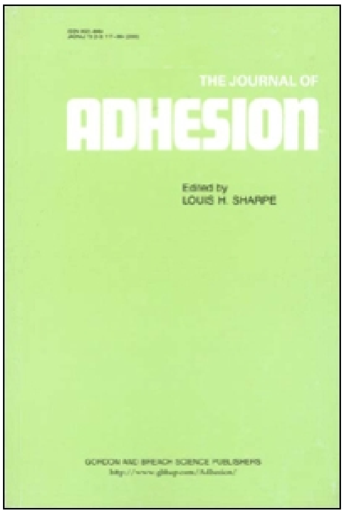

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Surface Characterization of Polymers by Physico-Chemical Measurements*

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The possibility of characterizing dispersion forces and acid-base interactions by means of physico-chemical measurements is demonstrated by the examples of contact angle and zeta potential measurements, with special attention being given to the latter. This method has been applied, to characterize the effect of plasma and flame treatment on the adhesion behaviour of injection moulded poly(propylene) specimens. The results with respect to acidic or basic functional surface sites, as obtained by zeta potential measurements, correlate with the elemental surface compositions determined by XPS. There is no general interrelation between acidic and basic parameters determined by contact angle measurements and the results of zeta potential and XPS measurements.

KEY WORDS Adhesion; dispersion forces; acid-base interactions; zeta potential measurements; polymer pre-treatments.

INTRODUCTION

Like other parameters, such as contact area and distance or diffusion, the adhesion strength between soild polymers and other substances is strongly influenced by the type and magnitude of intermolecular forces at the contact area between the adhesion partners.

In order to elucidate the adhesion mechanism between solids, as well as to change the adhesion properties of polymers, detailed information about the interrelation between chemical composition of the interface and intermolecular forces between the adhesion partners is necessary.

Three principal kinds of methods can be used for the characterization of adhesion forces, including:

- direct force measurements
- spectroscopic determination of the chemical composition of solid surfaces
- physico-chemical measurements of interactions energetics

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This paper is dedicated to Prof. Dr. Hansjörg Sinn on the occasion of his 65th brithday with thanks and best wishes.

This paper will deal with the application of physico-chemical measurements, especially zeta potential measurements, for characterization of the adhesion properties of polymers.

INTERACTION FORCES AT POLYMER SURFACES

Table I summarizes the interaction forces at solid surfaces which can influence the adhesion strength between polymers and other solids, and the magnitude of the interaction energy to be expected.

It is well known that the occurrence of covalent chemical bonds and Coulomb forces in adhesion systems lead to high values of adhesion strength whereas exclusive occurrence of dispersion forces accounts for weak adhesion forces. It is assumed that acid-base interactions indicate higher interaction energy than dispersion interactions. Thus, numerous modifications of polymer surfaces have been carried out to improve the adhesion properties by the creation of acidic or basic sites at the surface.

The term "displacement forces" describes the effect of adsorbed substances, impurities and auxiliaries on adhesion phenomena. In the following, the theoretical background of dispersion, acid-base interaction and displacement forces will be briefly discussed.

DISPERSION INTERACTIONS

The dispersion interaction energy between solids can be sufficiently described by the "microscopic" theory which assumes summation of intermolecular forces between the molecules in a solid. According to this approach (see Refs. 1,2) the dispersion energy between solids is given by their Hamaker constant and the adhesion distance (eq. 1).

$$E_{\mathrm{disp}} = -\frac{A}{12 \cdot \pi \cdot d^2} \tag{1}$$

with E_{disp} = interaction energy
A = Hamaker constant
d = distance

TABLE I
Interaction forces at polymer surfaces

Interacting component	Range	Parameter to be determined	Interaction energy [kJ · mol^{-1}]
Covalent bond	short	reactivity of functional groups	60 – 600
Coulomb interaction	short	charge of functional groups	> 400
dispersion forces	long	Hamaker constant	≤ 40
acid-base	short		≤ 50
interactions		pK values	
• Brønsted theory		constant acc. to many	
• Lewis theory		approaches	
"displacement forces"	short	adsorption free energy	≤ 40

The Hamaker constant is approximately proportional to the London constant of the molecules and the squared number of molecules per unit volume (Eq. 2).

$$A = \pi^2 \cdot \beta \cdot q^2 \tag{2}$$

with β = London constant
q = number of particles per unit volume

Therefore, the adhesion force of solids should decrease with increasing porosity of the solids.

ACID-BASE INTERACTIONS

Acid-base interactions at interfaces can be attributed to

- dissociation of functional surface groups according to the Brønsted theory and specific adsorption of H^+ or OH^- on surface groups
- electron transfer between the adhesion partners according to the Lewis and Pearson theories.

