Chemical Structure, Thermal Properties, and Free-Surface Energy Parameters of Coatings Synthesized from Poly(urethane-dimethylsiloxane) Anionomers

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ABSTRACT: Poly(urethane-dimethylsiloxane) (PU-PDMS) anionomers with increased hydrophobicity and fixed amount of elastic segments (51 wt %) at 3- and 4-stage methods were obtained. The anionomers were synthesized from isophorone diisocyanate, poly(oxytetramethylene)diol, and α,ω-polydimethylsiloxanediol (PDMS). 2,2-bis(hydroxymethyl)propionic acid (DMPA) was used as ionic center. The anionomers were extended with ethylenediamine (EDA) in water. ^{1}H NMR and IR methods were employed to confirm the chemical structures of the anionomers. Suitable defined structural factors κ and α were calculated on the basis of selected bands of the spectra. The factors were employed to perform detailed quan-

tity and polarity analysis of the anionomers structures. The free-surface energy (FSE) of the anionomers was evaluated on the basis of physical model by Owens and Wendt. The effect of chemical structures on polarity of the materials was discussed. It was found that the FSE and its polar and dispersive components distinctly decrease with the increasing polisiloxane content in the anionomer chain. © 2008 Wiley Periodicals, Inc. J Appl Polym Sci 110: 3488–3500, 2008

Key words: segmented polyurethane; chemical structure of polyurethane anionomers; IR and ^{1}H NMR spectra; structures polarity and dispersivity estimation; free-surface energy parameters estimation by Owens–Wendt method

INTRODUCTION

In recent years, significant progress in synthesis of polyurethane coatings and elastomers with control polarity that are utilized in production of membranes, protection coatings, and biomedical materials has been observed.[1–3] From free-surface energy (FSE) results evaluated by Owens–Wendt method on the basis of the contact angles measurement by suitable chosen set of polar (e.g., water, formamide) and nonpolar (diiodomethane, hexane) liquids which were placed on the polyurethane coating surface, one can be concluded that the FSE of regular polyurethane obtained from diisocyanates and polyols is more than 40 mJ/m^2.[4–6] It appears that the FSE of the polyurethane based on 4,4′-diphenylmethane diisocyanate and poly(propylene)glycol ($M = 1000$ g/mol) may increase to about 47 mJ/m^2, when additional —CH$_3$ groups are incorporated into urethane segments. This effect is beneficial, for instance in adhesives with good adhesion to aluminum production, and can be realized as a result of urethane-isocyanate prepolymers extension with the mixture of 2-methyl-1,3-propanediol and 1,4-butanediol.[6] The

same effect was gained as a result of incorporation into polyurethane —COOH groups from 2,2-bis (hydroxymethyl)propionic acid (DMPA) at the stage of prepolymers extending.[7]

Much more attention is paid to structural modification of the polyurethanes, leading to the decrease in the FSE. The polyurethane elastomers with the lowered FSE are definitely hydrophobic, and because of that, they are significantly less chemical reactive. Additionally, good mechanical and thermal properties cause, that those polymers may be applied as blood compatibility materials or polymer surface modificators, which allow bioactive compounds as for example, biosensors to attach.[3,8,9]

There are many approaches to lower the FSE of the polyurethane polymers. For instance, incorporation of hydrophobic macromonomer with perfluoralkyl group into a polyurethane anionomer results in a material with an FSE less than 19 mJ/m^2.[10] Another approach may be exchange of the aromatic MDI diisocyanate for its cycloaliphatic counterpart i.e., 4,4′-methylene dicycloheksyl diisocyanate (H$_{12}$MDI).[11] The most often utilized method of lowering the FSE of the polyurethanes, while maintaining their good physicomechanical properties, is polyaddition by using diisocyanates, polyethers, and suitable amounts of polysiloxane diols.[12] The coatings from the poly(urethane-dimethylsiloxane)

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(PU-PDMS) can be applied as membranes for separation of vapors and gases mixtures for example, n-C_4H_{10}/CH_4 or $CO_2/O_2/N_2$.[13,14,15]

Previous research on the synthesis of the poly(urethane-dimethylsiloxane) polymers have mainly concerned an improvement in mechanical properties and thermal stability of that polymers.[16–20] Two articles[18,19] depict an interesting comparison of the measurement between water contact angles of polyurethane elastomer coatings with waterborne polyurethane, modified with aminoethylaminopropyl-substituted polydimethylsiloxane. In both cases, the increase in the water-contact angle of the polymer coatings with the increasing amount of the incorporated polydimethylsiloxane was observed. The hydrophobic influence of the polysiloxane is confirmed by the above-described effect. It is interesting that the contact angles of the anionomers were distinctly lesser: $78° \pm 2°$ at 9 wt % of the polisiloxane content, whereas for the analogous copolymer it is $101 \pm 3.4°$. In our opinion, it results from definitely larger polarity of the polyurethane anionomers. In other article, the water-contact angles of the polyurethane anionomer coatings which were modified by various molecular weights α,ω-poly(dimethylsiloxane)diols (PDMS) were determined. In that case, the water-contact angles reached maximum at 6 wt % of the polydimethylsiloxane content in the anionomer.[20] There are only few articles concerning the FSE evaluation of the PU-PDMS copolymers as well as dealing with, more particularly, researches on the influence of the poly(urethane-siloxane) chain structure on the FSE components estimated by Owens–Wendt method.

The aim of our research was to find an opportunity of lowering the FSE values of the polyurethane polymers as a result of exchanging a part of poly(oxytetramethylene)glycol (PTMO) for α,ω-poly-dimethylosiloxanodiol at the first stage of polyurethane synthesis, i.e., the prepolymerization with isophorone diisocyanate (IPDI) and PTMO. Taking into account the possible application of the polymers as membranes, we considered the study of only selected group of polymers, namely waterborne poly(urethane-siloxanes), suitable.

The FSE (γ_S) of the PU-PDMS coatings was calculated from the contact angles measurement, with the use of two pairs of the model measuring liquids: water-diiodomethane and formamide-diiodomethane, on the basis of physical model by Owens–Wendt. The model enables to evaluate polar (γ_S^p) and dispersive component (γ_S^d) of the FSE. The factors κ and α calculated by the means of ^{1}H NMR and IR spectral methods, respectively were employed to make structural interpretation.

