Studies of plasma treated styrene-based ionomers

Jolanta Kowalonek[1), *)], **Halina Kaczmarek**[1)], **Edyta Mikuła**[2)]

Abstract: The aim of the work was to study changes in the surface polarity of styrene ionomers containing Li⁺, Na⁺, K⁺ and Cs⁺ acrylates after air plasma treatment and then to observe the hydrophobic recovery of these samples. Changes in the surface properties were studied by atomic force microscopy (AFM), by measuring contact angles and calculating the surface free energy and its components. The values of surface free energy and its polar component increased considerably after air plasma treatment, which indicated the presence of polar groups on the surfaces. However, these alterations in the sample surfaces were impermanent.

Keywords: low temperature plasma, styrene ionomers, contact angle, surface free energy, aging.

Badania jonomerów styrenowych poddanych działaniu plazmy

Streszczenie: Zbadano zmiany polarności powierzchni jonomerów styrenowych, zawierających akrylany litu, sodu, potasu lub cezu, wywołane działaniem plazmy wytworzonej w powietrzu w funkcji czasu. Do oceny właściwości powierzchniowych zastosowano mikroskopię sił atomowych (AFM) oraz goniometrię. Na podstawie pomiarów kąta zwilżania obliczono swobodną energię powierzchniową i jej składowe. Pod wpływem działania plazmy wytworzonej w powietrzu wartości swobodnej energii powierzchniowej i jej składowej polarnej znacznie wzrosły, co wskazuje na zwiększenie liczby grup polarnych obecnych na powierzchni badanych próbek. Duża hydrofilowość modyfikowanej powierzchni, wywołana działaniem plazmy, zmniejszała się w funkcji czasu.

Słowa kluczowe: plazma niskotemperaturowa, jonomery styrenowe, kąt zwilżania, swobodna energia powierzchniowa.

Low temperature plasma, as used as a sample surface modifying factor, is a complex mixture. It consists of neutral molecules (mostly), electrons, ions, radicals, excited species and UV-irradiation [1—3]. All plasma species can interact with sample surfaces and, due to the complexity of the processes in the plasma, the results may be unpredictable [3, 4]. If the surface is modified with non-polymerizing gases (*e.g.* O_2, N_2, NH_3), polar functional groups are generally formed that cause an increase in the hydrophilicity of surfaces [5, 6]. Species, having sufficient energy to break chemical bonds take part in the formation of free radicals at the polymer surface. Then, these free radicals can react with plasma species and produce new functional groups on the surface. When oxygen or air plasma is applied, oxygen containing groups are created [4, 6]. However, the resulting decrease in water contact angle, increase in surface free energy and its polar component are not durable. These hydrophilic properties of the samples tend to decline during storage. This phenomenon is called hydrophobic recovery or aging. It is assumed that hydrophobic recovery is caused by the reorientation of polar groups that become buried beneath the surface [1, 7—9] and the driving force of this process is that the interface between sample surface and the surrounding medium tends to achieve a state with as low an energy as possible [3, 10]. Such behaviour of plasma modified polymers is not favourable from the industrial point of view as the polymer surfaces are modified in order to obtain better wettability and improve their adhesion to other materials such as dyes, printing inks, adhesives or metal layers [4]. Thus, the polymers are treated again just before these processes although less energy is demanded than the first time. It was noted that plasma sourced ion implantation (PSII) generated more polar groups on the surfaces and more cross-linked structures than conventional plasma. Moreover, PSII treated samples have a slower hydrophobic recovery compared with plasma treated ones [8, 9].

Kim J.-S., Lee Y. and co-authors examined the surface properties of ionomers after plasma or plasma source ion implantation (PSII) treatment. They studied changes in the outer layers of ionomers based on styrene-acrylic acid copolymers neutralised with sodium or caesium hydroxide, styrene–methacrylic acid, styrene-styrenesulfonic acid, ethyl acrylate-acrylic acid or methyl methacry-

---

[1)] Nicolaus Copernicus University, Faculty of Chemistry, Gagarin 7, 87-100 Toruń, Poland.

[2)] Institute of Animal Reproduction and Food Research of Polish Academy of Science, Tuwim 10, 10-748 Olsztyn, Poland.

[*)] Author for correspondence; e-mail: jk@chem.umk.pl

late-methacrylic acid copolymers. It was found that the hydrophobic recovery was much slower for ionomers than for polystyrene or the initial copolymers. Moreover, samples treated with PSII showed a slower hydrophobic recovery in comparison with samples treated with plasma. In addition, styrene ionomers containing caesium ions were less stable during aging than ionomers with sodium ions [11—14].

According to the Eisenberg theory [15], ionomers are polymers that are comprised of two types of aggregates: smaller multiplets — made of only ion pairs without segments of polymer chains, and larger clusters, which are created from multiplets surrounded by polymer chains. Such regions start overlapping and forming one phase.

The surface properties of styrene based–ionomers after UV-irradiation were previously investigated [16, 17].

The goal of the work was to examine styrene ionomers containing Li^+, Na^+, K^+ or Cs^+ cations in terms of their behaviour after air plasma treatment and to determine the influence of salt content and of the type of cations in ionomers on hydrophobic recovery.

EXPERIMENTAL PART

Materials and samples preparation

The preparation of styrene (S) and acrylic acid (AA) copolymers was described in previous papers [18, 19]. The appropriate ionomers were obtained as a result of neutralisation of acid groups in the copolymers with lithium, sodium, potassium or caesium hydroxide.

