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Journal of the European Ceramic Society 26 (2006) 2241–2248

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Determination of free surface energy values for ceramic materials and polyurethane surface-modifying aqueous emulsions

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Received 17 December 2004; received in revised form 5 April 2005; accepted 9 April 2005
Available online 3 June 2005

Abstract

Taking advantage of physical models developed by van Oss-Good and Neumann, which describe relations between surface free energy values for solids and wetting liquids, and making use of the contact angle values for Al_2O_3 and ZrO_2 surfaces and standard liquids with known values of surface energy, which were measured by means of the optical goniometer, surface free energy values as well as their components representing long-range interactions and acid–base interactions for the surfaces of the studied solids were evaluated. Analogical calculations were carried out for the comparative polymer materials—PTFE and PET. On the basis of the obtained data, and based on measured contact angle values for PET surfaces with water emulsions, free energy values were determined for newly synthesised polyurethane ionomers as well as for those ionomer emulsions additionally modified with vinyl monomers. It was found that the surface energy values for the synthesised polyurethane emulsions were predominantly affected by the structure of polyol and urethane segments, while the type of ionogenic segments influenced the quantity of acid–base interactions as well as the quantity of dispersal interactions. The effect of interactions between the surface of ceramic powders and aqueous emulsions on applicability of such systems as efficient binders in moulding green ceramic ware was discussed.

Keywords: Tape casting; Surfaces; Al_2O_3; ZrO_2; Engine components; Contact angle; Surface energy

1. Introduction

The surface free energy is equal in respect of figures to the work required to form a new unit surface when separating two phases which remain in equilibrium, in a reversible isothermal process. It is measured and expressed in mJ/m^2, and it is employed to evaluate the surface layer of a polymeric or ceramic material. The relation between the surface free energy (γ) and the surface tension (σ) can be presented by the equation as below, which comes directly from the Young equation:

$$\sigma = \gamma + S\frac{d\gamma}{ds} \tag{1}$$

where S is a unit surface area for a given body.

The notion of surface free energy is applicable both for liquids and for solids. However, there is a relation which is effective for liquids only:

$$\frac{d\gamma}{ds} = 0 \Rightarrow \sigma = \gamma, \quad \text{for } S \neq 0 \tag{2}$$

According to the Gibbs theory, the surface tension in a solid is equal to the surface free energy only when adsorption on the surface of that solid is equal to zero.[1]

The knowledge of the surface free energy value is very important in the ceramics processing industry. That figure is used to assess the possibility of decorating ceramic surfaces, gluing and painting on them with the use of polymeric materials, and the possibility of obtaining smooth coatings of ceramic slurry (blend of ceramic powder, e.g. Al_2O_3, solvent, polymeric binders, de-flocculants and plasticisers) in the so-called *tape casting* process.[2]

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doi:10.1016/j.jeurceramsoc.2005.04.011

The difference between the surface free energy for a ceramic powder, e.g. Al_2O_3 or ZrO_2, and a liquid organic binder is generally known to be essential for good wettability of oxide grains, and hence for covering them with organic solution(s) of polymers or with tailored aqueous dispersion(s). Those processes are important in moulding green ceramics which – after the final firing – have been intended for special applications, i.e. where high heat resistance must be accompanied by improved corrosion resistance, and the final product is expected to offer additionally high mechanical parameters. The examples cover non-conducting and corrosion-resistant components employed in the chemical process equipment, in control instruments, etc. A key issue in the production of ceramic elements with complicated shapes, like for example spark plug insulators, is the need of mechanical working (turning, milling, grinding, etc.). That is very burdensome, labour-consuming and expensive in case of refractory materials as their hardness is considerable. Hence, the tools to be used must be made of extremely hard and expensive materials, like diamond or boron nitride.[3] Moreover, ceramics are not only very hard but highly brittle at the same time. In that situation it is frequently impossible to employ some mechanical working methods, e.g. turning is not applicable. In some cases, the profiling costs reach as high as 80% of the total manufacturing costs for a ceramic product. Mechanical working cannot be completely eliminated, yet one can try to reduce its scope by the use of improved moulding methods and/or by application of working to the biscuit material. Still better economic performance can be expected from profiling of pressed semi-finished products, with said profiling applicable to green ceramics. A major barrier faced here is insufficient mechanical strength of compression moulded ceramic intermediates which becomes responsible for the damage of materials/products during their machining. It is therefore a basic problem for profiling at as-moulded condition to select a suitable organic binder. The lowest possible admixture of such a binder should provide a ceramic material with the mechanical strength sufficiently high for machining.[4] That technology is currently applicable for the manufacture of small-size products only since no binders have so far been developed which could firmly fix the oxide grains together by forming interlayers and hence prevent the material from cracking under local thrust during intense mechanical working.[4,5]