Bolger's approach[3] can be applied to describe acid-base interactions between amphoteric metal oxide hydrates and organic acids or bases according to the Brønsted theory (Eqs. 3 and 4).

$$\mathrm{MOH} + \mathrm{HXR} \rightleftharpoons \mathrm{MOH_2^+} + \mathrm{XR^-} \quad K_A = \frac{a[\mathrm{MOH_2^+}] \cdot a[\mathrm{XR^-}]}{a[\mathrm{MOH}] \cdot a[\mathrm{HXR}]} \tag{3}$$

$$\mathrm{MOH} + \mathrm{YR} \rightleftharpoons \mathrm{MO^-} + \mathrm{HXR^+} \quad K_B = \frac{a[\mathrm{MO^-}] \cdot a[\mathrm{HYR^+}]}{a[\mathrm{MOH}] \cdot a[\mathrm{YR}]} \tag{4}$$

with MOH = metal hydroxide
HXR = organic acid
YR = organic base
$a[i]$ = activity of species i

$$\Delta A = \log K_A = pK^{\mathrm{inorg}}_{A(B)} - pK_{A(A)} \tag{5}$$

$$\Delta B = \log K_B = pK^{\mathrm{inorg}}_{A(A)} - pK_{A(B)} \tag{6}$$

with ΔA, ΔB = energy term according to Bolger.

According to this approach, the acid-base interaction energy is given by the parameters ΔA or ΔB. The adhesion strength is the higher the more negative the values of ΔA or ΔB.

The energy due to acid-base interactions according to the Lewis theory can be expressed for example by the Drago constants or the donor or acceptor numbers of solids according to Gutmann (for more details see Ref. 4).

"DISPLACEMENT FORCES"

We used the term "displacement forces" to explain the effect of sorption layers on adhesion. The mass-action law was simply applied to adhesion phenomena as shown in Eq. (7).

$$AB + 2C \rightleftharpoons AC + BC \qquad K = \frac{a[AC]\cdot a[BC]}{a[AB]\cdot a^2[C]} \tag{7}$$

The link between the standard interaction free energy, $\Delta_R G^\theta$, and the equilibrium constant K is given by Eq. (8).

$$\Delta_R G^\theta = -R\cdot T\cdot \ln K \tag{8}$$

with R = gas constant
T = temperature
where

$$\Delta_R G^\theta = \Delta_B G^\theta_{AC} + \Delta_B G^\theta_{BC} - \Delta_B G^\theta_{AB} \tag{9}$$

with $\Delta_B G^\theta_i$ = standard free energy of formation.

According to this approach, the equilibrium in an adhesion system containing two solids and one (or more) "third" substances is given by the standard free energy of formation between all the partners and the activity ($\approx$ concentration) of the "third" substance (see also Ref. 5).

Interrelations have been found[5] between free energy of adsorption of water vapour on fibres, determined by microgravimetrical methods, and the decrease of the free energy of adhesion between fibres and other solids. They confirm the approach of "displacement forces".

PHYSICO-CHEMICAL SURFACE CHARACTERIZATION METHODS

Physico-chemical measurements may be applied for the determination of dispersion and acid-base interaction and "displacement forces".

Generally, these measurements are based on the investigation of interaction energies between low molecular test molecules and solids. Gaseous, liquid and dissolved substances can be used as low molecular test substances.

In the case of solid-gas interactions, inverse gas chromatography (IGC) has been established for the determination of parameters characterizing dispersion and acid-base interactions according to the Lewis acid-base theory.[6,7] Correlations between surface characteristics determined by IGC and practical adhesion phenomena have been found experimentally by different authors.[8–10]

The most frequently used physico-chemical method to characterize the surface properties of polymers is the measurement of the contact angle of a sessile liquid drop which is sensitive to changes in the surface free energy of the solid. The interrelations between contact angle, surface free energy and work of adhesion are shown in the following equations.

$$W_{12} = \gamma_1 + \gamma_2 - \gamma_{12} \qquad \text{or } W_a = \gamma_s + \gamma_l - \gamma_{sl} \tag{10}$$

$$\gamma = \left(\frac{\partial \mathscr{F}}{\partial A}\right)_{T,V} \tag{11}$$

$$\gamma_{sv} = \gamma_{sl} + \gamma_{lv} \cdot \cos(\Theta) \tag{12}$$

with W_{12} = reversible thermodynamic work of adhesion
γ_1, γ_2 = surface free energy of the phases 1 and 2 in vacuum
γ_{12} = interfacial free energy
γ_{sv}, γ_{lv} = interfacial free energy between solid and gaseous phase and liqud and gaseous phase, respectively
γ_l, γ_s = surface free energy of the liquid and the solid, respectively
γ_{sl} = interfacial free energy
Θ = contact angle
$\mathscr{F}$ = Helmholtz free energy
A = surface area
V = volume

Combination of the Dupré equation (10) and the Young equation (12) permits one to calculate the thermodynamic work of adhesion W_a from contact angle measurements (Eq. 14).

$$\gamma_l \cdot \cos(\Theta) = \gamma_s - \gamma_{sl} - \pi_e \tag{13}$$

$$W_a = \gamma_l \cdot [1 + \cos(\Theta)] + \pi_e \tag{14}$$

with π_e = equilibrium spreading pressure.

Table II summarizes empirical approaches to calculate the surface free energy of solids, which have been used by different authors to characterize the adhesion properties of polymers.

A general correlation between surface free energy and adhesion cannot be described. The limitations of contact angle measurements and the surface free energy concept are especially due to

- limited theoretical background
- morphological factors influencing the contact angle in addition to surface free energy
- influence of adsorption phenomena on contact angle and surface free energy

ZETA POTENTIAL MEASUREMENTS

Conclusions with regard to the occurrence of dispersion, acid-base, and displacement forces in adhesion systems can be drawn from the results of zeta potential measurements using the Gouy-Chapman-Stern-Grahame model (GCSG model) of the electrical double layer.