To prepare thin films, 2 % (m/v) polymeric solutions in tetrahydrofuran were made and then these solutions were cast onto levelled glass plates. After evaporation of the solvent, the samples were dried to a constant weight at 50 °C in a vacuum. The thickness of the films ranged from 70 μm to 90 μm.

The notation of samples is P(S-x-AY), where x denotes the content of acrylic acid (AA) in the copolymer or content of salt in the ionomer in mol %, Y = A, Li, Na, K, Cs.

Plasma treatment

The samples were placed on microscope glasses in a quartz tube and then this tube was put into a plasma system. The apparatus operated at an air pressure of 4.5 Pa ($4.5 \cdot 10^{-2}$ mbar), current intensity 140 mA and frequency 2860 MHz. The treatment time was 30 s.

Methods of testing

Contact angle measurements and surface free energy calculations

To analyse the surface properties of the samples, contact angle measurements were made using a DSA G10 goniometer from Krüss GmbH (Germany). In these studies,

a drop of test liquid (water or diiodomethane) was placed onto the sample surface with a microsyringe and the value of the contact angle was calculated by the computer on the basis of the obtained image of the liquid drop. Contact angles were measured before, immediately after plasma treatment, and after storage of plasma treated samples. The samples were stored at room temperature in a desiccator. The contact angle values are an average of *ca*. 8 measurements and the deviation from the average was within ± 2°. All measurements were carried out at room temperature.

On the basis of contact angle measurements, the surface free energy (γ_s), as well as its dispersive (γ_s^d) and polar (γ_s^p) components, were calculated by the Owens-Wendt method [20] using an appropriate computer program.

Atomic force microscopy (AFM) measurements

AFM images were recorded on a MultiMode NanoScope III, Veeco Mertology Inc. (USA) with a silicon probe (Veeco) in tapping mode, in air, at room temperature. Besides images of the samples, roughness parameters (R_q, R_a) were gained from this method, where R_q is the root mean square and R_a is the arithmetic mean of the measurements. AFM images were obtained in three different sample regions for each sample and the most representative image was chosen. The R_q and R_a parameters were calculated for a defined scan area (2 μm × 2 μm) and averaged in the three regions of the sample surfaces.

RESULTS AND DISCUSSION

Surface free energy

Effect of content of acrylic acid in P(S-AA) copolymers on surface properties

Table 1 shows the surface free energy values and its components for polystyrene and styrene-acrylic acid copolymers with 5.16 or 11.67 mol % of acrylic acid before, immediately after plasma treatment, and after storage of the plasma treated samples. Before the plasma treatment, the surface free energy and its polar component values were higher for the copolymer with 5.16 mol % of acrylic acid than for the copolymer with 11.67 mol % of acid. This indicated a more hydrophilic surface for the copolymer with lower content of acrylic acid compared with the surface of copolymer with the higher content of the acid. The reason for this may be the existence of acrylic acid groups on the surface in the case of the lower content. However, when the content of acid in the copolymer becomes higher, the majority of carboxylic groups are dimerized, not free, and may be situated below the outer layer.

The plasma treatment induced a significant increase in the surface free energy and its polar component. Such alterations suggested the presence of a high amount of

T a b l e 1. **The values of surface free energy (γ_s) and its polar (γ_s^p) and dispersive (γ_s^d) components for polystyrene and styrene-acrylic acid copolymers with different contents of acrylic acid, before and after plasma treatment**

Sample		γ_s, mJ/m²	γ_s^p, mJ/m²	γ_s^d, mJ/m²
PS	untreated	32.3	6.4	25.9
	plasma treated (immediately)	67.8	44.1	23.7
	plasma treated (after 7 days)	54.1	32.1	22.0
	plasma treated (after 14 days)	47.6	25.8	21.8
	plasma treated (after 25 days)	45.1	24.3	20.8
P(S-5.16-AA)	untreated	38.7	8.0	30.7
	plasma treated (immediately)	69.3	46.7	22.6
	plasma treated (after 7 days)	59.0	36.9	22.1
	plasma treated (after 14 days)	51.8	29.2	22.6
	plasma treated (after 25 days)	46.6	24.1	22.5
P(S-11.67-AA)	untreated	35.7	3.3	32.4
	plasma treated (immediately)	69.1	46.2	22.9
	plasma treated (after 7 days)	55.9	32.2	23.7
	plasma treated (after 14 days)	47.4	23.3	24.1
	plasma treated (after 25 days)	42.8	20.9	21.8

T a b l e 2. **The values of surface free energy (γ_s) and its polar (γ_s^p) and dispersive (γ_s^d) components for polystyrene and styrene ionomers with different contents of sodium ions, before and after plasma treatment**