Problems presented in the article are essential not only for research but also for the application pur-

poses. The FSE is a factor that decides on chemical and biological resistance of the polymer, which has been presented in the references. Those properties are important in case when the poly(urethane-siloxane) anionomers are utilized as selective membranes, anticorrosive coatings as well as medical implants.
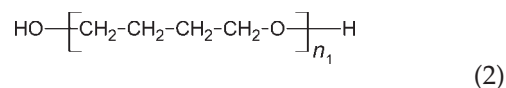
EXPERIMENTAL

Raw materials and reagents

IPDI [5-isocyanato-1-(isocyanatomethyl)-1,3,3-trimethylcyclo-hexane] from Aldrich. The reagent was used as purchased.

$$\text{(1)}$$
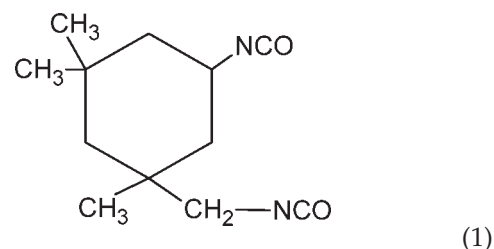
Poly(oxytetramethylene)diol (PTMO) (M_n = 1000 g/mol) from Aldrich.

$$\text{HO}-\left[\text{CH}_2\text{-CH}_2\text{-CH}_2\text{-CH}_2\text{-O}\right]_{n_1}-\text{H}$$
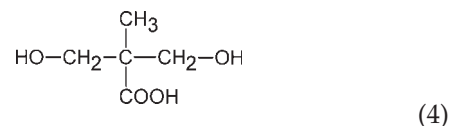
$$\text{(2)}$$

where $n_1 \approx 22$

Melting point is 33°C. Solid product. The reagent was used as purchased.

α,ω-poly(dimethylsiloxane)diol type X-22-160AS (PDMS, M_n = 1000 g/mol) was kindly donated from Shin-Etsu (Japan). Transparent and odorless liquid, silica oil consistence.
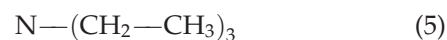
$$\text{(3)}$$
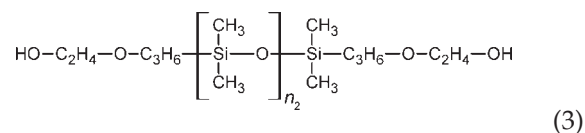
where $n_2 \approx 10$

DMPA from Aldrich.

$$\text{(4)}$$

Melting point is 190°C. Hygroscopic product. That reagent was dried directly before its use in a cabinet drier, at 120°C.
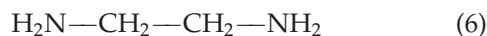
Triethylamine (TEA) from Aldrich.

$$\text{N}-(\text{CH}_2-\text{CH}_3)_3 \qquad \text{(5)}$$

Ethylenediamine (EDA) from Aldrich.

TABLE I
Chemical Compositions of the Anionomers

Sample No.	IPDI, n	PTMO, m_1	PDMS, $m_2 = 1-m_1$	DMPA, q	NCO : OH	TEA, p	EDA, r	Calculated content of —NCO groups (wt %) After 1st stage	After 2nd stage	Contents of soft segments (wt %) Segments from PTMO	Segments from PDMS
1	4	1	0	1	2.0	1	2	13.4	8.35	45	0
2	4	0.9	0.1							40	5
3	4	0.8	0.2							36	9
4	4	0.7	0.3							31	13
5	4	0.6	0.4							27	18
6	4	0.5	0.5							22	22
7	3	1	0		1.5		1	10.1	4.7	51	0
8	3	0.9	0.1							46	5
9	3	0.8	0.2							41	10
10	3	0.7	0.3							36	15
11	3	0.6	0.4							31	20
12	3	0.5	0.5							25	25
13	3	1	0						2.1	51	0
14	3	0.9	0.1							46	5
15	3	0.7	0.3							36	15
16	3	0.5	0.5							25	25

$$H_2N—CH_2—CH_2—NH_2 \qquad (6)$$

N-methylpyrrolidone (NMP) (Aldrich).

TEA, EDA, and NMP were dried over 4 Å molecular sieves 1 week before being used.

Dibutyltin dilaurate (DBTDL) from Aldrich, is used as the catalyst in the production of urethane-isocyanate prepolymers.

Method for the synthesis of urethane anionomers

Anionomers were synthesized in the glass stand composed of three-necked flask, heating bowl, mechanical agitator, dropping funnel, thermometer, reflux condenser, and nitrogen supply nozzle.

In the first case of the study, anionomers were synthesized at 4-stage method as follows.

Stage I: Synthesis of urethane-siloxane prepolymer terminated with isocyanate groups

Molten PTMO (A_1) or alternatively PTMO (A_1) mixed with PDMS (A_2) were added drop by drop to the flask containing adequate amount of IPDI (B). The amounts of the monomers were so selected to maintain the molar ratio: IPDI to the mixture of PTMO and PDMS equal $n : (m_1 + m_2) = 4 : 1$ or $3 : 1$. Then, the catalyst (DBTDL) was added, and the reaction was allowed to proceed at 50°C till theoretical content of free-isocyanate groups reached end point. The content of —NCO groups in the mixture, which was analyzed every 30 min, was compared with the expected value based on the assumed stoichiometry (Table I).

At different initial ratios of monomers, the urethane-isocyanate polymers (Sample Nos. 1, 7, and 13) (Table I) from IPDI (B) and PTMO were synthesized as follows:

$$nB + m_1A_1 \rightarrow B(A_1B)_{m-1}A_1B + (n - m_1 - 1)B \qquad (7)$$

Significant excess of IPDI, with a predominance of dissolved monomeric IPDI-NCO in the mixture, results in urethane-isocyanate prepolymer of type BA_1B.

In the next synthesis, urethane–siloxane–isocyanate prepolymers were obtained. The molar ratios of monomers are presented as follows:

$$nB + m_1A_1 + m_2A_2 \rightarrow B(A_1B)_{m_1}(A_2B)_{m_2} + (n - 2)B \qquad (8)$$
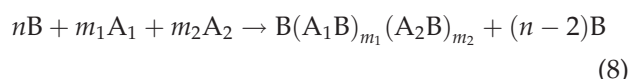
where n, m_1, m_2 are stoichiometric factors given in Table I.

In the case of the urethane–siloxane–isocyanate prepolymers, —NCO-terminated prepolymers dissolved in IPDI were also obtained, as it is shown in eq. (8).

Stage II: Incorporation of 2,2-bis(hydroxymethyl) propionic acid into the polymer chain

The reaction of the isocyanate mixture from Stage I with the IPDI and DMPA (X) may be presented as follows:

$$B(A_1B)_{m_1}A_1B + (n - m_1 - 1)B + m_1X$$
$$\rightarrow BX(BA_1)_{m_1}A_1B + B(XB)_{m_1-1}B + (n - 3)B \quad (9)$$
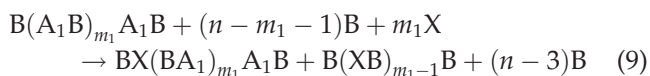
Adequate amount of DMPA, dissolved in NMP, was added drop by drop to the mixture of the obtained at Stage I urethane prepolymers in the time of 10 min at 85°C. Then, the catalyst DBTDL was added. The total content of catalyst was about 0.3 wt % with regard to the introduced polyols. Thus, the urethane–isocyanate prepolymers were extended. From eq. (9), in the reaction at NCO : OH = 1.5 ($n = 3$) the remaining IPDI together with DMPA were built into the urethane–isocyanate chain.