As shown in Figure 1, the existence of an electrical double layer in the solid polymer/aqueous electrolyte solutions is due to dissociation processes of acid or basic molecular groups and to preferential adsorption of one kind of ion in competition with

TABLE II

Calculation of the surface free energy of polymers from contact angle by different approaches

Approach	Equation
Neumann[11]	$\cos\Theta = \frac{(0.015\cdot\gamma_s - 2)\cdot\sqrt{\gamma_s\cdot\gamma_l} + \gamma_l}{\gamma_l\cdot(0.015\cdot\sqrt{\gamma_s\cdot\gamma_l} - 1)}$
Owens, Wendt[12] Kaelble[13]	$[1+\cos(\Theta)]\cdot\gamma_l = 2\cdot\left[\sqrt{\gamma_s^d\cdot\gamma_l^d} + \sqrt{\gamma_s^p\cdot\gamma_l^p}\right]$
Wu[14]	$[1+\cos(\Theta)]\cdot\gamma_l = 4\cdot\left[\frac{\gamma_l^d\cdot\gamma_s^d}{\gamma_l^d+\gamma_s^d} + \frac{\gamma_l^p\cdot\gamma_s^p}{\gamma_l^p+\gamma_s^p}\right]$
Fowkes[15]	$[1+\cos(\Theta)]\cdot\gamma_l = 2\cdot\sqrt{\gamma_s^d\cdot\gamma_l^d}$
van Oss, Chaudhury and Good[16]	$[1+\cos(\Theta)]\cdot\gamma_l = 2\cdot\left[\sqrt{\gamma_s^{LW}\cdot\gamma_l^{LW}} + \sqrt{\gamma_s^+\cdot\gamma_l^-} + \sqrt{\gamma_s^-\cdot\gamma_l^+}\right]$

γ_l	surface free energy of liquid	γ_s	surface free energy of solid
γ_l^d	dispersion term	γ_s^d	dispersion term
γ_l^p	polar term	γ_s^p	polar term
γ_l^{LW}	Lifshitz-van der Waals term	γ_s^{LW}	Lifshitz-van der Waals term
γ_l^+	electron acceptor term	γ_s^+	electron acceptor term
γ_l^-	electron donor term	γ_s^-	electron donor term

adsorption of water. Since anions are preferentially adsorbed in a neutral 1:1-electrolyte solution the zeta potential of most polymers is negative.

Figure 2 shows schematically the build up of the electrical double layer according to the GCSG model.[17] As is well known, the electrokinetic or zeta potential, which is accessible by electrokinetic experiments, is assumed to be the potential of the outer Helmholtz plane.

In 1924 Otto Stern[18] derived equations for the interrelations between the zeta potential of solids in 1:1-electrolytes (*e.g.*, KCl) and the free energies of adsorption of K^+ and Cl^- ions. As shown schematically in Figure 3 most polymers show a parabolic dependence on concentration of KCl solutions. The concentration at maximum zeta potential, c_{max}, and the maximum zeta potential ζ_{max} permit the calculation of the molar adsorption free energies, Φ_{K^+}, for K^+ and Φ_{Cl^-} for Cl^- ions (Eqs. 15 and 16).

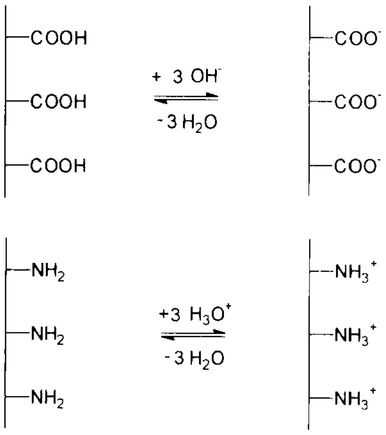
$$\Phi_{Cl^-} - \Phi_{K^+} = 2\cdot F\cdot\zeta_{max} \tag{15}$$

$$\Phi_{Cl^-} + \Phi_{K^+} = 2\cdot R\cdot T\cdot\ln[c_{max}] \tag{16}$$

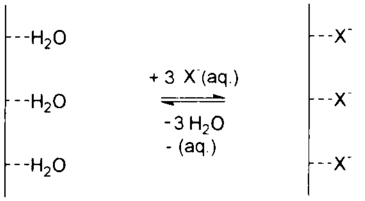
with F = Faraday constant.

Assuming that anions are partially dehydrated and adsorbed in the inner Helmholtz plane by dispersion interactions and that the hydrated cations are suitable as counter ions in the diffuse part of the double layer, the value of ζ_{max} in KCl solutions should correspond with the dispersion forces occurring at solid surfaces.

As shown in Eq. (1) the dispersion interaction energy between parallel plates is given by the Hamaker constant of the substances, in which the porosity of the materials is involved. Figure 4 shows that the ζ_{max} values of poly(acrylonitrile) fibres increase with



a) Dissociation of surface functional groups



b) Preferential adsorption of dehydrated anions due to dispersion interaction hydrated surface ⇌ hydrated anion

FIGURE 1 Mechanism of double layer formation at the polymer/electrolyte interface.

