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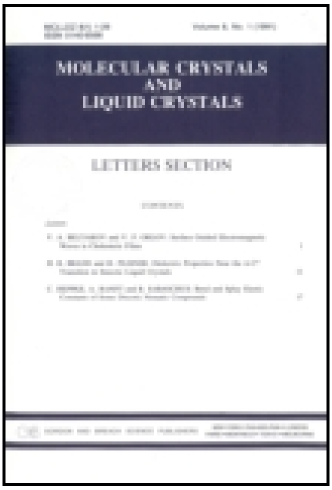

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The Influence of UV-Irradiation or Plasma on Ionomer Surfaces

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Films of polystyrene and styrene ionomers with various content of sodium acrylate were studied in terms of changes in surface properties after UV-irradiation or plasma action. The alterations were examined by contact angle measurements and FTIR-ATR spectroscopy.

Both UV-irradiation (3h and 4h) and the plasma action (30s) induced a growth in the sample hydrophilicity owing to appearance of polar groups on the surfaces. More effective alterations of surface polarity were caused by the plasma action. However, these changes were reversible, contrary to the results caused by UV-irradiation. Photons can penetrate deeper into the sample rendering the changes more durable.

Keywords styrene ionomers; UV-irradiation; air-plasma treatment

Introduction

Because of their poor adhesion properties, polymers are subject to the action of the modifying agents, which transform their surfaces from hydrophobic into hydrophilic. Among the variety of techniques deployed to enhance hydrophilicity and surface free energy of polymers one can distinguish plasma treatment and UV-irradiation [1–4].

Low-temperature plasma consists of neutrals, ions, atoms, radicals, electrons and photons. Some of them may exist in ground or excited state. Photons and electrons as the species having high energy can initiate processes (oxidation, cross-linking) in polymer surface by breaking chemical bonds and producing polymer radicals, which in turn can react with radicals from plasma and create new functionalities by embedding new oxygen-containing groups into the polymer surfaces. The active species coming from plasma are responsible for the changes in polymer surface [5,6,2]. Moreover, surface oxidation is accompanied by etching and cleaning [5,6,2].

High energy UV-irradiation causes oxidation, degradation and cross-linking of polymers. This technique is based on selective processes of absorption of UV-light by photoreactive groups, which are able to absorb radiation of suitable wavelength [2].

The aim of this work was to compare the influence of the plasma treatment or UV-irradiation on surface properties of styrene-b-sodium acrylate ionomers, derived from emulsion copolymers, containing varied amount of sodium salt. Additionally, durability of these alterations was the subject of interest.

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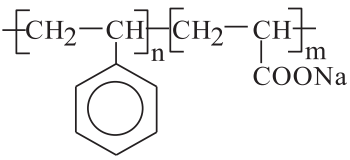

Figure 1. Structure of poly(styrene-co-sodium acrylate).

Ionomers are polymers consisting of hydrophobic hydrocarbon backbone along which ionic side groups are randomly distributed. Interactions between ionic groups and counterions lead to the creation of aggregates called multiplets, in which only firmly packed ionic pairs are present. With increasing ion content in ionomers, larger aggregates, called clusters, appear. Clusters contain multiplets as well as polymer chains and they constitute separate phase. Interactions between ionic groups in multiplets lead to the physical cross-linking improving mechanical properties and enhancing glass transition temperature [7–9].

Experimental

Copolymers of styrene (S) with acrylic acid (AA) were obtained by emulsion polymerization which was performed in the following conditions: weight ratio of water to the sum of monomers was 2:1, temperature 80°C, potassium persulfate as an initiator (6 mmol/dm^3), 3% (w/w) of emulsifier [10]. It was pointed out that such copolymers had partially random and block structure [11].

Ionomers (Fig. 1) were acquired as a result of neutralisation of acid groups in copolymers with sodium hydroxide. 3–5% solutions of copolymers in benzene were titrated under nitrogen with a standard solution of sodium hydroxide in methanol (a mixture of benzene and methanol 9:1 (v/v) was used for copolymers containing about or above 5 mol% of acid).

Thin polymeric films were obtained by casting 2% (m/v) solutions in tetrahydrofuran onto the levelled glass plates. After solvent evaporation, films were dried to a constant weight at 50°C in vacuum. The film thickness was about 80 μm to 90 μm.

The polymeric films on microscopic glasses were placed in a quartz tube and then this tube was put into a plasma system, which is a home-made equipment. The apparatus was working at air pressure 4.5×10^{-2} mbar, current intensity 140 mA and frequency generator of 2860 MHz. Treatment time was 30s.