In the same way, the poly(urethane-siloxane)prepolymers-containing isocyanate groups were extended as follows:

$$B(A_1B)_{m_1}(A_2B)_{m_2} + (n - 2)B + X$$
$$\rightarrow BXB(A_1B)_{m_1}(A_2B)_{m_2} + (n - 3)B \quad (10)$$
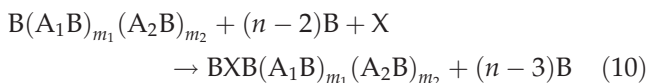
It arises from eqs. (9) and (10) that 1 mol of the unreacted IPDI remains in the products of the Reaction Nos. 1–4 after the chain extension with DMPA is terminated (Table I) $n = 4$. Then, a new isocyanate prepolymer is obtained:

$$BXB(A_1B)_{m_1}(A_2B)_{m_2} \quad (11)$$
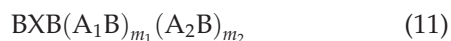
To complete the reaction, 2 mol of an extender EDA ($r = 2$) (Table I) should be added to the mixture at the next stage. There should not be the monomeric IPDI in the products of Reaction Nos. 5–12 ($n = 3$) after the second stage was completed. Thus, in the next stage, only the polymer presented in formula (11) will react with 1 mol of EDA ($r = 1$). It is obviously quite formal reasoning in fact the complex mixture of the prepolymers will react according to the stoichiometry, given in Table I.

In the obtained prepolymers,

$$BXB(A_1B)_{m_1}(A_2B)_{m_2} \text{ and } BXB(n = 4) \quad (12)$$

$$BXB(A_1B)_{m_1}(A_2B)_{m_2}(n = 3) \quad (13)$$
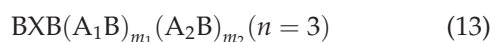
—COO$^-$ groups which are derived from structural fragments of the DMPA are present. It was necessary to make durable connection between the prepolymers and DMPA before the extension step, to be sure, that the obtained anionomer makes a macroanion for an ammonia cation, which is produced at the next stage with TEA addition. That structure will allow to obtain the anionomer, which will be able to dissociate in water and will be easily dispergate in water.

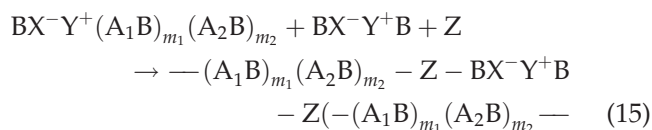Stage III: Synthesis of quaternary ammonium salts with the use of TEA

To obtain the quaternary ammonium salts, after the content of free —NCO groups was analyzed, the mixture of the isocyanate anionomers, without the monomeric IPDI content, was cooled down to 60°C. Then, TEA (Y) was added, and the mixture was reacted for 30 min. The number of moles of TEA added to the mixture corresponded to the number of moles of the built-in DMPA acid ($q = p$).

$$BXB(A_1B)_{m_1}(A_2B)_{m_2} + BXB + Y$$
$$\rightarrow BX^-Y^+(A_1B)_{m_1}(A_2B)_{m_2} + BX^-Y^+B \quad (14)$$
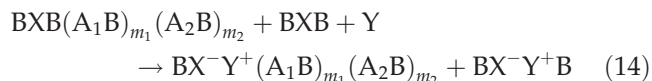
Stage IV: Dispersion step and extension of the isocyanate anionomers with the use of ethylenediamine (EDA) in aqueous medium

Deionized water was added to the isocyanate anionomers by rapid stirring at room temperature for 5 min. The amount of water was suitably selected, to obtain dispersion comprising about 25% of solids. Than EDA (Z) in equimolar ratio ($r = 2$ or 1) was added drop by drop to the dispersion for 5–7 min, to extend the isocyanate anionomers.

$$BX^-Y^+(A_1B)_{m_1}(A_2B)_{m_2} + BX^-Y^+B + Z$$
$$\rightarrow \text{---}(A_1B)_{m_1}(A_2B)_{m_2} - Z - BX^-Y^+B$$
$$- Z(-(A_1B)_{m_1}(A_2B)_{m_2}\text{---} \quad (15)$$

However, the chemical formula not only influences the polyurethane properties but also polyaddition conditions, as for example, an order of the monomers introduction. Thus, independent of the 4-stage synthesis for comparison, the anionomers were obtained from the 3-stage method (Sample Nos. 13–16) (Table I).

At Stage 1, the 1st and 2nd steps from the 4-stage method were connected and the urethane–isocyanate anionomer (Sample No. 13), or the urethane–siloxane–isocyanate anionomers (Sample Nos. 14–16) $n = 3$ with built-in DMPA were obtained.

Suitable amount of PTMO, DMPA, and alternatively PDMS were dissolved in NMP and placed into the flask. When the mixture reached 50–55°C, suitable amount of IPDI and of the catalyst (DBTDL) were added. Then, the mixture was heated to 85°C, and the temperature was maintained during the synthesis. The content of free —NCO groups was analyzed every 30 min. The 2nd and 3rd steps of the 3-stage method are analogous to Steps 3 and 4 of the 4-stage method, i.e., the neutralization with TEA and the chain extension with EDA in aqueous medium, respectively.

A total of Sixteen anionomer samples were obtained as described earlier. Amounts of PTMO and PDMS that create elastic segments were selected such as to obtain a total elastic segment content of 44–45 wt % (Anionomers Nos. 1–6) or 50–51 wt % (Anionomers Nos. 7–16), independent of the method of synthesis. The remaining amounts, i.e., 55–56 wt % or 49–50 wt %, respectively, were derived from

hard segments. The hard segments are made from significantly more polar urethane or urea structures, derived from IPDI, DMPA, and EDA.

The weight method was employed to determine solid content. It was found that the dispersion contains 26 ± 1.3 wt % of solids. The polymer coatings were prepared by pouring the dispersion on the apolar surface of poly(tetrafluoroethylene) (PTFE) followed by drying in a circular oven at 65°C for 5 h. Then, the samples were conditioned at room temperature for 10 days.

Determination of —NCO group content

The method of determination was a well-known one, and dibutylamine was used in the tests. Excess of unreacted amine was titrated with the HCl solution, and bromophenol blue was used as an indicator.[21]

NMR spectroscopy

^{1}H NMR spectra of the polymers were recorded using FT NMR Bruker Avance 500[II] spectrometer. The samples of coatings (i.e., produced anionomers) were dissolved in CDCl$_3$, and the solutions with the concentration of about 0.2 g/dm^3 were prepared. TMS was used as a standard.

IR spectroscopy

IR spectra were recorded with the spectrophotometer Paragon 1000 FTIR, within 4000–6500 cm^{-1}, with the use of ATR technique (the polymer film was placed between the prism walls). The obtained spectra were presented as the relationship of transmittance (%) versus wave number $\bar{\nu}$ (cm^{-1}).