The presence of polymers as organic ingredients is decisive for the processing profile and economics of two basic stages in the ceramics manufacturing process:

- dry pressing of ceramic powders, and
- profiling of unburnt biscuits.

The use of organic additives in the ceramics manufacturing processes has been practised for a long time, and selection of a suitable additive makes an inherent question in developing a manufacturing method for a specific ceramic product. Organic additives play a special role in moulding operations which involve non-plastic feeds, like oxide raw materials, non-oxide ones, ceramals and ceramic composites. Polymeric binders play a fundamental role in the *tape casting* process.[2]

Searching for efficient water-dilutable binders for ceramic powders, scientists have focused their interest recently on polymeric ionomers. Those polymers comprise high molecular weight compounds with a minor number of functional groups incorporated into their trunk chains—the groups would dissociate if in water. The organic backbone chains make hydrocarbon segments, while carboxyl or sulfo groups (in anionomers) and ammonium or phosphonium groups (in cationomers) are usually employed as dissociating segments.[5–7] The presence of ionic groups gives higher polarity to those polymers, hence making them partially water-soluble. Stronger ionic interactions, on the other hand, improve adhesion of the binders produced on the basis of those ionomers to polar ceramic materials, to glass and metals. And better adhesion results in higher mechanical strength of compression moulded ceramic elements.

We found it advisable to look from that point of view on polyurethane (PU) ionomers which are capable of forming stable aqueous dispersions.[8] It seems also promising to use hybrid poly(acryl-urethane) polymers as binders for ceramics. That system can be produced in the reaction of isocyanate prepolymer and 2-hydroxyethyl acrylate, followed by free-radical co-polymerisation of so obtained macro-monomer with acrylates.[9]

The study on polymer coatings prepared from modified poly(acryl-urethane) emulsions revealed that their thermal stability, mechanical strength and adhesion to substrate were superior to coatings obtained from homopolymeric polyacryl or polyurethane emulsions.[10]

Resulting from the above observation, a research programme was initiated to develop methods for the production of new type PU ionomers and to utilise those materials as binders for oxide ceramic powders to be processed by compression moulding and then subjected to mechanical working as green ceramics.

Another important issue needs to be addressed when employing polymeric binders: these materials must be selected carefully to provide sufficient wettability of grain surface in oxide ceramics by polymeric emulsions. The latter should fix the grains together firmly enough after evaporation of organic solvents and water, so that it should be possible to subject the material to forming in a moulding press and then to mechanical pre-treatment.

Hence, this paper presents a method to calculate – on the basis of measured contact/wetting angle – the value of the surface free energy for selected ceramic materials (Al_2O_3 and ZrO_2) and synthesised waterborne PU ionomers. Also, an attempt was made to provide interpretation for the findings from the viewpoint of expected application benefits at moulding ceramic products.

Table 1
Properties of ceramic materials used

Property	Unit	Al_2O_3	ZrO_2
Apparent density	(G/cm^3)	3.8	6.0
Flexural strength	(MPa)	300	770
Young's modulus	(GPa)	220	200

2. Experimental

2.1. Materials

Substrates:

- Polished ceramic test pieces, $d = 20$ mm, $h = 5$ mm, made of corundum (Al_2O_3) and ZrO_2 (Table 1). Producer: Institute for Power Engineering, "CEREL" Dept. of Ceramics in Boguchwała, Poland.
- Polymer materials

Polymer plates 100 mm × 50 mm × 10 mm (Table 2):

- Polytetrafluoroethylene (PTFE) (TARFLEN type),
- Producer: Zakłady Azotowe in Tarnów-Mościce S.A., (Poland)
- Polyethyleneterephtalate (PET), ERTALYTE TX type,
- Producer: Plastics Engineering (Tielt, Belgium).