Sample		γ_s, mJ/m²	γ_s^p, mJ/m²	γ_s^d, mJ/m²
PS	untreated	32.3	6.4	25.9
	plasma treated (immediately)	67.8	44.1	23.7
	plasma treated (after 7 days)	54.1	32.1	22.0
	plasma treated (after 14 days)	47.6	25.8	21.8
	plasma treated (after 25 days)	45.1	24.3	20.8
P(S-3.85-ANa)	untreated	33.2	4.8	28.4
	plasma treated (immediately)	68.4	47.2	21.2
	plasma treated (after 7 days)	54.6	33.8	20.8
	plasma treated (after 14 days)	48.8	26.5	22.3
	plasma treated (after 25 days)	45.9	22.9	23.0
P(S-5.16-ANa)	untreated	36.5	1.2	35.3
	plasma treated (immediately)	67.3	49.2	18.1
	plasma treated (after 7 days)	51.7	31.0	20.7
	plasma treated (after 14 days)	46.4	25.6	20.8
	plasma treated (after 25 days)	46.4	24.5	21.9
P(S-6.41-ANa)	untreated	33.3	4.2	29.1
	plasma treated (immediately)	67.2	46.4	20.8
	plasma treated (after 7 days)	52.7	30.9	21.8
	plasma treated (after 14 days)	44.3	22.5	21.8
	plasma treated (after 25 days)	43.4	20.3	23.1
P(S-11.67-ANa)	untreated	34.4	5.3	29.1
	plasma treated (immediately)	65.0	46.3	18.7
	plasma treated (after 7 days)	53.8	31.7	22.1
	plasma treated (after 14 days)	47.8	26.4	21.4
	plasma treated (after 25 days)	44.0	21.6	22.4
P(S-14.05-ANa)	untreated	36.2	6.3	29.9
	plasma treated (immediately)	66.3	46.7	19.6
	plasma treated (after 7 days)	51.9	31.0	20.9
	plasma treated (after 14 days)	46.8	27.4	19.4
	plasma treated (after 25 days)	44.6	22.7	21.9

polar groups on the sample surfaces, which might have been related to the incorporation of species from the plasma into the surfaces leading to the creation of new functional groups. Moreover, the reorientation of existing polar groups in copolymers could also occur. However, the dispersive component of surface free energy decreased insignificantly, which suggested that the dispersive interactions between the studied surface and test liquid did not change greatly.

A hydrophobic recovery was observed after storage of the plasma treated samples although the samples did not achieve the initial values of surface free energy and its components, even after 25 days of storage. The decrease in the surface free energy and its polar component may have been related to the reorientation and entering of polar groups beneath the surfaces [3, 7, 8, 10].

Effect of different content of sodium or caesium acrylates in ionomers on surface properties

Tables 2 and 3 show the surface free energy values and their polar and dispersive components for ionomers with different contents of sodium or caesium ions. Before the plasma treatment, the samples with lower content of salts had lower values of polar components compared with samples with a higher content of salts. The ionomers having lower content of salts had less hydrophilic surfaces than the samples with a higher content of salt, which might have resulted from the location of aggregates or ion pairs under the surfaces. Y. Lee, J.-S. Kim *et al*. presented similar results [12]. However, the surface free energy and its components for these ionomers did not differ considerably. The results suggest that the above-mentioned quantities depended rather on the amount of salt introduced into the copolymer than on the type of ions.

After the plasma action, the surface free energy and its polar component increased markedly but the dispersive component decreased for all samples. Such changes indicated an increase in hydrophilicity of the sample surfaces, which was caused by the appearance of new polar groups or by reorientation of single ionic pairs or ionic aggregates, existing in ionomers. It was proved earlier that plasma (PSII) caused an appearance of the ionic groups from ionomers on their surfaces [12, 14].

The changes in the plasma treated samples were not durable and the processes on the surfaces were dynamic. The surface free energy and its polar component dropped steadily with aging time; however, the dispersive compo-

T a b l e 3. The values of surface free energy (γ_s) and its polar (γ_s^p) and dispersive (γ_s^d) components for polystyrene and styrene ionomers with different contents of caesium ions, before and after plasma treatment

Sample		γ_s, mJ/m²	γ_s^p, mJ/m²	γ_s^d, mJ/m²
PS	untreated	32.3	6.4	25.9
	plasma treated (immediately)	67.8	44.1	23.7
	plasma treated (after 7 days)	54.1	32.1	22.0
	plasma treated (after 14 days)	47.6	25.8	21.8
	plasma treated (after 25 days)	45.1	24.3	20.8
P(S-3.85-ACs)	untreated	37.9	4.2	33.7
	plasma treated (immediately)	66.9	45.3	21.6
	plasma treated (after 7 days)	43.6	25.0	18.6
	plasma treated (after 14 days)	37.3	19.2	18.1
	plasma treated (after 25 days)	35.4	11.5	23.9
P(S-6.41-ACs)	untreated	36.9	3.4	33.5
	plasma treated (immediately)	66.5	44.9	21.6
	plasma treated (after 7 days)	51.9	31.0	20.9
	plasma treated (after 14 days)	37.0	17.8	19.2
	plasma treated (after 25 days)	37.7	13.1	24.6
P(S-11.67-ACs)	untreated	37.0	5.3	31.7
	plasma treated (immediately)	62.9	41.9	21.1
	plasma treated (after 7 days)	49.0	29.1	19.9
	plasma treated (after 14 days)	43.2	20.3	22.9
	plasma treated (after 25 days)	42.4	19.7	22.7
P(S-14.05-ACs)	untreated	37.0	8.4	28.6
	plasma treated (immediately)	60.6	37.4	23.2
	plasma treated (after 7 days)	48.1	32.5	15.6
	plasma treated (after 14 days)	37.1	17.9	19.2
	plasma treated (after 25 days)	38.0	14.3	23.7

nent did not alter much. This was a consequence of new formed polar groups or ionic groups from multiplets entering beneath the sample surfaces. The rate and the effectiveness of hydrophobic recovery for polystyrene and ionomers with sodium acrylates were similar but for ionomers with caesium acrylates slightly higher, which might have been a result of weaker interactions in multiplets owing to the larger size of caesium ions. Moreover, the weaker interactions between ions in multiplets might not constitute such a hindrance for polar groups to overturn.