Determination of the mechanical properties of the coatings obtained from poly(urethane-dimethylsiloxane) anionomers

The samples with dimensions of 60 mm × 10 mm × 0.3 mm were submitted to tensile tests. Strength tests of the samples were carried out with the use of a testing machine type Fp-100 from Heckert (Germany), in accordance with a standard procedure.[22] The crosshead speed was 500 mm/min, and the gauge length of the specimens was 25 mm. Tensile force versus sample tensile strain was recorded and the relationship was plotted as function of tensile stress versus sample elongation.

Tensile strength (TS$_b$) in MPa was calculated from the formula:

$$TS_b = \frac{F_b}{ab} \qquad (16)$$

where F_b, force recorded at break (N); b, width of measuring length (mm); d, thickness of measuring length (mm).

Elongation at break (E_b) in % was calculated from the relationship:

$$E_b\% = \frac{L_b - L_o}{L_o} \times 100 \qquad (17)$$

where L_b, length measured at break (mm); L_o, initial measuring length (mm).

Method for determination of the free-surface energy components for solids

Physical parameters of the FSE for solid γ_S were found in this study on the basis of the Owens–Wendt model.[23]

The model assumes that the FSE γ_S of the solid state may be presented as a sum of two components:

$$\gamma_S = \gamma_S^d + \gamma_S^p \qquad (18)$$

where γ_S^d, FSE connected with long-range dispersion interactions (dispersion, polar and induction interactions); γ_S^p, FSE connected with polar interactions.

Taking into account the FSE components in the meaning as it was described earlier, Owens and Wendt proposed an equation that establishes the relationship between the FSE parameters of the standard liquids (L) and of the investigated surface of solid (S):

$$\gamma_L \frac{1 + \cos \Theta}{2} = (\gamma_S^d \gamma_L^d)^{0.5} + (\gamma_S^p \gamma_L^p)^{0.5} \qquad (19)$$

where Θ is the experimentally found contact angle between a liquid drop and a solid surface under investigation.

To find as well as to validate the values of FSE (γ_S) and the components γ_S^d and γ_S^p of FSE, two sets of standard liquids (water-formamide and diiodometane-formamide) for the anionomer surface investigation were used. The standard liquids have known γ_S values. The values of the components γ_S^d and γ_S^p differ in significant degree (Table VII). Solving the set of eq. (19) for the given pair of standard liquids the γ_S^d and γ_S^p values were calculated. Then, based on eq. (18), γ_S value of the polyurethane anionomer coatings was calculated.

The angles Θ were measured using the method suggested by Zisman,[24] i.e., by means of optical goniometer (Cobrabid Optica-Warsaw) with a digital camera installed instead in axial extension of its lens. The liquid drops with the constant volume (about 5 μdm^3) were applied to the surfaces of studied samples with the use of a special micropipette.

The samples were fixed on the stage of the goniometer. The measurements were taken in a room at $21 \pm 1°C$. The values of contact angles were found from the geometric analysis of pictures taken for liquid drops, which involved the use of the original software developed by Kontrast (Pasłęk, Poland) for interpretation of the Young's equation. The measuring errors for angles Θ come from two sources. The first of them results from different shapes of liquid drops placed on the investigated coatings, and from possible interactions between the standard liquid and that subgrade, as well as from different liquid vaporization rates observed when the pictures were taken. Nine drops were analyzed each time which were placed on the surface simultaneously. Another source of potential errors is inaccuracy in graphical interpretation of the pictures with the use of the computer software. For each picture recorded (i.e., for each liquid drop), the geometrical shape analysis was repeated 10 times: the extreme values were rejected, and the arithmetic mean value was calculated for the accepted findings. The measured values of contact angles and the FSE components for the anionomer coatings according to those measurements were presented in Table VIII.

RESULTS AND DISCUSSION

Chemical structures as well as polarity and dispersity nature of the polyurethane anionomers

Figure 1 shows an exemplary ^1H NMR spectrum of the Sample No. 12 of the poly(urethane-siloxane) anionomer. Interpretation of that spectrum is presented in Table II, where the protons' signals were assigned to the particular structural parts of the anionomer chain, according to eq. (9). The recorded NMR spectra fully confirmed the structure of the obtained anionomers, which allowed us to use the recorded spectra for quantity interpretation. In Table III, the signals of the protons and their conventional integration (I) were presented based on the arbitrary selected signal of f-type protons in IPDI ($I = 1.00$).

Assuming that magnitude of polar and dispersion interactions in the polymer is proportional to the number of polar and apolar structures in the macromolecule and based on integrated signals of ^1H NMR spectra, polarity (p) and dispersity (d) of chemical structures of the synthesized anionomers was evaluated. Factor κ was defined for that purpose as follows:

$$\kappa\% = \frac{I_p}{I_p + I_d} \times 100 \qquad (20)$$

where

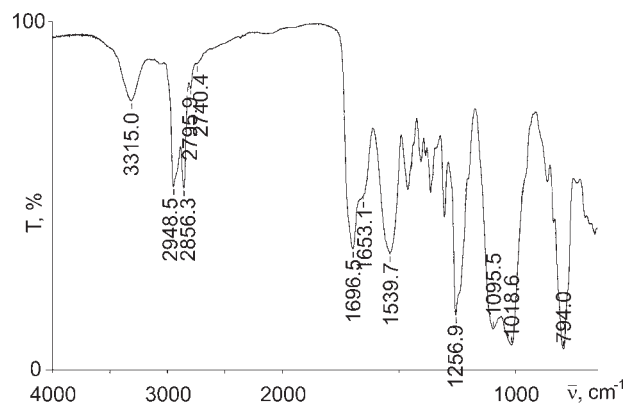$$I_p = \sum_{i=1}^{4} (I_g + I_h + I_i + I_j) \qquad (21)$$

Figure 1 ^1H NMR spectrum of the Anionomer No. 12.

is the sum of integrated four signals recorded over a wide range of $\delta = 2.5$–4.1 ppm (designated as g, h, i, j) and representing the protons in groups $-CH_2-$ bonded to polar ether groups, nitrogen atoms, $-OH$ groups, and urethane or urea groups, whereas

$$I_d = \sum_{i=1}^{6} (I_a + I_b + I_c + I_d + I_e + I_f) \qquad (22)$$

is the sum of six integrated signals for protons of dispersible $-CH_3$ groups, which are present in structural units derived from PDMS, TEA, DMPA, and IPDI as well as $-CH_2-$ groups derived from PDMS, PTMO, the employed IPDI diisocyanate and amino chain extender EDA.