2.2. Standard liquids

Diiodomethane CH_2I_2 (Sigma – Aldrich)
Formamide $HCONH_2$ (Sigma – Aldrich)
Redistilled water

Surface parameters for employed standard liquids have been presented in Table 3.

Table 2
Selected properties of comparative polymer materials[16,17]

Property	Unit	PTFE (TARFLEN)	PET (ERTALYTE TX)
Density	(g/cm^3)	2.3	1.44
Tensile stress at yield	(MPa)	25–35	90
Unit elongation	(%)	350–500	15
Tensile stress at yield	(MPa)	350	320
Melting point	(°C)	>500	255
Glas transition temperature	(°C)	−120	80

Table 3
Literature-derived surface properties of standard liquids employed[13]

Standard liquids	Surface parameters [mJ/m^2]				
	γ_L	γ_L^{LW}	γ_L^{AB}	γ_L^-	γ_L^+
Redistilled water	72.8	21.8	51	25.5	1.6
Formamide	58.0	39.0	19.0	39.6	0.9
Diiodomethane	50.8	50.8	0	0	0.4

2.3. Aqueous emulsions of polyurethane ionomers

- Emulsion of PU anionomer obtained from the reaction of 2,4- tolylenediisocyanate and 2,6-tolylenediisocyanate (2,4- and 2,6-TDI), polyoxyethylene glycol (Rokopol 7p) ($M_n = 450$) and 2,2-bis(hydroxymethyl)propionic acid (DMPA), neutralised with triethylamine (TEA) and extended by means of 1,6-hexamethylenediamine (HMDA); that anionomer offers the increased content of ions (5.19 wt.% COO^-) (sample no. 1),[9]
- Emulsion of PU anionomer obtained from the reaction of 2,4- and 2,6-TDI, Rokopol 7p and DMPA, neutralised with TEA and extended by means of HMDA (sample no. 2a) (2.31 wt.% COO^-),[9]
- Emulsion of PU anionomer obtained in the reaction of 2,4- and 2,6-TDI, polycaprolactone diol ($M_n = 530$) (PCD) and DMPA, neutralised with TEA and extended by means of HMDA (sample no. 2b) (2.13 wt.% COO^-),[9]
- Emulsion of PU cationomer obtained in the reaction of 2,4- and 2,6-TDI, Rokopol 7p and *N*-methyldiethanolamine (*N*-MDA), neutralised with formic acid (HCOOH) and extended by means of HMDA (sample no. 3),[11]
- Emulsion of urethane-vinyl macro-anionomer obtained in the reaction of isocyanate prepolymer anionomer and HEA, extended at the final stage by means of HMDA (sample no. 4),[9]
- Emulsion of urethane-vinyl macro-anionomer obtained in the reaction of isocyanate prepolymer anionomer and HEA, extended at the final stage by means of HMDA and additionally subjected to radical copolymerisation with styrene and vinyl acetate (sample no. 5),
- Emulsion of urethane-vinyl macro-anionomer obtained from the reaction of isocyanate prepolymer anionomer and HEA, extended at the final stage by means of HMDA and additionally subjected to radical polymerisation with styrene (sample no. 6).

2.4. Method for determination of contact angle

The contact angle values Θ for the PTFE and ceramics surfaces and standard liquids as well as aqueous emulsions of PU ionomers were measured by means of computer-aided analysis of shapes of liquid drops, as observed in an optical goniometer and recorded by a digital camera installed below the eyepiece, in axial extension of the lens. Due care had to be exercised since even minor deviations from the pre-fixed conditions resulted in considerable errors. The dispersion drops were applied by means of a micro-pipette on a perfectly smooth surface of PTFE or on polished surfaces of Al_2O_3 or TiO_2 test specimens (Fig. 1). The drops were applied from the height of about 3 mm above the substrate surface. The pictures taken of the drops were then analysed with the use of PC and specialised software, and the contact/wetting angle values were found. The read-outs were taken for 10 pictures for different drops of the same liquid studied and the arithmetic mean value was reported. Standard