Our data are contrary to the results obtained by J.-S. Kim, Y. Lee *et al*. [11—14] who observed no hydrophobic recovery for ionomers, or a much smaller effect. The reason for such varied behaviour might have been different conditions of the plasma treatment and a different way of preparing the samples. In this experiment, the samples were treated by air plasma; however, O_2 plasma or O_2 plasma source ion implantation (PSII) were applied in experiments conducted and described by the other research group [11—14]. Many factors influence the alterations of the polymer surface during plasma modification, which makes the comparison of different results difficult to interpret. It was possible to compare the pressure in the chamber during the plasma action. In our experiments, the pressure of the working gas was higher (the vacuum was weaker) than the pressure applied by J.-S. Kim, Y. Lee *et al*. [11—14]; 4.5 Pa ($\approx$ 33 mTorr) and 0.13 Pa ($\approx$ 1 mTorr), respectively. This meant that these two quan-

tities differed by 1.5 orders of magnitude. Changes in sample surfaces induced by PSII treatment were more durable compared with the changes caused by plasma treatment [8, 9], which meant that hydrophobic recovery was much slower in the case of PSII treated samples than in the case of plasma treated ones. PSII modified a thicker surface layer and, in this way, a more stable surface was created that might partially explain the variances in the results [9].

FT-IR ATR spectra of untreated and plasma-treated samples are not included in the paper as there were no noticeable alterations in these spectra. This technique provides information from a depth of about 1 μm [21]. However, plasma modifies the surface to a depth of a few nm (1—3 nm) [21] so contact angle measurements are a useful method to obtain information from such a thin layer [22].

Effect of type of cations in ionomers on surface properties

Tables 4 and 5 contain the surface free energy values and their polar and dispersive components for ionomers with 5.16 or 11.67 mol % of various cations. Before plasma modification, ionomers with 5.16 mol % of Na^+, K^+ cations had somewhat lower polar component values than ionomers with 11.67 mol %. This may indicate that the ionomers with a higher content of salts had more hydrophilic surfaces than ionomers with lower content of salts.

T a b l e 4. The values of surface free energy (γ_s) and its polar (γ_s^p) and dispersive (γ_s^d) components for styrene-acrylic acid copolymer with 5.16 mol % of acrylic acid and ionomers with 5.16 mol % of Li^+, Na^+ and K^+ ions, before and after plasma treatment

Sample		γ_s, mJ/m^2	γ_s^p, mJ/m^2	γ_s^d, mJ/m^2
P(S-5.16-AA)	untreated	38.7	8.0	30.7
	plasma treated (immediately)	69.3	46.7	22.6
	plasma treated (after 7 days)	59.0	36.9	22.1
	plasma treated (after 14 days)	51.8	29.2	22.6
	plasma treated (after 25 days)	46.6	24.1	22.5
P(S-5.16-ALi)	untreated	35.9	5.6	30.3
	plasma treated (immediately)	65.4	43.2	22.2
	plasma treated (after 7 days)	54.0	33.4	20.6
	plasma treated (after 14 days)	53.2	29.7	23.5
	plasma treated (after 25 days)	50.6	28.3	22.3
P(S-5.16-ANa)	untreated	36.5	1.2	35.3
	plasma treated (immediately)	67.3	49.2	18.1
	plasma treated (after 7 days)	51.7	31.0	20.7
	plasma treated (after 14 days)	46.4	25.6	20.8
	plasma treated (after 25 days)	46.4	24.5	21.9
P(S-5.16-AK)	untreated	36.9	2.7	34.2
	plasma treated (immediately)	67.8	43.2	24.6
	plasma treated (after 7 days)	54.8	33.4	21.4
	plasma treated (after 14 days)	38.0	16.8	21.2
	plasma treated (after 25 days)	36.5	15.3	21.2

T a b l e 5. The values of surface free energy (γ_s) and its polar (γ_s^p) and dispersive (γ_s^d) components for styrene-acrylic acid copolymer with 11.67 mol % of acrylic acid and ionomers with 11.67 mol % of Li$^+$, Na$^+$, K$^+$ and Cs$^+$ ions, before and after plasma treatment