The total integration for the particular anionomers that is evaluated from (21) and (22) is presented in Table IV. With that assumption, eq. (21) gives the shares of chemical structures which have the dominant effect on polar interactions, whereas eq. (22) is specific for dispersion interactions which occur in the structures of synthesized anionomers (Table I). One can assume then that the κ factor value, as calculated from eq. (20), provides physical characterization of the polarity degree for a given anionomer. The obtained data show that the κ factor values vary within 22–30% for the anionomers group obtained at $-NCO : -OH = 2.0$ and within 24–36% for the anionomers group at $-NCO : -OH = 1.5$. Independent of the above, the highest κ values among those groups were observed for polyurethane Anionomer Nos. 1 and 7, obtained from PTMO only. From the performed calculation, one can be clearly concluded that the PDMS presence in the anionomers causes decrease in polarity (increase in dispersity). It is interesting that the anionomers containing similar parts from PDMS and PTMO (Sample Nos. 6 and 12) have distinctly various dispersity ($\kappa = 25$ i 27.6%). Slightly larger dispersity of the anionomers obtained at $-NCO : -OH = 2.0$ (Sample No. 4) can be explained in the larger share of rigid segments. Thus, the rigid segments derived from

δ (ppm)	Structural elements of the anionomer chain	Marking of the protons	Descent of the structural fragment
0.07	—Si—$(CH_3)_2$—O— —CH_2—Si(CH_3)—O—	(a)	PDMS (A_2)
0.84–0.96	NH^+—$(CH_2$—$CH_3)_3$	(b)	TEA (Y)
1.06		(c)	DMPA (X)
1.25		(d)	IPDI (B)
1.50–1.68	—O—CH_2—$(CH_2)_2$—CH_2—O—	(e)	PTMO (A_1)
1.99–2.07		(f)	IPDI (B)
2.36–2.39	NH^+—$(CH_2$—$CH_3)_3$	(g)	TEA (Y)
2.84	—NH—CH_2—CH_2—NH—CO—NH—	(h)	EDA +IPDI (BZ)
3.36–3.41	-CH_2-CH_2-O-CH_2- 	(i)	PTMO (A_1) IPDI (B) DMPA (X)
4.05–4.06	-NH-CO-O-CH_2-CH_2-O- 	(j)	PTMO+IPDI (A_1B) IPDI+DMPA (BX)

TABLE III
Chemical Shifts δ (ppm) and Integrations Signals (Conventional Unit) in ¹H NMR Spectra of the Synthesized Anionomers

Type of protons (by Table II) and integration of signals

Sample nos.	a δ (ppm)	a I	b δ (ppm)	b I	c δ (ppm)	c I	d δ (ppm)	d I	e δ (ppm)	e I	f δ (ppm)	f I	g δ (ppm)	g I	h δ (ppm)	h I	i δ (ppm)	i I	j δ (ppm)	j I
1	0.07	0.0441	0.84–0.93	0.5103	0.96–1.1	0.31	1.25	0.967	1.55–1.73	1.7501	1.99–2.07	0.259	2.33–2.39	0.2588	2.84	0.3909	3.37–3.42	1	–	–
2	0.04–0.80	0.2346	0.84–0.93	0.8967	1.01–1.05	0.29	1.25	0.703	1.55–1.73	2.2075	1.99–2.07	0.2634	2.35–2.46	0.2217	2.84	0.3447	3.37–3.46	1	4.05	0.0291
4	0.04–0.08	0.600	0.84–0.98	1.0013	1.01–1.1	0.43	1.25	1.321	1.55–1.73	2.8735	1.85–2.07	0.2673	2.36–2.39	0.2697	2.84	0.3782	3.36–3.46	1	3.6–3.78	0.1777
6	0.04–0.09	1.0565	0.84–0.97	0.7488	1.01–1.1	0.5	1.25	0.83	1.55–1.72	2.934	1.99–2.07	0.3558	2.36–2.39	0.3387	2.85	0.5554	3.36–3.41	1	3.75–4.32	0.2429
7	0.07	0.039	0.84–0.96	0.3305	1.06	0.29	1.25	0.257	1.50–1.68	1.1465	1.99–2.07	0.0991	2.36–2.39	0.0597	2.84	0.0844	3.36–3.41	1	4.05–4.06	0.0869
8	0.07	0.2293	0.84–0.98	0.7188	1.01–1.1	0.39	1.25	1.543	1.55–1.73	2.6642	1.99–2.07	0.4384	2.36–2.39	0.3812	2.84	0.5479	3.37–3.41	1	–	–
10	0.04–0.11	0.4493	0.84–0.98	0.5713	1.01–1.1	0.38	1.25	0.986	1.55–1.73	2.2021	1.99–2.07	0.3571	2.36–2.39	0.3215	2.84	0.4716	3.37–3.41	1	–	–
12	0.04–0.08	0.9784	0.86–0.92	0.5404	1.06	0.57	1.25	0.309	1.55–1.69	1.1607	1.99–2.07	0.2522	2.35–2.39	0.1162	2.84	0.1681	3.37–3.41	1	4.05–4.2	0.1677

TABLE IV
Integrations of Signals (Conventional Unit) in ¹H NMR Spectra of the Polyurethane Anionomers and Their Polarity or Dispersity Degrees Calculated by eqs. (20)–(22)

Sample No.	I_p	I_d	Degree of polarity, κ (%)	Degree of dispersity, $100 - \kappa$ (%)
1	1.6497	3.8394	30.05	69.95
2	1.5955	4.5962	25.77	74.43
4	1.8256	6.4886	21.97	78.03
6	2.1370	6.4266	24.95	75.05
7	1.2310	2.1621	36.28	63.72
8	1.9291	5.9880	24.37	75.63
10	1.7931	4.9489	26.60	73.40
12	1.4520	3.8124	27.58	72.42

the apolar IPDI influence the dispersion interaction. It is very interesting conclusion, because the rule is, that the rigid urethane segments influence mainly the polar interaction. Although from the elastic segments mainly the dispersion interaction should be expected, the rigid segments influence the polar as well as dispersion interaction, as can be noticed. It should be expected that the anionomers' anionic structures influence the polar interaction (—COO⁻ anions, derived from the build-in DMPA acid) as well as the dispersion interaction (counterions: alkylammonia cation, $NH^+(C_2H_5)_3$).

Figure 2 shows the IR spectrum of the Sample No. 12, and Table V presents the interpretation of the most important bands as well as the absorbance of the anionomers. The build in of the PDMS segments into the anionomer chains was confirmed by the increase in the ratio of the Si—CH₃ bands absorbances (700–805 cm⁻¹) to C—H (in CH₂ groups) (2852–2859 cm⁻¹) based on IR spectra. The absorbance ratio of the N—H band (3300 cm⁻¹) as well as the first and second amide bands (1700 cm⁻¹ and 1540 cm⁻¹) to the C—H band absorbance (2852–2859 cm⁻¹) is definitely larger for the anionomers spectra at —NCO : —OH = 2.0. The difference in the hard
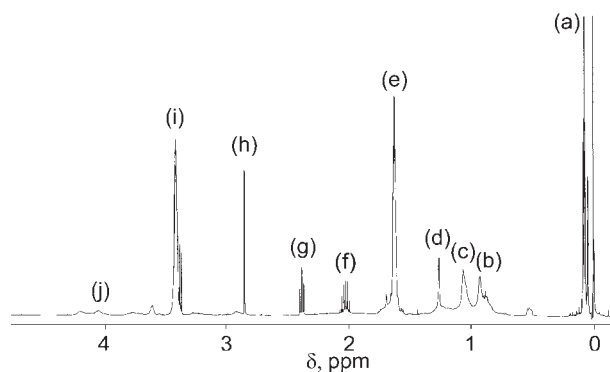

Figure 2 IR spectrum of the Anionomer No. 12.