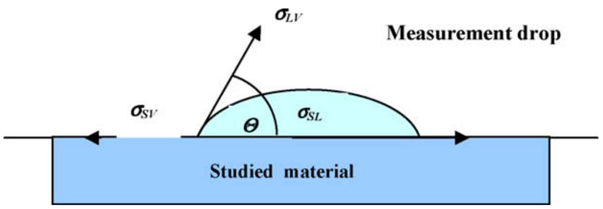

Fig. 1. Graphical interpretation of the Young's equation: $\sigma_{SV} = \sigma_{SL} + \sigma_{LV} \cos \Theta$ where: σ_{SV} – surface tension of solid being in equilibrium with saturated vapour of liquid. σ_{SL} – Interfacial surface tension of solid and liquid. σ_{LV} – Surface tension of liquid being in equilibrium with its saturated vapour. Θ – Equilibrium contact angle.[12]

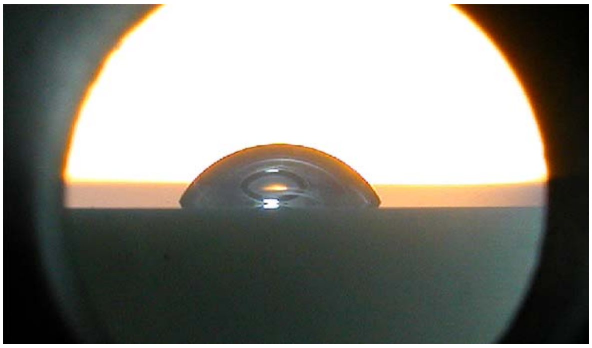

Fig. 2. Exemplary photo of a water drop carefully applied on the surface of a disk made of ZrO_2 ($\Theta = 65.1°$).

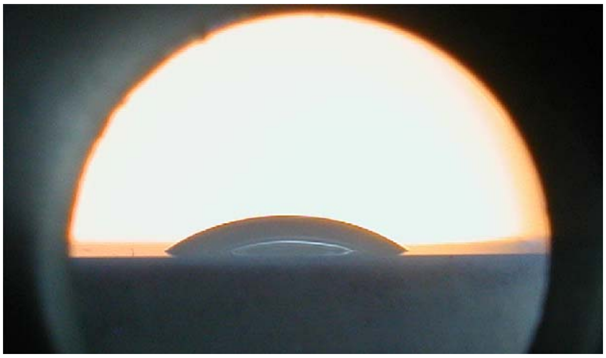

Fig. 3. Exemplary photo of a drop of anionomer 2a aqueous dispersion carefully applied on the surface of a disk made of Al_2O_3 ($\Theta = 36.1°$).

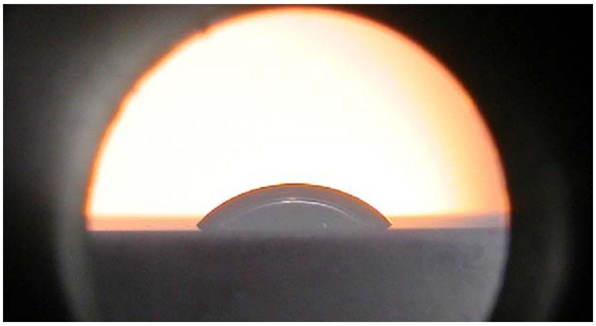

Fig. 4. Photo of a drop of anionomer 4 aqueous dispersion carefully applied on the surface of a disk made of Al_2O_3 ($\Theta = 46.5°$).

deviations were determined for every series of measurements. The pictures were taken in comparably similar time intervals from the moment of drop application, for every series of measurements. That was intended to minimise the effect of liquid evaporation from a drop. The drops applied to the substrate had the same volume of about 1.0 mm^3, and the measurements were taken at the constant temperature of 23 °C. The measurement consisted in measuring the angle between the surface of a solid in contact with a liquid and the tangent line to the liquid drop which had been drawn from the contact point of three phases. Figs. 2–4 present exemplary pictures of liquid drops on various ceramic substrates. The pictures in just this form were used to find the wetting angle values. Those values for the studied solids were presented in Tables 1, 2 and 4.