Sample		γ_s, mJ/m^2	γ_s^p, mJ/m^2	γ_s^d, mJ/m^2
P(S-11.67-AA)	untreated	35.7	3.3	32.4
	plasma treated (immediately)	69.1	46.2	22.9
	plasma treated (after 7 days)	55.9	32.2	23.7
	plasma treated (after 14 days)	47.4	23.3	24.1
	plasma treated (after 25 days)	42.8	20.9	21.8
P(S-11.67-ALi)	untreated	35.5	5.3	30.2
	plasma treated (immediately)	67.5	47.6	19.9
	plasma treated (after 7 days)	55.7	33.3	22.4
	plasma treated (after 14 days)	52.5	29.3	23.2
	plasma treated (after 25 days)	47.1	25.3	21.8
P(S-11.67-ANa)	untreated	34.4	5.3	29.1
	plasma treated (immediately)	65.0	46.3	18.7
	plasma treated (after 7 days)	53.8	31.7	22.1
	plasma treated (after 14 days)	47.8	26.4	21.4
	plasma treated (after 25 days)	44.0	21.6	22.4
P(S-11.67-AK)	untreated	37.3	4.8	32.5
	plasma treated (immediately)	69.6	46.6	23.0
	plasma treated (after 7 days)	52.6	28.2	24.4
	plasma treated (after 14 days)	40.0	12.9	27.1
	plasma treated (after 25 days)	33.4	7.4	26.0
P(S-11.67-ACs)	untreated	37.0	5.3	31.7
	plasma treated (immediately)	62.9	41.9	21.1
	plasma treated (after 7 days)	49.0	29.1	19.9
	plasma treated (after 14 days)	43.2	20.3	22.9
	plasma treated (after 25 days)	42.4	19.7	22.7

When the content of ions in the ionomers increase, some of the aggregates, also single ionic pairs, may be situated on the ionomer surfaces.

The plasma caused a substantial increase in surface free energy and its polar component and a decrease in its dispersive component, which indicated a greater surface

T a b l e 6. Values of roughness parameters (R_q, R_a) for polystyrene, styrene-acrylic acid copolymer with 11.67 mol % of acrylic acid, styrene ionomers with 11.67 mol % of Li$^+$, Na$^+$, K$^+$ and Cs$^+$ ions, before and immediately after plasma treatment

Sample		Roughness parameters, nm	
		R_q	R_a
PS	untreated	5.78	4.35
	plasma treated (immediately)	7.03	5.72
P(S-11.67-AA)	untreated	33.29	23.90
	plasma treated (immediately)	20.71	16.94
P(S-11.67-ALi)	untreated	20.80	15.45
	plasma treated (immediately)	20.88	15.94
P(S-11.67-ANa)	untreated	0.91	0.55
	plasma treated (immediately)	1.75	1.14
P(S-11.67-AK)	untreated	0.90	0.56
	plasma treated (immediately)	2.13	1.57
P(S-11.67-ACs)	untreated	1.76	1.24
	plasma treated (immediately)	1.86	1.30

hydrophilicity caused by a greater number of polar groups, *i.e.* new oxidized groups and ionic groups, emerging from the inside of the samples.

After several days of storage, the surface free energy and its polar component decreased but the changes in the dispersive component were negligible, which meant that the acquired hydrophilicity of these ionomer surfaces declined during this time. Hydrophobic recovery was the result of conformational alterations and reorientation of polar groups, hiding beneath the surface due to the hydrophobic surroundings. The most effective hydrophobic recovery was observed for ionomers with potassium acrylates, especially for ionomers with 11.67 mol % of

these ions. Potassium ions have a larger radius than lithium and sodium ions but smaller than caesium, so the multiplets existing in ionomers containing lithium or sodium cations are supposed to be more stable than multiplets formed in ionomers with potassium ions. The specific structure of these ionomers favoured the effective hydrophobic recovery. For these ionomers, the surface free energy values after 25 days of aging were slightly lower than the initial values. However, the polar component values were still higher than those for the untreated surfaces, so the hydrophilic character of the samples was sustained. As the surface free energy is the sum of polar and dispersive components, the decrease in surface free
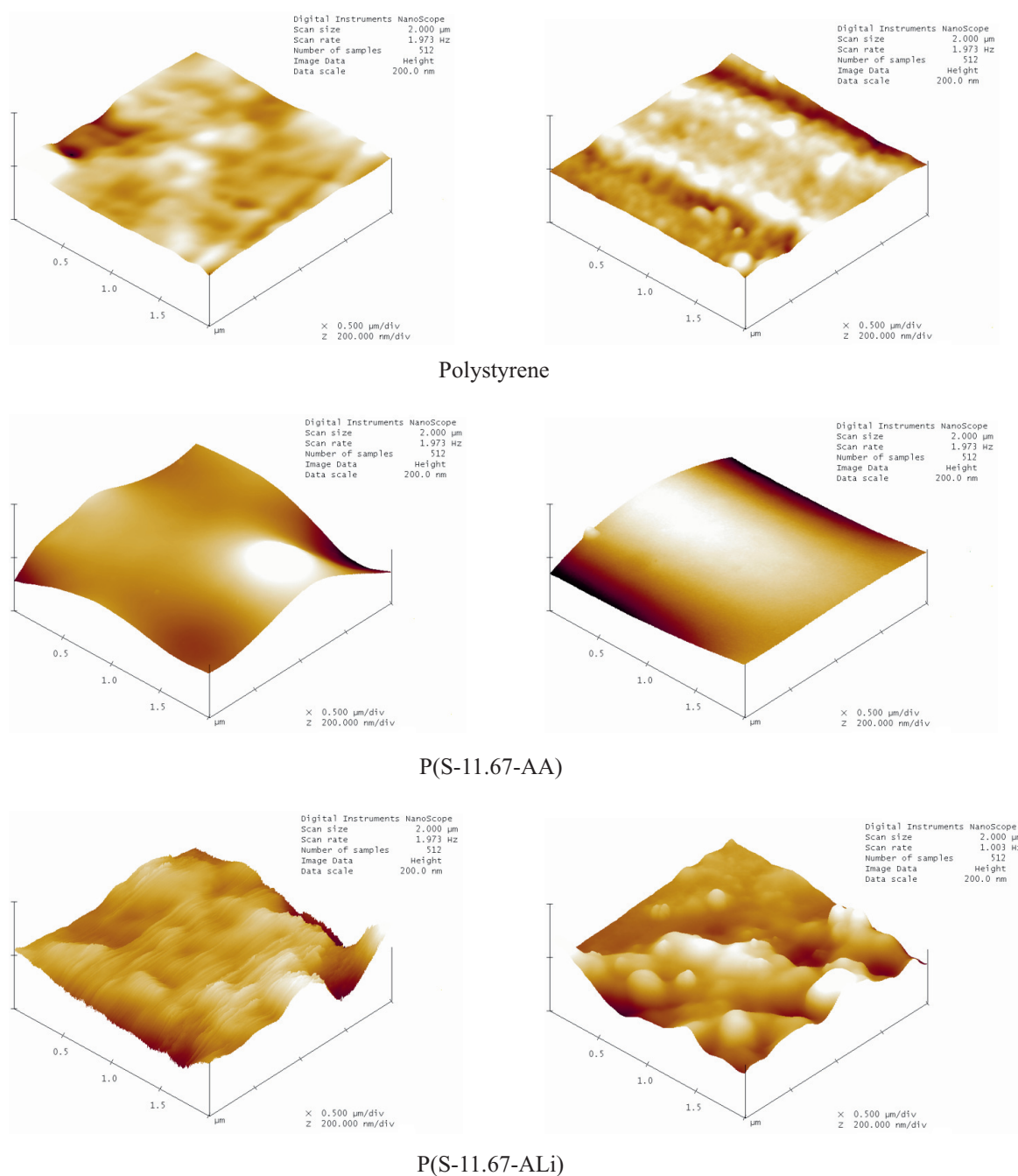