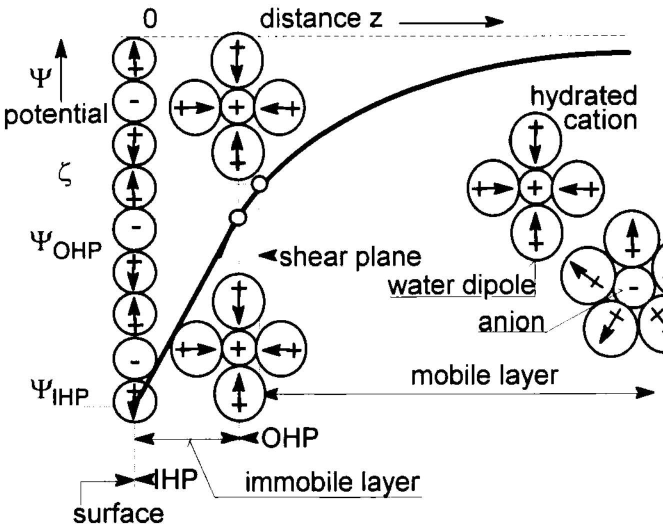


FIGURE 2 Build-up of an electrochemical double layer according to Gouy-Chapman-Stern-Grahame model.

increasing Hamaker constant when the porosity is kept constant and that they decrease with increasing porosity as expected from the microscopic theory of dispersion forces. (The values of Figure 4 were taken from Ref. 5).

Since adsorption of ions at the solid electrolyte interface takes place in competition with adsorption of water, the ζ_{max} values in KCl solutions are lower the higher the hydrophilicity of the solid. Figure 5 shows the experimental confirmation of these assumptions. ζ_{max} correlates linearly with the cosine of the contact angle between polymers and water.[19]

Experiments have shown that ζ_{max} corresponds very well with the adhesion behaviour of solids due to dispersion forces. Examples are given in Ref. 5 for pigment soil adhesion on fibers and for reinforcement of polymers.[20] Thus, the influence of the Hamaker constant (influenced by the chemical constitution as well as by the porosity) and of sorption phenomena on the adhesion force can be explained by zeta potential

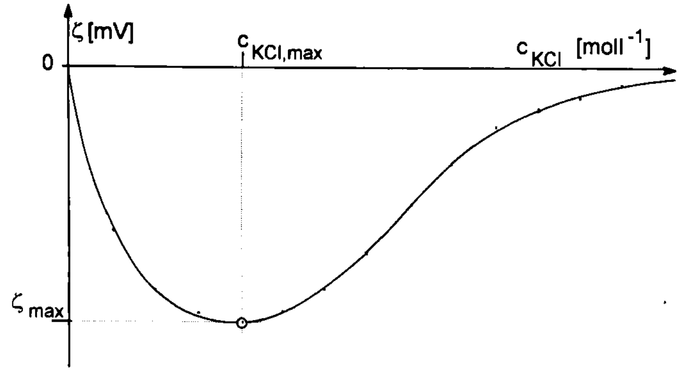


FIGURE 3 Zeta potential of polymers as a function of KCl concentration.

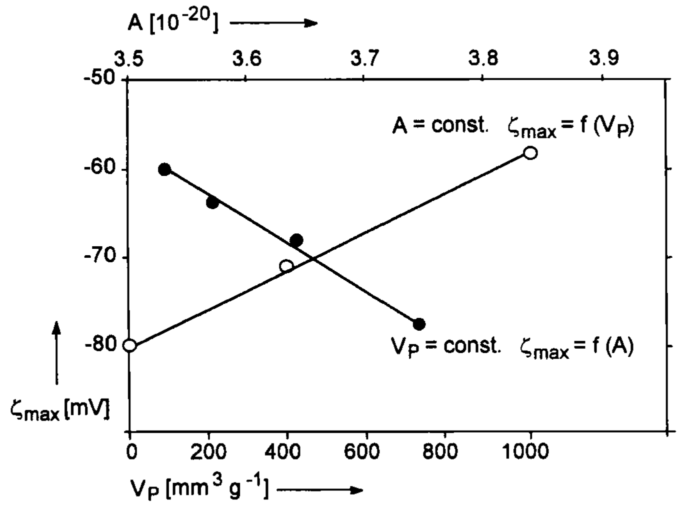


FIGURE 4 Maximum zeta potential of PAN fibres in KCl solution as a function of Hamaker constant A (●) and specific pore volume Vp (○).

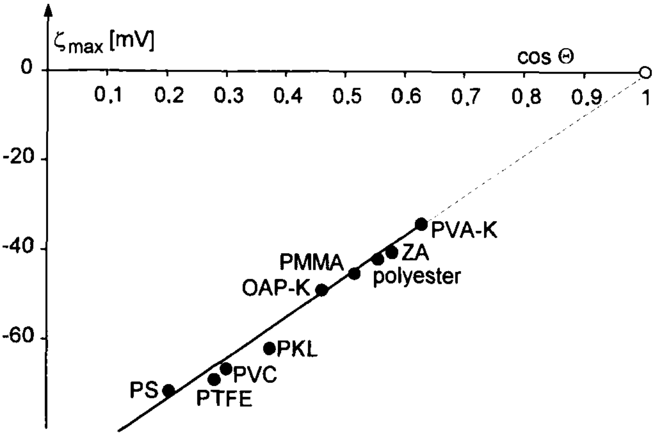


FIGURE 5 Maximum zeta potential in KCl solution and cosine of the contact angle of water for different polymers (PKI, OAP-K, ZA and PVA-K polymers used for offset printing).

measurements. Zeta potential measurements can also be applied for characterizing the acid-base characteristics of solids. Generally, the presence of acidic or basic functional groups corresponds with the ζ-pH plot, as can be seen in Figure 6.