2.5. Method applied in finding components of surface free energy for solids

The model by van Oss-Good made grounds for finding physical parameters of the surface energy for a solid γ_S as presented in this study. The model is based on the hypothesis by Owen-Wendt which assumes that the surface free energy $\gamma_{S,L}$ may be presented as a sum of two different components

Table 4
Surface free energy values for studied solids

Type of surface	Wetting angles			Surface parameters [mJ/m^2]				
	Standard liquids	Θ [°]	σ	γ_S	γ_S^{LW}	γ_S^{AB}	γ_S^-	γ_S^+
PTFE (TARFLEN)	Diiodomethane	72	–	21.8	21.8	0	0	0
Al_2O_3	Redistilled water	65.1	1.0	41.1	35.1	6.0	16.10	0.56
	Formamide	49.6	0.7					
	Diiodomethane	48.5	0.4					
ZrO_2	Redistilled water			45.6	35.7	9.90	11.96	2.05
	Formamide	63.6	1.6					
	Diiodomethane	39.0	0.9					
PET (ERTALYTE TX)	Redistilled water	66.3	0.9	46.0	42.9	3.1	13.1	0.18
	Formamide	46.2	0.7					
	Diiodomethane	33.0	0.7					

σ: Standard deviation.

(Fig. 1):[12,13]

$$\gamma_{S,L} = \gamma_{S,L}^{LW} + \gamma_{S,L}^{AB} \tag{3}$$

where:

γ_S^{LW}-surface energy connected with long-range interactions (dispersion, polar and induction interactions),
γ_S^{AB}-surface energy connected with acid–base interactions, as results from the Lewis theory,

and where the Eq. (3) applies generally to solids (subscript S) and to liquids (subscript L), both standard liquids and tested liquids.

When the symbol of $\gamma_S{}^+$ is used for the component $\gamma_S{}^{AB}$, which corresponds to the surface free energy of a Lewis acid, and the symbol of $\gamma_S{}^-$ is used for the component representing a Lewis base, the Berthelot theory (interactions between the particles of different bodies located on the surface are equal to the geometric mean of the interactions between the particles within each of those bodies) will produce the following relations:[14]

- for bipolar substances (liquids and surfaces of solids), which can be represented by the studied ceramics and synthesised PU ionomers;

$$\gamma_i^{AB} = 2(\gamma_i^+ \gamma_i^-)^{0.5} \tag{4}$$

- for liquids and surfaces of non-polar solids (diiodomethane, PTFE);

$$\gamma_i^{AB} = 0 \tag{5}$$

(where: i = S – solid L – liquid).

The van Oss-Good equation establishes a relation between the parameters of surface free energy for solids (S) and the liquids which interact with them (L):

$$(\gamma_S^{LW} \gamma^{LW})^{0.5} + (\gamma_S^+ \gamma_L^-)^{0.5} + (\gamma_S^- \gamma_L^+)^{0.5} = \gamma_L \frac{(1+\cos\Theta)}{2} \tag{6}$$

and with the wetting angle Θ which is formed by a liquid drop on the investigated surface.

After having measured the wetting angle values Θ for the surfaces of ceramics and three standard liquids (water, diiodomethane and formamide) with known parameters γ_L, γ_L^{LW}, γ_L^+ and γ_L^- (Table 2), we utilised the Eq. (6) to find the values of γ_S^{LW}, γ_S^+ and γ_S^- for the surfaces of the test pieces made of Al_2O_3 and ZrO_2 as well as for a plate made of PET (ERTALYTE TX) to compare. Then, the Eqs. (4) and (3) were employed to calculate the values of γ_S^{AB} and γ_S. Since the relation (7) applies for the non-polar PTFE surface:

$$\gamma_S^{AB} = 0 \tag{7}$$

one can find the energy $\gamma_S = \gamma_S^{LW}$ from a simplified van Oss-Good equation:

$$(\gamma_S^{LW} \gamma_L^{LW})^{0.5} = \gamma_L \frac{(1+\cos\Theta)}{2} \tag{8}$$

and on the basis of the measured wetting angle value for PTFE and one non-polar standard liquid – diiodomethane, for which $\gamma_L^{AB} = 0$. The obtained findings were provided in Table 4.