Irradiation was conducted with a low-pressure mercury-vapour lamp (TUV 30W, Philips, Holland) emitting light with a wavelength of 254 nm. The intensity of incident light, measured with electronic radiometer HD 9021 (Delta OHM, Italy), was 20.02 W/m^2.

Surface properties of the samples were analysed by contact angle (Θ) measurements using a DSA G10 goniometer (Krüss GmbH, Germany). A drop of water was placed onto a sample surface with microsyringe and the value of contact angle was calculated by the computer on the basis of the obtained image of the liquid drop. Measurements of contact angles were made for non-treated, treated and aged samples. The value of contact angle is average of ca. 8 measurements and the deviation from the average is within ±2 deg. All measurements were carried out at room temperature.

FTIR-ATR spectra of the samples were collected using FTIR Genesis II (Mattson, USA) spectrophotometer equipped with ATR (Pike Technologies, Inc.) containing ZnSe crystal.

Table 1. The values of water contact angle (deg) for polystyrene and styrene ionomers with various content (mol%) of sodium salts before, after UV-irradiation and after aging process. Minus "–" means immeasurable contact angle

	Water contact angle (deg)			
Sample	0 h	3 h	4 h	Aged 7 days after 3 h UV-irradiation
PS	80.8	73.3	49.0	57.0
S-b-ANa(3.7)	80.2	48.3	44.2	45.3
S-b-ANa(5.3)	69.1	44.2	33.9	39.8
S-b-ANa(9.7)	87.6	64.2	—	61.5
S-b-ANa(14.7)	55.6	35.0	—	30.3

The notation of samples is S-b-ANa (x), where x in brackets means the content of sodium acrylate (ANa) in ionomer in mol%, letter "b" means that the samples were obtained by emulsion copolymerization.

Results and Discussion

Table 1 contains the results of water contact angle measurements for the ionomers. Values of contact angles of non-irradiated samples decreased with increasing content of sodium ions in ionomers, which suggests that the more sodium salts were introduced into ionomer the more polar the surface was. It is acknowledged that different types of aggregates (multiplets, clusters and ionic pairs) can exist in ionomers and it is dependent on the amount of salts in them [7–9]. When the content of sodium acrylate rises, it is possible that smaller aggregates or ionic pairs may appear on the sample surface. Thus, higher surface hydrophilicity of the sample with 14.7 mol% of sodium ions may be related to a great number of aggregates. These aggregates might be placed not only beneath the surface but also on the surface. While, the ionomer with 9.7 mol% of sodium ions is the exception to the rule owing to its highest hydrophobicity. Probably, aggregates formed (their amount and the size) in this ionomer were capable of existing under the surface, making this surface hydrophobic.

Table 1 shows the changes in water contact angle of UV-irradiated samples as well. It is evident that short-wavelength irradiation caused a decrease in water contact angle, especially 4 h irradiation, which indicated an increase in surface polarity owing to the presence of polar groups on the surfaces as a consequence of photo-oxidation process. Ionomers with higher amount of sodium acrylate were more sensitive to UV-light. After 4h irradiation, the drop of water was very flat and contact angle was difficult to estimate. Probably the presence of acrylate groups makes the ionomers sensitive to UV-light because carbonyl groups are able to absorb UV-irradiation.

The samples were irradiated 3 h or 4 h and then they were aged under ambient conditions for one week. For 3 h samples the values of contact angles were slightly lower compared to those just after irradiation without aging, which suggests that photo-oxidation processes continued as a result of either atmospheric oxygen reacting with trapped polymer radicals or mechanical changes influencing subsequent photo-oxidative degradation processes. In the case of 4h samples, irradiation and then aging made water contact angle immeasurable.