Polystyrene

P(S-11.67-AA)

P(S-11.67-ALi)

Fig. 1. continued on the next page

Fig. 1. (continued)

P(S-11.67-ANa)

P(S-11.67-AK)

P(S-11.67-ACs)

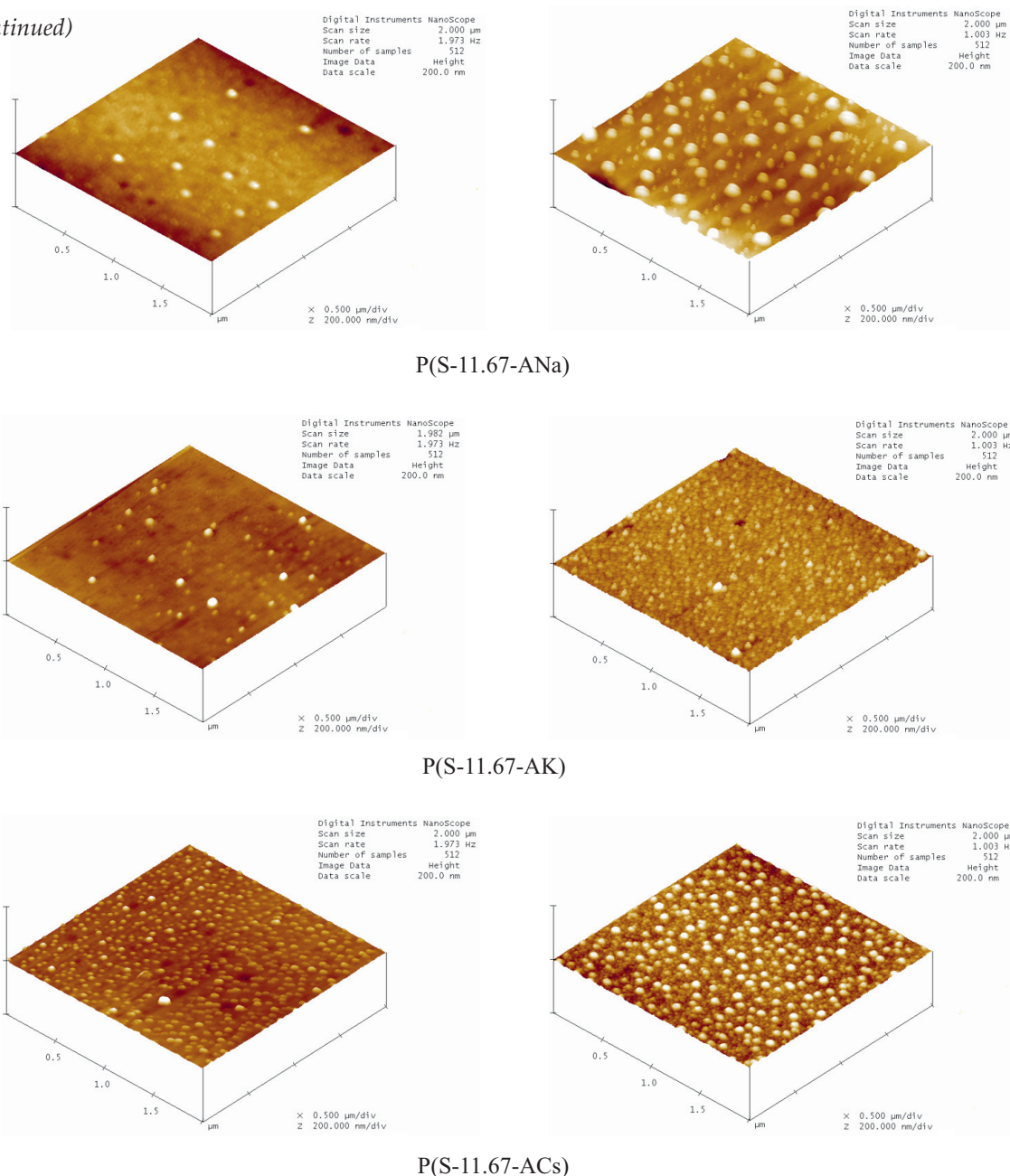**Fig. 1. AFM images of samples: left column — untreated samples, right column — plasma-treated samples; scan area: 2 μm × 2 μm, z-scale: 200 nm**