TABLE V
Absorbance of the Fundamental IR Bands in the Anionomers

Sample nos.	CH $\bar{\nu}$	CH A_1	N—H $\bar{\nu}$	N—H A_2	C—N $\bar{\nu}$	C—N A_3	C=O $\bar{\nu}$	C=O A_4	Si—C Bending bonds $\bar{\nu}$	Si—C Bending bonds A_5	Si—C rocking bonds $\bar{\nu}$	Si—C rocking bonds A_6	A_2/A_1	A_3/A_1	A_4/A_1	A_5/A_1
						$\bar{\nu}$ cm^{-1}, Absorbance bands, conventional units									Relative absorbance		
1	2852.0	0.2076	3319.6	0.0686	1550.6	0.4441	1696.4	0.2988	–	–	–	–	0.330	2.139	1.439	–
2	2854.9	0.1436	3308.5	0.0511	1552.9	0.3666	1698.5	0.2407	799.0	0.3705	–	–	0.356	2.553	1.676	2.580
3	2854.6	0.2731	3311.0	0.1074	1550.5	0.5657	1696.1	0.3897	799.0	0.6102	1256.1	0.6327	0.393	2.071	1.427	–
4	2854.5	0.1661	3313.5	0.0685	1552.7	0.4087	1696.5	0.2630	797.5	0.6802	1257.0	0.4087	0.412	2.461	1.583	4.095
5	2856.0	0.1660	3316.3	0.0751	1553.5	0.4109	1699.4	0.2797	796.8	0.8420	1257.0	0.5576	0.452	2.475	1.685	5.072
6	2858.5	0.1100	3316.3	0.0506	1552.2	0.3473	1698.0	0.2292	795.0	0.9306	1257.0	0.5460	0.460	3.157	2.084	8.460
7	2852.9	0.4153	3314.6	0.1035	1539.5	0.4597	1696.3	0.4503	–	–	–	–	0.249	1.107	1.084	–
8	2853.8	0.4476	3320.0	0.1216	1538.5	0.5251	1699.0	0.5034	801.4	0.3494	–	–	0.272	1.173	1.125	0.781
9	2853.7	0.4505	3316.5	0.1424	1539.6	0.5895	1696.6	0.5478	798.4	0.7016	1255.8	0.7224	0.316	1.309	1.216	1.557
10	2854.1	0.4117	3321.4	0.1303	1539.8	0.5495	1696.3	0.5284	797.6	0.8629	1256.5	0.7521	0.316	1.335	1.283	2.096
11	2856.0	0.2596	3312.0	0.0953	1538.4	0.4578	1699.4	0.4155	796.1	1.0695	1256.9	0.7143	0.367	1.763	1.601	4.120
12	2856.3	0.2816	3315.0	0.1104	1539.7	0.4775	1696.5	0.4594	794.0	1.2385	1256.9	0.8066	0.392	1.696	1.631	4.398
13	2852.2	0.4262	3314.1	0.1159	1540.1	0.5018	1699.5	0.4519	–	–	–	–	0.272	1.177	1.060	–
14	2852.8	0.4035	3321	0.1151	1540.1	0.4845	1698.7	0.464	802.0	0.376	–	–	0.285	1.201	1.150	0.932
15	2856	0.3397	3316.5	0.1167	1540.5	0.4811	1699.5	0.4718	797.6	0.8779	1256.6	0.7021	0.344	1.416	1.389	2.584
16	2855	0.2299	3321	0.0904	1541.3	0.377	1699.0	0.372	794.3	1.0529	1257.0	0.6652	0.393	1.640	1.618	4.580

TABLE VI
Values of the α Parameter Calculated by Eq. (23)

	$\Delta\bar{v}$ (cm^{-1})							
	3100–3400	1690–1710	1520–1560	1010–1110	2730–3000	790–805	1255–1257	
Sample nos.	Summary absorbance							α
1	0.0686	0.5946	2.6479	1.7865	0.4460	0.0000	0	0.92
2	0.0511	0.2407	0.7332	1.2627	0.3132	0.3705	0	0.77
3	0.1074	0.7771	3.3586	1.7587	0.6022	0.6102	0.6327	0.76
4	0.0685	0.5226	1.6233	1.3541	0.3738	0.6802	0.5193	0.69
5	0.0751	0.8180	3.1118	1.4657	0.3831	0.8405	0.5576	0.75
6	0.0506	0.2292	0.3473	1.3879	0.2229	0.9306	0.546	0.54
7	0.1035	0.8961	0.9169	2.1493	0.8611	–	–	0.83
8	0.1216	0.5034	0.5251	2.5265	0.9429	0.3494	–	0.74
9	0.1424	1.0829	1.1745	2.0995	0.9750	0.7016	0.7224	0.65
10	0.1303	0.5284	0.5495	3.0785	0.8965	0.8629	0.7521	0.63
11	0.0953	1.2254	2.6675	1.9920	0.5827	1.0695	0.7143	0.72
12	0.1104	0.4594	0.4775	2.9218	0.6509	1.2385	0.8066	0.60
13	0.1159	0.4519	0.5018	2.2297	0.8966	–	–	0.79
14	0.1151	0.4640	0.4845	1.7922	0.8500	0.3760	0	0.70
15	0.1167	0.4718	0.4811	1.9553	0.7443	0.8779	0.7021	0.57
16	0.0904	1.0926	1.1327	1.7451	0.5240	1.0529	0.6652	0.64

segment structure between the anionomers obtained at —NCO : —OH = 1.5 and at —NCO : —OH = 2.0 was confirmed by that fact.

The total absorbance for the selected band ranges of the IR spectra was employed to establish quantity criterion which would enable the comparison of the polar and dispersity compound of the FSE (Table VI). According to that, α factor was defined as:

$$\alpha = \frac{A_p}{A_p + A_d} \quad (23)$$

where

$$A_p = A_{3100-3400} + A_{1690-1732} + A_{1520-1560} + A_{1010-1110} \quad (24)$$

is the total absorbance, based on the first Lambert-Beer Law, which is determined in the maximum of the favoring polar interactions functional groups.

$A_{3100-3400}$, the total band absorbance of N—H valence bonds in urethane and urea; $A_{1690-171}$, total band absorbance of C=O valence bonds in urethane and urea; $A_{1520-1560}$, total band absorbance of N—C vibration in urethane group; $A_{1030-1110}$, total band absorbance of C—O valence bonds in urethane, ethers as well as Si—O in siloxanes. On the contrary,

$$A_d = A_{2730-3000} + A_{1255-1257} + A_{790-805} \quad (25)$$

is the total band absorbance of the indicating mainly dispersion interaction groups, i.e., valence bonds of C—H (—CH$_3$, —CH$_2$— groups) and bending of Si—C (1255 cm^{-1} and 800 cm^{-1}). The functional groups assignment to the suitable kinds of interaction

according to (24) and (25) is rough, because the structures considered here as "polar" for example —O—C—O— or —Si—O—Si— (1010–1110 cm^{-1}) also occur in dispersion interaction. Similarly, Si—C bonds because of markedly electronegative difference between C and Si atoms also affect the polar interactions.