2.5.1. *Method for finding surface parameters of aqueous emulsions of PU ionomers*

The surface parameters γ_L, γ_L^{LW} and γ_L^{AB} for the synthesised PU emulsions have the capacity of intensive thermodynamic parameters and they should be dependent solely on the type and structure of PU ionomers, concentration of polymer in the emulsion system, and on temperature. In case of those systems, i.e. bipolar liquids, the total surface energy γ_L was found by means of the independent Neumann method,[15] with the use of the following equation:

$$\cos\Theta = -1 + 2\left(\frac{\gamma_S}{\gamma_L}\right)^{0.5} \exp[-0.0001247(\gamma_L - \gamma_S)^2] \tag{9}$$

and on the basis of measured Θ angles for those emulsions and earlier investigated PTFE surface, for which $\gamma_S = 21{,}8\ \mathrm{mJ/m^2}$ (Table 2). The obtained values for γ_L were provided in Table 5 (column 5).

The γ_S^{LW} values for aqueous emulsions of synthesized PU anionomers were found from the van Oss-Good Eq. (6), basing on the values of angles as measured on PTFE, taking for γ_L the value which had been determined before with Neumann's method, and assuming that $\gamma_S = \gamma_S^{LW} = 21.8\ \mathrm{mJ/m^2}$.

If the determined values satisfy the condition $\gamma_L > \gamma_L^{LW}$, then the Eq. (3) can be used to calculate the value of γ_L^{AB} for PU emulsions studied.

The obtained results are presented in Table 5.

3. Discussion of findings

As can be concluded from the data presented in Table 4, the surface free energy for the studied ceramic materials results predominantly from long-range interactions γ_S^{LW}. However, both oxides are characterized by a considerable share

Table 5
Wetting angles and calculated surface parameters for selected PU anionomer emulsions

Sample no.	Type of polyol	Content of COO^- anions [wt.%]	Θ (Measured on PTFE) [°]	γ_L [mJ/m^2]	γ_L^{LW} [mJ/m^2]	γ_S^{AB} [mJ/m^2]
1	Rokopol 7p	5.19	75.2	47.3	40.4	6.9
2a		2.31	63.8	39.0	36.2	2.8
2b	PCD	2.13	68.4	42.1	38.0	4.1

of the surface free energy γ_S^{AB} which results from acid–base interactions, with the share of the surface energy resulting from base interactions γ_S^- being much higher, what is in particular true for ZrO_2. That is easy to understand since the surface of Al_2O_3 is amphoteric-basic in its nature while the surface of TiO_2 is amphoteric-acidic. The radii of Ti^{+4} and Al^{+3} ions which are close to each other (0.68 and 0.55 Å, respectively) can make the explanation for the similar values of the dispersion components γ_S^{LW}. The surface energy values calculated for the studied ceramic materials are only slightly lower (41–46 mJ/m^2) than the energy for the polar polymer like poly(ethyleneterephthalate) (46 mJ/m^2), which has been calculated for comparison. For the latter material, the dispersion interactions γ_S^{LW} are decisive, too, and a weak alkaline nature is revealed in the Lewis interactions.

Table 5 presents the values of the parameters γ_L^{LW} for emulsions of selected PU anionomers which have been found from the van-Oss-Good relation (6), on the basis of wetting angles between the emulsion studied and the non-polar PTFE surface. The calculations made use of the values γ_L for those emulsions which have been found from the Neumann relation (9). Then, the values of the parameter γ_L^{AB} were found from the relation (3).