energy can be induced by the dispersive component making a contribution to the surface free energy. Dispersive interactions are supposed to be responsible for the reduction in the surface free energy as the polar component values were higher than the original ones [23]. It is also possible that hydrophobic groups can migrate to the surface during storage [24].

The same situation was observed for the ionomer with 3.85 mol % of caesium ions. The specific structure of this sample may be related to the lowest content of salts in the ionomer and to the larger size of caesium ions, which better influences hydrophobic recovery.

The slowest hydrophobic recovery was noted for ionomers with lithium ions. The multiplets in these iono-

mers are the most compact on account of the smaller size of Li^+ ions. To some extent, this property might prevent the polar groups on the surface from entering under the surface. Moreover, it was previously pointed out that the properties of these ionomers might be similar to the initial copolymers due to the existence of covalent bonds between lithium cations and carboxylate anions [25, 26].

The presence of aggregates in the ionomers did not disturb the hydrophobic recovery especially in the case of ionomers with Cs^+ or K^+. The nature of the polymers and the conditions of obtaining the plasma influence the behaviour of samples during storage.

After 25 days of aging, values of surface free energy above 40 mJ/m^2 are still high enough to use the polymeric

materials in further technological processes like printing or painting [4, 27].

AFM results

AFM images of polystyrene, styrene-acrylic acid copolymer with 11.67 mol % of acid and ionomers containing 11.67 mol % of Li^+, Na^+, K^+, Cs^+ ions are shown in Fig. 1. In the left column there are images of untreated samples and in the right column — just after the plasma treatment. It is interesting to note that the surface morphologies of ionomers with Na^+, K^+ and Cs^+ cations are similar but different from the morphology of ionomers with Li^+ ions, which may indicate that the samples varied in structure. On the surfaces of these three ionomers, there are some small hills but they are generally smooth. The surface of polystyrene is flatter than that of the copolymer and ionomer with Li^+ ions, but all are folded. More information about the surfaces are contained in Table 6, which lists the calculated roughness parameters (R_q, R_a). Ionomers containing Na^+, K^+ and Cs^+ ions are characterised by the lowest values of these quantities, but the ionomer containing Li^+ ions and copolymer have the highest ones. The similarity between the morphologies of ionomer containing lithium ions and the initial copolymer may result from the similarity of the structures as it was found that the covalent bonds are between Li^+ and carboxylate anion [25, 26].

There are subtle changes between plasma treated and untreated surfaces, which may indicate that plasma influences the morphology and the roughness of sample surfaces slightly. Surface roughness does not change during aging; however, the lack of extensive alterations in surface roughness may facilitate hydrophobic recovery. No changes or slight changes in AFM results were observed by other researchers [28, 29].

CONCLUSIONS

— Air plasma brought about a significant rise in the surface free energy and its polar component, which suggested the formation of new polar groups (species from plasma) and appearance of ionic groups from inside of the samples.

— Plasma treated samples partially restored their former surface properties, which indicated that the alterations in surfaces induced by plasma were impermanent and reversible.

— Hydrophobic recovery was slower and less effective for ionomers containing sodium cations compared with that for ionomers with caesium ions and it did not depend on the content of sodium ions in ionomers. However, the hydrophobic recovery was faster for an increased content of caesium ions in ionomers.

— The hydrophobic recovery was the slowest for ionomers containing lithium ions, but the most effective — for ionomers with potassium ions, which might result

from the size of the ions and the strength of the multiplets formed.

— AFM techniques revealed that the surfaces of ionomers with Na^+, K^+ and Cs^+ ions were similar and very smooth. The surfaces of ionomers with Li^+ ions were similar to the surface of the initial copolymer. Plasma treated samples showed minimal changes in morphology and roughness.

REFERENCES

[1] Inagaki N., Narushim K., Tuchida N., Miyazaki K.: *Journal of Polymer Science, Part B: Polymer Physics* **2004**, *42*, 3727. http://dx.doi.org/10.1002/polb.20234

[2] Bryjak M., Gancarz I., Smolińska K.: *Advanced Colloid Interface Science* **2010**, *161*, 2. http://dx.doi.org/10.1016/j.cis.2010.09.004

[3] Deshmukh R.R., Sherty A.R.: *Journal of Applied Polymer Science* **2007**, *104*, 449. http://dx.doi.org/10.1002/app.25554

[4] Żenkiewicz M.: „Adhezja i modyfikowanie warstwy wierzchniej tworzyw wielkocząsteczkowych", PWN, Warszawa 2000, str. 146—156.