The α factor defined in (23) may be considered as notably less representative than the κ factor defined in (20) also by other reason. The signal integration in the NMR spectrum depends directly on the number of protons. On the contrary, for given —CH$_2$ band (2852 cm^{-1}) in IR spectrum, according to the first Lambert-Beer law:

$$A_{CH_2} = \varepsilon_{CH_2} d_1 c_{CH_2} \quad (26)$$

the concentration (number of groups), molar extinction factor ε_{CH2} as well as sample thickness d_1 influence the band absorbance. The sample thickness does not influence the values (23), but ε factors of the investigated bands may markedly differ.

However, as resulted from the data presented in Table VI, the observed trend of changes in α factor characterizes the reciprocal influence of the polar and dispersity components of the FSE on the intermolecular interactions. One can be concluded, that with the increasing amount of PDMS in the polyurethane anionomer chains, the drop in polarity should be expected. The trend is more distinctly marked in the Anionomer Nos. 1–12, obtained at the 4-stage method. That procedure generally favors obtaining more ordered structures of the polymer chains.

TABLE VII
Surface Properties of the Model Measuring Liquids[25]

Model measuring fluids	Free surface energy parameters [mJ/m²]		
	γ_L	γ_L^d	γ_L^p
Water	72.8	21.8	51
Formamide	58.0	39.0	19.0
Diiodomethane	50.8	48.5	2.3

Free-surface energy of the polyurethane coatings obtained from anionomers

The above presented admission was confirmed by the observed changes in contact angles Θ as well as in the markedly decrease in the FSE. After 6 wt % of PDMS instead of PTMO (Anionomer Nos. 2 and 8) into the polyurethane chains was introduced, the γ_s value decreases from about 47 to 35 mJ/m² (Table VIII).

The least contact angles Θ were observed for the coatings which were obtained from the polyurethane Anionomer Nos. 1 and 7. The contact angles increase with the increasing polarity of the model liquids in order: dijodomethane, formamide, and water. The contact angles Θ for every model liquid in the poly (urethane-siloxane) case were larger than in the polyurethane anionomer case and reach the value of almost 85° for water (Anionomer Nos. 6) at equal PTMO and PDMS content (25 wt %). The hydrophobic polysiloxane influence is confirmed by that fact.

Table VIII shows the FSE (γ_s) values and its polar (γ_s^p) and dispersity (γ_s^d) components evaluated by Owens and Wendt method [eqs. (18) and (19)] on the basis of the investigated Θ with the use of two model liquids pairs with considerably different polarity: water-diiodomethane and formamide-diiodomethane. Because of some difficulties in the precise determination of the contact angles Θ to validate the FSE results on the basis of the Zisman method adapted in our study (relatively high-standard deviation), two sets of the model liquids were used (Table VIII). The obtained with the use of both sets of model liquids γ_s values are similar, as resulted from the data presented in Figure 3. Slightly larger are: the γ_s values of the anionomers at $-NCO : -OH = 2.0$ as well as the α factor evaluated from the band absorbance in the IR spectrum.

The changes in γ_s and γ_s^p are considerably more sensitive on the increase in the hydrophobicity of the anionomers than on the changes in the degree of polarity κ. The factors κ and α (Tables IV and VI) as well as γ_S decrease with the increasing content of the hydrophobic PDMS in the anionomer chain. As it can be concluded from the data presented in Table VIII, the dispersion interaction (γ_S^d) influence more on the total FSE, but the share in the FSE of the polar compound (γ_S^p) is also considerably 12–30%. When the set of the model liquids, water-diiodomethane with the notable polarity difference, was applied (Fig. 4), the mentioned effect was more visible. From the data presented in Table VIII one cannot be concluded that with the increasing PDMS

TABLE VIII
Experimental Values of the Contact Angles and Calculated by Owens and Wendt Method of the FSE Parameters of the Anionomer Coatings

Sample no.	Contact angles Θ (°)						Water-diiodomethane			Formamide-diiodomethane		
	Model measuring fluids						Parameters of the FSE [mJ/m²]					
	CH_2I_2	Standard deviation	Formamide	Standard deviation	H_2O	Standard deviation	γ_S^p	γ_S^d	γ_S	γ_S^p	γ_S^d	γ_S
1	30.77	1.13	56.19	2.51	68.77	3.35	8.58	37.72	46.30	0.82	43.38	44.21
2	47.73	3.24	62.96	2.59	74.01	4.55	8.61	29.81	38.42	1.80	33.75	35.56
3	58.77	1.77	72.41	2.93	79.38	4.32	7.96	24.22	32.18	1.08	28.23	29.32
4	48.48	2.10	67.59	3.57	79.80	1.47	5.64	30.77	36.41	0.50	34.97	35.47
5	62.97	3.47	68.39	3.39	77.69	3.13	10.06	21.26	31.32	4.70	23.35	28.04
6	57.95	1.58	68.51	1.72	84.85	1.45	4.95	25.99	30.93	2.46	27.48	29.94
7	31.20	2.69	59.16	2.43	73.10	3.62	6.33	38.67	45.00	0.26	44.34	44.61
8	56.25	3.93	76.51	5.22	80.62	2.65	6.71	26.09	32.80	0.01	32.01	32.01
9	60.32	1.77	78.50	3.44	82.69	2.42	6.48	23.98	30.46	0.05	29.25	29.30
10	62.86	3.26	74.77	2.29	83.51	1.82	6.60	22.56	29.16	1.28	25.66	26.95
11	67.63	2.51	79.12	3.63	83.93	2.55	7.49	19.69	27.18	0.99	23.24	24.22
12	67.06	1.83	79.45	2.75	83.52	1.79	7.58	19.95	27.54	0.75	23.83	24.58
13	23.38	1.80	57.95	1.92	72.80	0.74	5.62	41.97	47.60	0.05	48.35	48.40
14	48.74	4.00	69.90	1.53	79.08	0.63	6.04	30.43	36.47	0.14	35.71	35.85
15	58.79	1.98	75.43	5.14	81.03	0.88	7.04	24.58	31.62	0.31	29.37	29.68
16	58.98	1.64	75.04	1.45	84.66	1.42	5.23	25.28	30.51	0.41	29.06	29.46

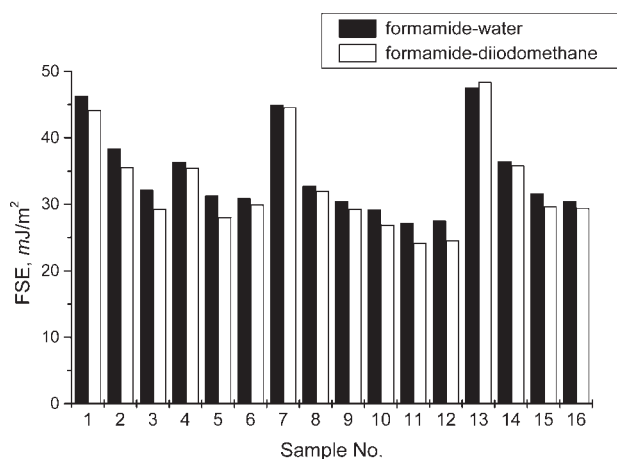**Figure 3** FSE diagrams of the poly(urethane-siloxane) anionomer coatings.