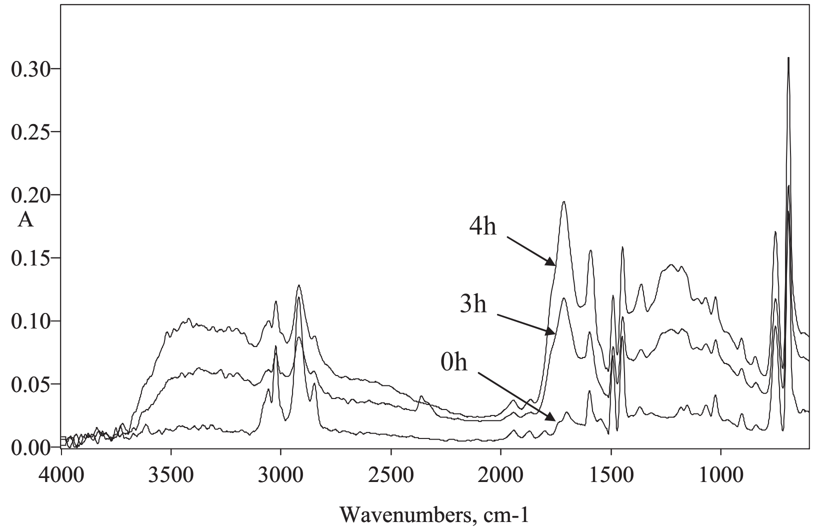

Figure 2. FTIR-ATR spectra of S-b-ANa(3.7) ionomer before (0h) and after (3h and 4h) UV-irradiation.

The FTIR-ATR spectra of UV-irradiated samples proved that new groups containing oxygen were formed on the sample surfaces studied. Figure 2 shows the example of infrared spectra of ionomer with 3 mol% of sodium ions. It is seen that absorbance increased in three regions: 3100–3700 cm^{-1} where absorption band comes from vibrations of OH/OOH groups; 1500–1850 cm^{-1} this absorption band is assigned to vibrations of C=O groups; vibrations of C—O groups in alcohols, phenols, ethers, carboxylic acids, esters are responsible for absorption in the 800–1400 cm^{-1} range [12].

Figure 3 depicts the dependence of water contact angle on the aging time. It can be observed that after 30s plasma action, the water contact angles decreased considerably for all

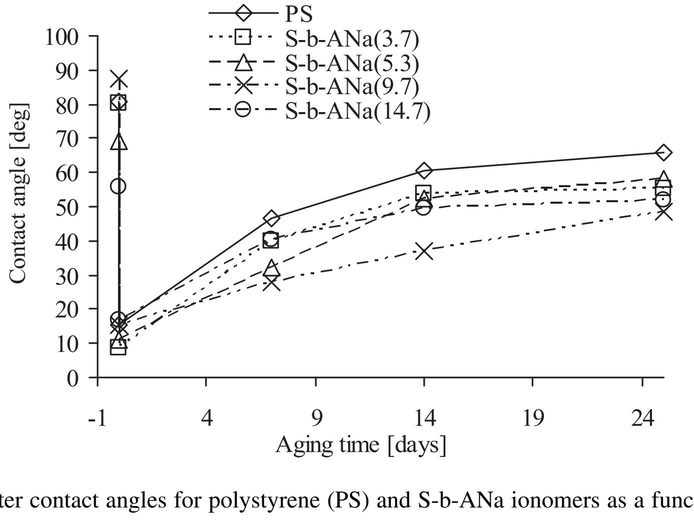

Figure 3. Water contact angles for polystyrene (PS) and S-b-ANa ionomers as a function of aging time.

samples acquiring about 10–15 deg. It indicates a significant increase in the surface polarity induced by the appearance of oxygen-containing groups on the top layer of the samples. The new functional groups may be formed from plasma species or may emerge from the inside of the samples as the ionomers based on styrene-acrylic acid copolymers contain polar groups [13,14]. However, no changes in FTIR-ATR spectra of the plasma-modified samples were detected.

After 7, 14 and 25 days of aging, water contact angle was measured for the plasma-treated samples (each time it was a new sample). It turned out that Θ became bigger after aging for specified period of time under ambient conditions. The phenomenon of regaining former surface properties by the samples is called hydrophobic recovery [14–16], where reorientation and migration of functional groups play an important role. The polar groups may rotate and hide beneath the surface reducing the hydrophilicity due to the hydrophobic surroundings [14–16,1]. Hydrophobic recovery behaviour was observed for both polystyrene and sodium ionomers. However, this process was effective in the case of ionomers containing 14.7 and 5.3 mol% of sodium acrylate, for which the contact angle values after 14 days of aging were close to those before the plasma treatment. These ionomers had the most hydrophilic surfaces before the plasma treatment. The slowest hydrophobic recovery was observed for ionomer with 9.7 mol% of sodium ions, whose surface was the most hydrophobic in the beginning.

In earlier works it was ascertained that hydrophobic recovery was much slower for ionomers than for non-ionic polymers [13,14] because of the presence of multiplets, which render the mobility of macrochains around them limited. Thus, the newly formed groups on the surface could not have entered beneath the surface. It might be also true for S-b-ANa ionomer with 9.7 mol% of sodium ions. In the case of ionomers with 14.7 and 5.3 mol% of sodium ions the initial higher hydrophilicity of the surfaces suggested that aggregates were on and under the surface, so there were no major hindrances making entrance of functional groups difficult. However, the conditions of the experiment in above-mentioned works and conditions of this experiment were different.