According to Hunter,[17] the pK values of dissociating functional groups of solids can be calculated from the ζ-pH plot at varied ionic strength. Using the GCSG model, Börner[21] developed an approach which allows the determination of the molar free energies of adsorption of H^+ and OH^- ions, which correspond with the pK_A and pK_B values of acidic or basic groups, as well as with the molar adsorption free energies of electrolyte ions from the ζ-pH-c plots. The principle of this approach is described in the following:

The charge densities of the inner and outer Helmholtz planes is given by Eqs. (17) and (18).

$$\sigma^{IHP} = \sum_i z_i \cdot x_i^{IHP} \cdot e \cdot N \tag{17}$$

$$\sigma^{OHP} = \sum_i z_i \cdot x_i^{OHP} \cdot e \cdot N \tag{18}$$

with z_i = stoichiometric number (in the case of 1:1-electrolytes $z = [-1]$ for anions and $z = [+1]$ for cations)
x_i^k = molar fraction of the ionic species in the k plane
e = elementary charge
N = number of adsorption sites

The charge density in the diffuse layer in the case of 1:1-electrolytes can be described according to the Stern model:

$$\sigma^{\text{diffuse}} = \sqrt{2 \cdot \varepsilon_r \cdot \varepsilon_0 \cdot R \cdot T \cdot c_{\text{bulk}}} \cdot \left\{ \exp\left[\frac{F \cdot \zeta}{2 \cdot R \cdot T}\right] - \exp\left[-\frac{F \cdot \zeta}{2 \cdot R \cdot T}\right] \right\} \tag{19}$$

The concentration of the ionic species in the plane k can be expressed by the bulk concentration by means of a Boltzmann approach which contains the adsorption

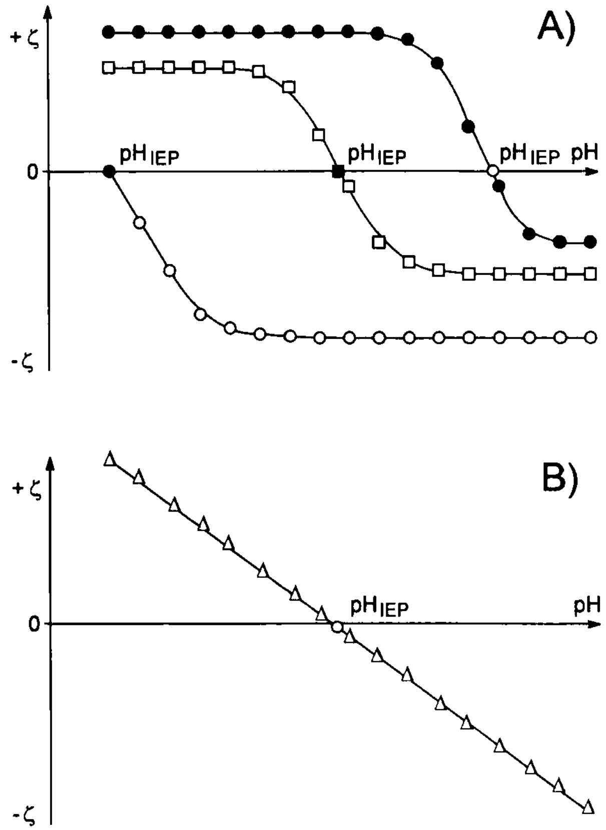


FIGURE 6 Schematic representation of zeta potential *versus* pH plot of solids A): • dissociable basic molecule groups; □ dissociable acidic and basic molecule groups; ○ dissociable acidic molecule groups. B): △ non-polar surface without dissociable molecule groups.

potentials for the ionic species, Φ_i. Eqs. (20) and (21) follow from Eqs. (17) and (18) in the case of 1:1-electrolytes.

$$\frac{\sigma^{IHP}}{e\cdot N}=\frac{\sum_i z_i\cdot c_i^{\text{bulk}}\cdot\exp\left[-\frac{z_i\cdot F\cdot\Psi_0-\Phi_i}{R\cdot T}\right]}{\sum_i |z_i|\cdot c_i^{\text{bulk}}\cdot\exp\left[-\frac{z_i\cdot F\cdot\Psi_0-\Phi_i}{R\cdot T}\right]+55.5\frac{\text{mol}}{l}} \tag{20}$$

$$\frac{\sigma^{OHP}}{e\cdot N}=\frac{\sum_i z_i\cdot c_i^{\text{bulk}}\cdot\exp\left[-\frac{z_i\cdot F\cdot\zeta-\Phi_i}{R\cdot T}\right]}{\sum_i |z_i|\cdot c_i^{\text{bulk}}\cdot\exp\left[-\frac{z_i\cdot F\cdot\zeta-\Phi_i}{R\cdot T}\right]+55.5\frac{\text{mol}}{l}} \tag{21}$$