[5] Sun D., Stylios G.K.: *Journal of Materials Processing Technology* **2006**, *173*, 172. http://dx.doi.org/10.1016/j.jmatprotec.2005.11.022

[6] Bogaerts A., Neyts E., Gijbels R., van der Mullen J.: *Spectrochimica Acta, Part B* **2002**, *57*, 609. http://dx.doi.org/10.1016/S0584-8547(01)00406-2

[7] Arefi F., Andre V., Montazer-Rahmati P., Amouroux J.: *Pure and Applied Chemistry* **1992**, *64*, 715. http://dx.doi.org/10.1351/pac199264050715

[8] Han S., Lee Y., Kim H *et al*.: *Surface Coating Technology* **1997**, *93*, 261. http://dx.doi.org/10.1016/S0257-8972(97)00057-1

[9] Lee Y., Han S., Lee J.-H *et al*.: *Journal of Vacuum & Science Technology, A* **1998**, *16*, 1710. http://dx.doi.org/10.1116/1.581289

[10] Murakami T., Kuroda S., Osawa Z.: *Journal of Colloid and Interface Science* **1998**, *202*, 37. http://dx.doi.org/10.1006/jcis.1997.5386

[11] Kim J.-S., Hong M.-C., Nah Y.H. *et al*.: *Journal of Applied Polymer Science* **2002**, *83*, 2500. http://dx.doi.org/10.1002/app.10265

[12] Lim H., Lee Y., Han S. *et al*.: *Journal of Polymer Science, Part B: Polymer Physics* **2003**, *41*, 1791. http://dx.doi.org/10.1002/polb.10536

[13] Song J.-M., Kim Y., Han S. *et al*.: *Journal of Applied Polymer Science* **2003**, *89*, 3100. http://dx.doi.org/10.1002/app.12498

[14] Lee Y., Han S., Kwon M.-H. *et al*.: *Applied Surface Science* **2003**, *203—204*, 875. http://dx.doi.org/10.1016/S0169-4332(02)00838-3

[15] Eisenberg A., Hird B., Moore R.B.: *Macromolecules* **1990**, *23*, 4098. http://dx.doi.org/10.1021/ma00220a012

[16] Suchocka-Gałaś K., Kowalonek J.: *Surface Science* **2006**, *600*, 1134. http://dx.doi.org/10.1016/j.susc.2005.12.047

[17] Kowalonek J., Suchocka-Gałaś K.: *Applied Surface Science* **2009**, *255*, 9159. http://dx.doi.org/10.1016/j.apsusc.2009.06.124

[18] Eisenberg A., Navratil M.: *Macromolecules* **1973**, *6*, 604. http://dx.doi.org/10.1021/ma60034a27

[19] Suchocka-Gałaś K., Wojtczak Z.: *Polimery* **1982**, *27*, 340.

[20] Owens D.K., Wendt R.C.: *Journal of Applied Polymer Science* **1969**, *13*, 1741. http://dx.doi.org/10.1002/app.1969.070130815

[21] Chan C.-M., Ko T.-M., Hiraoka H.: *Surface Science Reports* **1996**, *24*, 1. http://dx.doi.org/10.1016/0167-5729(96)80003-3

[22] Abbasian A., Ghaffarian S.R., Mohammadi N., Fallahi D.: *Journal of Applied Polymer Science* **2004**, *93*, 1972. http://dx.doi.org/10.1002/app.20672

[23] Chibowski E., Terpilowski K.: *Journal of Colloid and Interface Science* **2008**, *319*, 505. http://dx.doi.org/10.1016/j.jcis.2007.10.059

[24] Fernández-Blázquez J.P., Fell D., Bonaccurso E., del Campo A.: *Journal of Colloid and Interface Science* **2011**, *357*, 234. http://dx.doi.org/10.1016/j.jcis.2011.01.082

[25] Mattera Jr V.D., Risen W.M.: *Journal of Polymer Science; Polymer Physics Edition* **1984**, *22*, 67. http://dx.doi.org/10.1002/pol.1984.180220107

[26] Ostrowska-Czubenko J., Ostrowska-Gumkowska B.: *European Polymer Journal* **1988**, *24*, 65. http://dx.doi.org/10.1016/0014-3057(88)90128-0

[27] Navaneetha Pandiyaraj K., Selvarajan V., Deshmukh R.R., Gao Ch.: *Applied Surface Science* **2009**, *255*, 3965. http://dx.doi.org/10.1016/j.apsusc.2008.10.090

[28] Amornsudthiwat P., Mongkolnavin R., Kanokpanont S. *et al.*: *Colloids and Surfaces, B*: Biointerfaces **2013**, *111*, 579. http://dx.doi.org/10.1016/j.colsurfb.2013.07.009

[29] Kondyurin A., Gan B.K., Bilek M.M.M., Mizuno K., McKenzie D.R.: *Nuclear Instruments and Methods in Physics, Research Section B* **2006**, *251*, 413. http://dx.doi.org/10.1016/j.nimb.2006.06.027

Received 18 III 2014.

Instytut Inżynierii Materiałowej
Zachodniopomorskiego Uniwersytetu Technologicznego w Szczecinie

zaprasza do udziału

w VI Krajowej Konferencji
**"Nowe materiały – nowe technologie
w przemyśle okrętowym i maszynowym"**

Międzyzdroje – Ystad, 24—28 maj 2015 r.

www.nmnt.zut.edu.pl