Air-plasma induced more effective changes in polarity of sample surfaces compared to short-wavelength irradiation [2,3]. However, the alterations of top layers of plasma-treated samples were partially reversible in contrast to UV-irradiated samples, for which the changes were durable and secondary reactions probably took place [2,3].

Photo-oxidation reactions occur in deeper layers (in the order of a few μm), however, air-plasma causes changes only in a very thin surface layer about a few nm [3,4,7]. Thus, permanence of changes may be related to a depth where they occurred. Contact angle measurements provide information to a depth of about 1 nm [5] and FTIR-ATR spectroscopy detects information at a depth of about 1 μm [1]. It might be the reason why oxygen-containing products in the surface layer of the plasma–treated samples cannot be detected by FTIR-ATR method.

Conclusions

Surface hydrophilicity of styrene-b-sodium acrylate ionomers depended on the content of salts in a sample. Ionomer with 9.7 mol% of sodium ions had the most hydrophobic surface, but ionomer with 14.3 mol% of salt had the most hydrophilic surface. As a consequence of high amount of ionic groups in a sample, some of smaller aggregates or ionic pairs may have been placed on the surface.

UV-irradiation caused an increase in surface polarity as a result of photo-oxidation reactions. Ionomers with higher content of sodium ions were more sensitive to UV-light than ionomers with smaller amount of salts probably due to a great number of carboxylate groups, which were capable of absorbing UV-irradiation. The alterations of UV-irradiated samples were durable.

The plasma treatment (30s) caused more considerable changes in hydrophilicity of samples compared to UV-light. However, the aging effect related to the reorientation of polar groups was observed.

Modification with plasma occurs in a thinner layer compared to the depth of modification with UV-irradiation, which may explain the permanency of changes in irradiated samples because alterations of deeper layers can reduce probability of hydrophobic recovery.

References

[1] Chan, C.-M., Ko, T.-M., & Hiraoka, H. (1996). *Surf. Sci. Reports*, *24*, 1.
[2] Kessler, F., Kühk, S., Radtke C., & Weibel, D. E. (2013). *Polym. Int.*, *63*, 310.
[3] Barish, J. A., & Godard, J. M. (2011). *J. Appl. Polym. Sci.*, *120*, 2863.
[4] Onyiriuka, E. C. (1993). *J. Appl. Polym. Sci.*, *47*, 2187.
[5] Żenkiewicz, M. (2000). *Adhesion and modification of outer layer of high-molecular plastics*, WNT: Warsaw, Poland.
[6] Oehrlein, G. S., Phaneuf, R. J., & Graves, D. B. (2011). *J. Vac. Sci. Technol. B*, *29*, 010801–1.
[7] Eisenberg, A., Hird, B., & Moore, R. B. (1990). *Macromolecules*, *23*, 4098.
[8] Capek, I. (2004). *Adv. Colloid Interface Sci.*, *112*, 1.
[9] Capek, I. (2005). *Adv. Colloid Interface Sci.*, *118*, 73.
[10] Suchocka-Gałaś, K.. & Wojtczak, Z. (1982). *Polimery*, *27*, 340.
[11] Brown, C. W., & Taylor, G. A. (1969). *Appl. Polym. Sci.*, *13*, 629.
[12] Zieliński, W., & Rajca, A. (1995). *Spectroscopic methods and their application to identification of organic compounds*, WNT: Warsaw, Poland.
[13] Lim, H., Lee, Y., Han, S., Kim, Y., Song, J.-M., & Kim, J.-S. (2003). *J. Polym. Sci. Part B: Polym. Phys.*, *41*, 1791.
[14] Lee, Y., Han, S., Kwon, M.-H., Lim, H., Kim, Y.-S., Chun, H., & Kim, J.-S. (2003). *Appl. Surf. Sci.*, *875*, 203–204.
[15] Deshmukh, R. R., & Sherty, A. R. (2007). *J. Appl. Polym. Sci.*, *104*, 449.
[16] Han, S., Lee, Y., Kim, H., Kim, G., Lee, J., Yoon, J.-H., & Kim, G. (1997). *Surf. Coat. Technol.*, *93*, 261.
[17] Abbasian, A., Ghaffarian, S. R., Mohammadi, N., Fallahi, D. (2004). *J. Appl. Polym. Sci.*, *93*, 1972.
[18] Hopkins, J., Wheale S. H., & Badyal, P. S. (1996). *J. Phys. Chem.*, *10*, 14062.