$$C^{SP}=\frac{\sigma^{IHP}+\sigma^{\text{diff}}}{\zeta-\Psi_0} \tag{22}$$

Mathematical modelling of the electrokinetic double layer by means of the value tripletts zeta potential, ζ, bulk concentration of electrolyte ions, c_i^{bulk}, and pH as an expression of the bulk concentration of H^+ and OH^- ions, respectively, according to eqs. (17) – (21) and the equation for the integral Stern capacity, C^{SP}, (Eq. 21) permit the calculation of the adsorption potentials for all ionic species (Φ_i) of electrolyte solutions (*e.g.*, K^+,Cl^-,H^+,OH^- ions in the case of potassium chloride solutions), the charge densities in the two Helmholtz planes and the diffuse layer (σ^k), and the integral capacity of the Stern layer (C^{SP}). The adsorption potentials of H^+ and OH^- ions correspond, like the molar free energies of adsorption, $\Delta_{ads}G^\theta$, with the pK_A and pK_B values of acidic or basic groups according to Eqs. (23) and (24).[22]

$$\exp\left[\frac{-\Phi_{H^+}}{R \cdot T}\right] = \frac{10^{-pK_b} \cdot c[H_2O]}{K_w \cdot (l/\text{mol})} \tag{23}$$

$$\exp\left[\frac{-\Phi_{OH^-}}{R \cdot T}\right] = \frac{10^{-pK_a} \cdot c[H_2O]}{K_w \cdot (l/\text{mol})} \tag{24}$$

The molar adsorption potentials, Φ_i, represent the non-electrostatic adsorption and do not describe the electrostatic influence on the adsorption equilibration between the charged surface and ionic species, *i*, from the liquid phase. Hence, Φ_i is a characteristic value to describe the adsorption equilibration at the isoelectric point.

The application of the model mentioned above was investigated in detail for polymer-grafted silica particles by Simon.[23] Results are summarized in Figure 7a, 7b, and 7c. They show that the isoelectric points as well as the pK_A and the pK_B values of grafted silica correspond with the acidic or basic character of the surface.

It is possible to describe a pK_i dependence on pH and c^{bulk}, with respect to the electrostatic term of the molar free adsorption energy, $\Delta_{\text{ads}}G_i^\theta$ (Eq. (25).

$$\Delta_{\text{ads}}G_i^\theta = \Phi_i + z_i \cdot F \cdot \zeta(pH, c^{\text{bulk}}) \tag{25}$$