Figure 5 Tensile strength diagrams of the poly(urethane-siloxane) anionomer coatings.

content in the anionomers the dispersion interactions increase more than the polar interactions, as it could result from the analysis of degree polarity κ. To confirm that assumption much more precise FSE components analysis are needed. With the increasing PDMS content the amount of the structures increases which are responsible for the increase in the dispersion interactions ($100\text{-}\kappa$ increases and α decreases) as resulted from NMR and IR spectra structural analysis. The increase in hydrophobicity of the investigated anonomers was confirmed by that fact. On the contrary, the FSE analysis confirms that γ_S decreases with the increasing PDMS content as a result of the γ_S^d decrease which mainly influences the FSE. The polar component γ_S^p does not change practically with the increasing PDMS content but its share in the total FSE is notable.

It has been demonstrated in our previous study, that introduction of the PDMS into the analogous poly(urethane-siloxane) polymers, but not containing the ionic centers, much more significant affects the drop in the FSE from about 45 to 20 mJ/m^2. But in
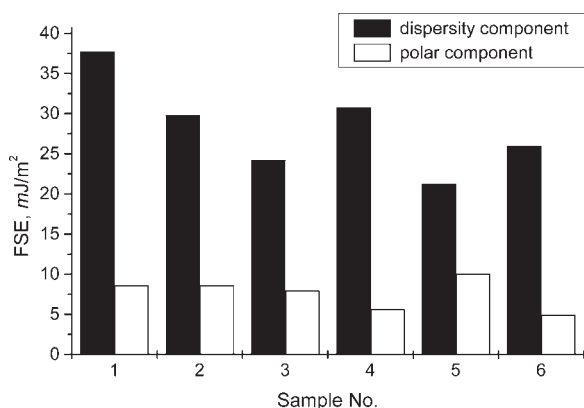
that case the FSE has been calculated on the basis of the novel method by van Oss-Good.[26] The presence of the anionic centers results in the additional growth in the FSE, but the polymers capable of producing the durable water dispersion are obtained. The water dispersion can be utilized for instance in production of the ecological polyurethane varnishes. The similar effect, as for the anionomers, has been observed for the water soluble polyurethane cationomers. The FSE results evaluated by van Oss-Good for the polyurethane cationomers were less than for the analogous nonionic polyurethanes. The main influence on the FSE values have the γ_S^{LW} component connected with the long-range interactions, but the influence of γ_S^{AB} component connected with acid–base interaction is also noticeable.[27,28] One should remember that in both methods the long-range interaction are of different meaning. The γ_S^{LW} compound evaluated by van Oss-Good method comprises γ_S^d as well as γ_S^p interactions evaluated by Owens and Wendt method but does not comprise γ_S^{AB} acid–base interactions.[29,30]

Figure 4 FSE components diagrams of the poly(urethane-siloxane) anionomer coatings (NCO : OH = 2.0) (Table I).
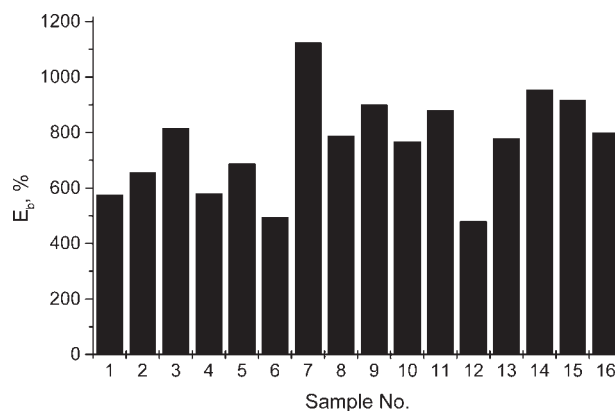

Figure 6 Elongation at break diagrams of the poly (urethane-siloxane) anionomer coating.

Mechanical properties

Tensile strength of the coatings varies within the range of 30–60 MPa and elongation at brake within the range of 400–1100%, as it was presented in Figures 5 and 6. The values are quite good as for coatings from polyurethane elastomers. The mechanical properties of the obtained coatings are influenced by the molar ratio of IPDI to the total amount of polyoles, the amount of PDMS in relationship to PTMO and the number of stages in polyaddition process. Tensile strength distinctly decreases with the increasing PDMS content, whereas elongation at break decreases. It can be explained by the decrease in the polar interactions, which can somehow order the phase structure of the polymer. The highest tensile strength (TS_b >50) was found for the Sample Nos. 7–9 at NCO : OH = 1.5. In those cases, the PDMS amount has secondary meaning because the chemical composition of the material is more important. Generally, the properties of coatings which were obtained at 3-stage method (Samples Nos. 13–16) are weaker, what probably results from the less molecular weight of the poly(urethane-siloxane) obtained at 3-stage method than at 4-stage method. To confirm that assumption more investigation are needed.

CONCLUSIONS

The presented study shows that the decrease in polarity of the polymers is affected by the introduction of the poly(dimethylsiloxane) into the polyurethane anionomer chains instead of the elastic segments from PTMO. That drop results from the changes in the long-range interactions inside elastic and rigid segments. The decrease of κ and α factors confirms that assumption. The κ and α factors can be calculated from the integration data for the proper signals in ^{1}H NMR spectra and from the absorbance changes for the selected bands in IR spectra, respectively.

The afore-mentioned structural changes are reflected in the drop in the FSE values from 47 to 35 mJ/m^2, with the PDMS introduction. From the FSE results, calculated by Owens and Wendt method, one can be concluded that the share of the dispersity component γ_S^d in the total FSE γ_S of the anionomer is distinct. The γ_S^d is mainly connected with the interactions between the alkyl groups of the elastic and rigid segments in the poly(urethane-siloxane) anionomer chains.

Introduction of the ionic structures into the polymers results in obtaining of the poly(urethane-siloxane) polymers that are capable of producing the durable water dispersions. It is possible to approximately evaluate the polar and dispersion interaction inside the elastic and rigid segments of the polymers on the basis of the chemical structure analysis by IR and ^{1}H NMR spectra. The interactions influence the FSE of the polymer coatings but the mechanical properties as well.

The obtained coatings have properties that are characteristic for elastomers, i.e., tensile strength within the range of 30–60 MPa and elongation at break 400–1100%. The drop in endurance parameters is affected by the introduction of the apolar PDMS segments, but the molar ratio of the monomers as well as the synthesis method are the determinant factors.

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