The obtained findings suggest that the component γ_L^{LW} brings the determining contribution to the total energy γ_L of the synthesised anionomers. That component is dependent on the dispersion interactions which are defined by the structure of PU macro-molecules, i.e. soft and flexible polyol segments, derived from PKD, Rokopol 7p or DMPA monomer (these introduce carboxyl groups), and rigid and more polar urethane segments, which involve 2,4- and 2,6-TDI derivatives and low molecular weight chain extender – HMDA. After comparing the findings for the samples 2a and 2b one can arrive at the conclusion that the structure of PKD polyester, which is more polar than the structure of polyether Rokopol 7p, gives more to the dispersion component γ_L^{LW}. On the other hand, the data collected for samples 1 and 2a suggest that the amount of the DMPA monomer is decisive for the amount of COO^- ions in the anionomer and it affects the dispersion component as well. Nevertheless, the amount of DMPA reveals the clear influence on the extent of Lewis interactions γ_L^{AB}. It is for that reason that anionomer 1, the one with the highest amount of COO^- ions, synthesised from Rokopol 7p, offers the highest value of the surface free energy γ_L.

We failed to find the values of the components γ_L^- and γ_L^+ for the synthesised anionomers despite fact that there was such a possibility in theory – the system of van Oss-Good algebraic Eqs. (9) needed to be solved. Those equations referred to three polar surfaces of solids, for which the values of γ_S^- and γ_S^+ are different from zero (Table 4). In our case, these were the surfaces of ceramic oxides Al_2O_3 and ZrO_2 and the surface of a polar polymer PET (ERTALYTE TX). The surface parameters for those materials were found by measuring the wetting angles for three standard liquids: water, diiodomethane and formamide. Additionally, the component values of the surface energy for those liquids were available in literature reports (Table 3). When solving the system of three equations like (9) for the measured wetting angles Θ for anionomer no. 1 (Table 6), we arrived at the contradiction: $(\gamma_L^-)^{0.5} < 0$ or $(\gamma_L^+)^{0.5} < 0$. A similar finding was obtained for anionomer no. 2a. That can be accounted for by the intrinsic inconsistence of the obtained values for γ_L and $\gamma_L{}^{LW}$ of the studied anionomers, which were taken for calculations, and which had been determined by two technically independent methods by Neumann and van Oss-Good.

The accuracy of findings is certainly affected not only by the errors in the models themselves but by random errors made when measuring the wetting angles Θ as well. In order to minimise the latter, the measurements should be taken with highest care. Precision of wetting angle measurements taken by means of the optical goniometer has been illustrated by Table 4 where the values of standard deviation σ for individual findings have been presented. Despite our efforts, the spread of some findings is considerable what can – in part – result from the differences in the surface quality of the solids. Surface roughness can eventually distort the images of PU emulsion drops applied to the studied surfaces.

When the surface energy values γ_L determined for the studied PU emulsions are compared to the surface energy values γ_S calculated for the test pieces made of Al_2O_3 and

Table 6
Wetting angles for studied ceramic substrates and polymer materials, with the use of PU ionomers

Sample no.	Type of ionomer	Type of vinyl co-monomer	Wetting angles		
			Type of substrate	Θ [°]	σ
1	Anionomer	–	Al_2O_3	46.0	0.8
			ZrO_2	45.7	1.2
			PET	47.2	3.2
2a	Anionomer	–	Al_2O_3	36.1	0.8
			ZrO_2	45.6	0.7
			PET	64.2	–
3	Cationomer	–	Al_2O_3	39.5	1.0
			ZrO_2	39.9	0.6
4	Anionomer	HEA	Al_2O_3	46.5	0.5
5		HEA, styrene, vinyl acetate	Al_2O_3	46.6	1.7
6		HEA, styrene	Al_2O_3	40.8	0.5

ZrO_2, one can arrive at much wider conclusions on reciprocal chemical affinity of the studied materials than the conclusions based solely on measured wetting angle values. The surface free energy γ_L of the studied aqueous emulsions of PU ionomers amounts to about 40 mJ/m^2. From that point of view, the anionic emulsions of synthesised PUs make liquids with moderate polarity, and with the surface energy much below that of water ($\gamma_L = 73$ mJ/m^2) used as a diluent (70 wt.%) for the studied emulsions. The values of the surface free energy γ_L were only slightly below the energy γ_S found for the surfaces of Al_2O_3 ($\gamma_S = 41$) and ZrO_2 ($\gamma_S = 46$ mJ/m^2). That suggests that the evaluated emulsions are not very efficient wetting agents for the surfaces of oxides in question, although the presence of water-soluble PU ionomer surely must reduce the surface tension of the emulsion. On the other hand, the values of wetting angles Θ themselves, which are below 45° for a few emulsions (Table 6), suggest something completely opposite. It is reasonable in that case to modify PU ionomers with hydrophobic vinyl monomers to reduce the surface free energy, in order to produce more efficient binding agents for ceramic powders. That way is confirmed by the values γ_L and γ_L^{LW} for the aqueous emulsion of styrene-modified copolymer no. 6. For anionomers nos. 5 and 6, which contain structural fragments derived from HEA and vinyl acetate (i.e. more polar units), higher values of the wetting angle are observed on the Al_2O_3 surface, what can be explained by a partial phase separation due to a lowered share of the ionic fragments responsible for water-solubility of the emulsions tested.