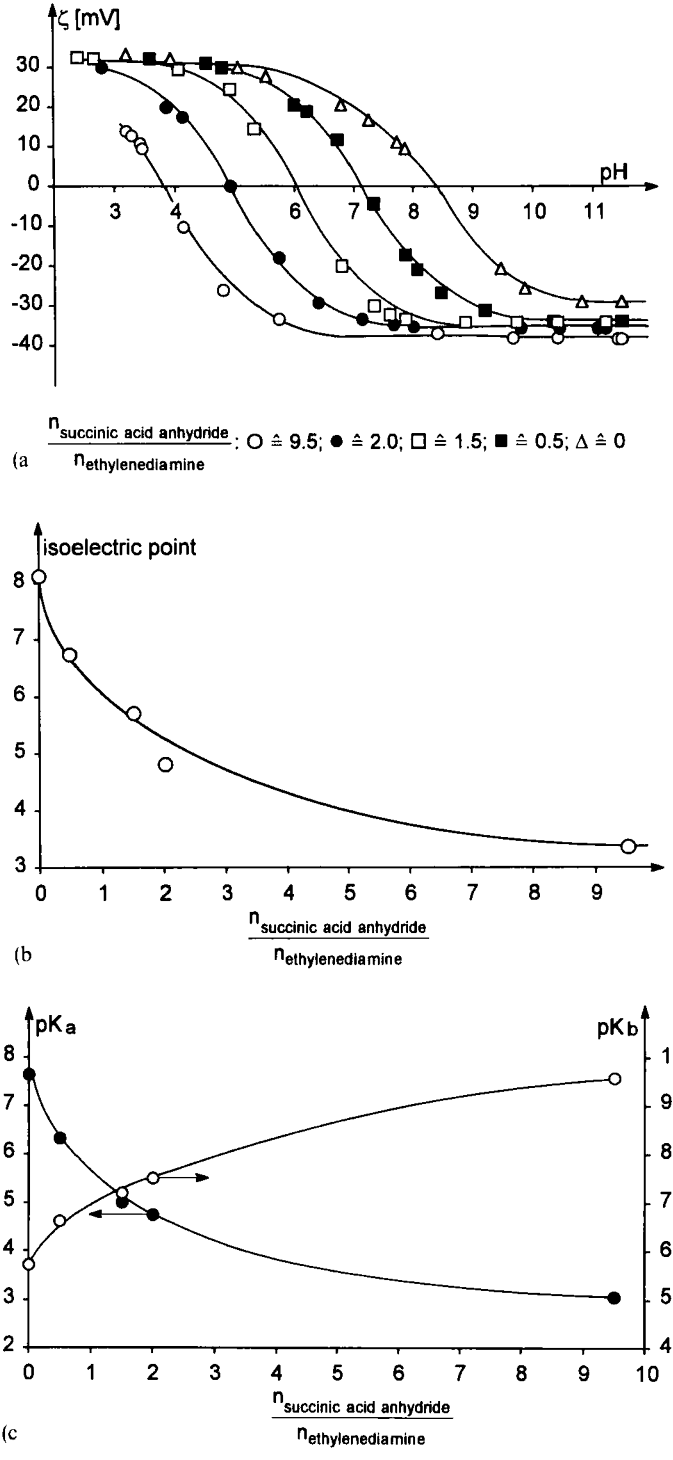
RESULTS AND DISCUSSION

Investigation of Surface Properties of Poly(propylene) Based Plastics

The applicability of zeta potential measurements and the model mentioned above to surface characterization was also proved with differently-treated poly(propylene) (PP) and PP/EPDM injection moulded sheets. In order to improve the adhesion properties of these polymers (*e.g.*, used as automotive bumpers) to poly(urethane) lacquers, washing procedures, flame or plasma pre-treatments are used in industry.

The zeta potential *versus* pH plots of differently pre-treated PP and PP/EPDM test specimens were obtained by means of the Elektrokinetic Analyzer EKA (Anton Paar KG, Graz, Austria). Figure 8 shows the ζ *versus pH* plots for untreated, power washed, flame treated, and oxygen plasma treated PP/EPDM sheets.

Qualitatively, the untreated sample shows the ζ-pH plot typical of non-polar surfaces whereas the "power washed" and flame treated specimens seem to have an


ζ [mV]
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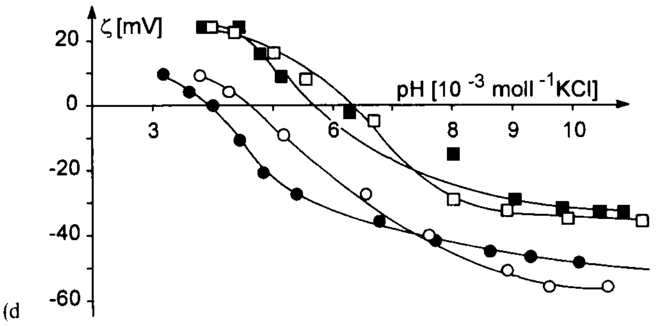

FIGURE 8 Zeta potential *versus* pH of differently treated PP/EPDM injection moulded sheets (Keltan TP 2600) ○ untreated, ■ "power wash" treated, □ flame treated, ● oxygen plasma treated.

TABLE III

Surface parameters of differently treated PP/EPDM (Keltan TP 2600) sheets calculated from ζ-pH-c_{KCl}^{bulk} plots

Sample	Dispersion interaction Φ_i [kJ·mol^{-1}]			Acid-base interaction Φ_i [kJ·mol^{-1}]				
	Φ_{K^+}	Φ_{Cl}	$\lvert\Phi_{Cl^-} - \Phi_{K^+}\rvert$	Φ_{H^+}	Φ_{OH^-}	$pK_{A(A)}$	$PK_{B(B)}$ $pK_{A(B)}$	*IEP*
untreated	−18.8	−21.1	2.3	−28.9	−56.9	5.7	10.6 3.4	4.6
power-wash treated	−7.8	−15.8	8.0	−38.2	−45.1	7.8	9.0 5.0	6.1
flame treated	−12.7	−20.0	7.3	−49.9	−60.3	5.1	6.9 7.1	6.3
O_2-plasma treated	−6.0	−13.5	7.5	−26.3	−62.8	4.6	11.1 2.9	3.8

IEP = isoelectric point

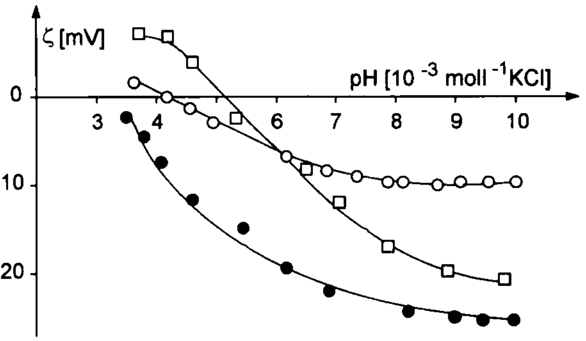

FIGURE 9 Zeta potential *versus* pH of differently treated PP injection moulded sheets (Hostalen PPN 1060) ○ unstreated, □ flame treated, ● oxygen plasma treated.

FIGURE 7 (a) Zeta potential measured in 10^{-3} mol·l^{-1} KCl *versus* pH of silica-poly (butadiene epoxide) composites differently grafted with ethylenediamine and succinic acid anhydride. (b) Isoelectric point of differently grafted silica-poly (butadiene epoxide) composites *versus* ratio of grafted substances. (c) pK_a and pK_b values of differently grafted silica-poly (butadiene epoxide) composites calculated by means of the GCSG model *versus* ratio of grafted substances.

