in the optimum range of PAA concentration is high and its character does not change, even though the degree of polymer oxidation in such coatings is vanishingly small and the formation of hydrogen bonds is difficult.

## Transmission



**Figure 12** IR transmission spectra: (1) heat-treated benzidine; (2) heat-treated benzidine with finely dispersed iron. Forming time, 20 min. Forming temperature, 220°C.

So, the molecules of PAA diffusing to the polymer–metal interface take part in the interface interaction, with the effect that one of the modified functional groups is chemically or physically connected with polymer macromolecules. The other group interacts with steel by an acid–base, donor–acceptor mechanism.

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