4. Conclusions

1. The values found for the surface free energy of the studied ceramic materials ($\gamma_S \approx 41$-45 mJ/m^2) result predominantly from long-range dispersion interactions ($\gamma_S^{LW} \approx 35$ mJ/m^2). Still, the values of surface energy resulting from acid–base interactions are considerable for both oxides ($\gamma_S^{AB} \approx 6$–10 mJ/m^2), with the contribution from basic interactions being much higher ($\gamma_S^- \approx 12$–16 mJ/m^2). Comparatively, a similar value of $\gamma_S \approx 45$ mJ/m^2 is offered by the polar PET material, wherein the component γ_S^{AB} is slightly lower, but the share of basic interactions is similar ($\gamma_S^- = 13.1$ mJ/m^2).
2. The total surface free energy for the synthesised polyurethane ionomers, which make essential components of aqueous emulsions, is dependent chiefly on the structures of soft and hard segments present in polyurethane, e.g. more on their polarity (decisive more for the component γ_L^{LW} of long-range interactions) than on the presence of ionic fragments (responsible for acid–base interactions γ_L^{AB}) which would appear to be more specific just for polymeric ionomers. The latter become active only in the systems with the increased amount of ions (anionomer no. 1). Hence, the acid–base structure of an ionomer should be supposed to be decisive mainly for its ability to dissociate in water, and it is significant for the production of homogeneous aqueous emulsions, while the value of free energy of an ionomer is controlled by the structure of chains as well as the structures of polyol and urethane segments. The value of γ_L for synthesised anionomers is decided primarily by the structure of polyol – higher values are obtained for polyester-derived anionomers. The presence of ionogenic structures, e.g. derived from DMPA and built-in into the urethane structures of PU ionomers, increases the values of both the dispersion γ_L^{LW} and ionic γ_L^{AB} components.
3. The measurements demonstrate constraints in the use of the Neumann and van Oss-Good models to analyse the surface properties of polyurethane emulsions when contacted with ceramic materials. Intrinsic inconsistencies in both the models adopted for determination of surface free energy, based on the Berthelot theory, made it impossible to find precise values of components γ_L^+ and γ_L^- in acid–base interactions γ^{AB}, as reveal themselves on polar ceramic and polymeric surfaces.
4. The values of the surface free energy γ_L which are only slightly below the values of energy γ_S found for the surface of Al_2O_3 ($\gamma_S = 41$) and ZrO_2 ($\gamma_S = 46$ mJ/m^2) justify the supposition that the studied emulsions are not the liquids capable of wetting efficiently the surfaces of those oxides, although the presence of PU ionomer dissolved in water surely reduces the surface tension value for emulsion when referred to that of water.
5. The measured values of wetting angles for the analysed surfaces of ceramic materials and synthesised PU emulsions reveal that the additional grafting of hydrophobic vinyl or acrylic chains on acryl-capped polyurethane ionomers can result in lower surface free energy of the emulsions so produced. That is advantageous from the viewpoint of improved wettability of ceramic powders. However, it should be verified in each individual case whether or not the additional vinyl co-monomer is responsible for increased value of γ_L due to reduced water solubility of the obtained polymeric dispersion. What should be additionally kept in mind is that it is not enough to provide the adequate value of the surface energy. The polymeric binder, in order to be efficient, should additionally offer the suitable mechanical strength of the bond between the ceramic material and polymer, and further investigations should focus just on that aspect.

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