TABLE IV

Surface parameters of differently treated PP (Keltan TP 2600) and PP/EPDM (Hostalen PPN 1060) injection moulded sheets

Surface treatment	Φ_i[kJ · mol^{-1}] calculated from ζ-pH-c_{KCl}^{bulk} plots			Surface free energy components γ_j^i [mJ · m^{-2}] determined by contact angle measurements				Elemental surface composition determined by XPS	
	Φ_{H^+}	Φ_{OH^-}	$\lvert\Phi_{Cl^-} - \Phi_{K^+}\rvert$	γ_s^d	γ_s^{p*}	γ_s^{-**}	γ_s^{+**}	O/C	N/C
Untreated PP/EPDM	−28.9	−56.9	−2.3	25.3	0.4	0.5	0.09	0.034	0
plasma treated PP/EPDM	−26.3	−62.8	−7.5	23.3	5.4	11.6	0.1	0.149	0
flame treated PP/EPDM	−49.9	−60.3	−7.3	25.9	9.0	30.3	2.6	0.154	0.013
untreated PP	−31.0	−56.1	−1.7	29.7	0.8	1.4	0	0.019	0
plasma treated PP	−31.3	−60.9	−6.1	28.0	9.6	9.2	1.0	0.120	0
flame treated PP	−48.0	−66.0	−7.0	32.9	9.6	16.9	0.01	0.118	0.022

* according to Owens and Wendt[12]

** according to van Oss *et al.*[16]

amphoteric surface character and the plasma treated specimen has obviously an acidic surface character. Similar results were obtained for poly(propylene) (Fig. 9).

The quantitative evaluation of the ζ *versus* pH plots summarized in Tables III and IV confirms the qualitative estimation.

Table III illustrates that the pre-treatment procedures of PP/EPDM increase the value of $(\Phi_{Cl^-} - \Phi_{K^+})$ characteristic of dispersion interaction as well as the Φ_{H^+} and Φ_{OH^-} values, which represent the acidity or basicity of the surface. Especially, it can be seen that the flame pre-treatment changes both acidity and basicity of the surface, whereas the plasma treatment only increases the acidic character.

Table IV shows similar results of *PP* specimens and, in addition, the comparison between the results of zeta potential measurements and those of XPS and contact angle measurements. It is evident that there is a good correlation between Φ_{H^+} or Φ_{H^-} and the elemental surface composition determined by XPS: the increase in acidity is connected with increasing O/C ratio and increase in basicity is due to the presence of nitrogen in the surface region.

The content of oxygen or nitrogen in the surface region increases the "polarity" of the surface according to Owens and Wendt's approach of the surface free energy. However,

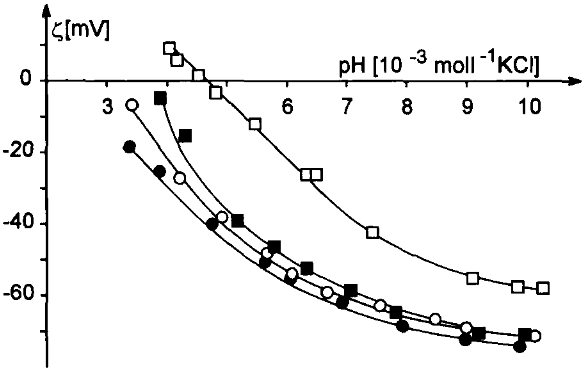

FIGURE 10 Zeta potential *versus* pH of untreated and oxygen plasma treated PP/EPDM without light stabilizers (Hostalen 8018 A) Plasma parameters: 13.56 MHz, 0.3 mbar, 200 W. Time of plasma treatment: □ untreated, ○ 10 sec, ■ 30 sec, ● 60 sec.

TABLE V

Surface parameters of PP/EPDM (Hostalen PPR 8018A) injection moulded sheets as a function of oxygen plasma treatment time

Time of O_2-plasma treatment [s]	Surface parameters of acid-base interaction determined by zeta potential measurements				
	Φ_{H^+} [kJ·mol^{-1}]	Φ_{OH} [kJ·mol^{-1}]	pK_A	pK_B	$\sigma^{diffuse}$ [μC·cm^{-2}]
10	−32.1	−60.2	5.1	10.1	0.68
30	−35.0	−57.3	5.6	9.5	0.71
60	−23.7	−72.8	2.8	11.5	0.82

plasma parameters: excitation frequency = 13.56 MHz, power = 200 W, pressure = 0.3 mbar.

we can see that the acidic character of the surface is under-estimated by the approach of van Oss and coworkers. Therefore, we can conclude that zeta potential measurements give more detailed information regarding the surface composition than contact angle measurements. The influence ot treatment time on the effect of plasma treatment can also be detected by zeta potential measurements as shown in Figure 10 and Table V.

The maximum effect is achieved after 60 seconds whereas a treatment time of 30 seconds gives only small effect. This kind of time dependence of plasma treatment was reported also by other authors.[24]

The effect of plasma and flame treatments on the adhesion behaviour of primarily non-polar polymers can be discussed in the following way:
Introduction of acidic or basic groups improves the ability to interact with corresponding acidic or basic substances. Furthermore, carboxylic groups react. *e.g.*, with OH groups at the surface of contacting materials by ester formation. This kind of interaction can be investigated by other methods (*e.g.* FT-IR).

CONCLUSIONS

The results presented show that zeta potential measurements are a valuable tool to characterize the surface properties of polymers. ζ-pH-c^{bulk} plots are useful in describing the dispersion and acid-base interactions of contacting substances. Dissociation constants of functional groups can be calculated. Due to the availability of automated and reproducible working zeta potential measuring devices, polymer surfaces can be easily characterized.

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