ISSN 1392–1320 MATERIALS SCIENCE (MEDŽIAGOTYRA). Vol. 18, No. 2. 2012

Plasma Surface Modification of Commercial SBS Rubbers for Enhanced Adhesive Bonding

Iwona KRAWCZYK-KŁYS [1], **Przemysław MAKOWSKI** [2], **Justyna WÓJCIK** [1], **Jacek TYCZKOWSKI** [2*]

[1] *Leather Research Institute, Zgierska 73, 91-462 Lodz, Poland*
[2] *Division of Molecular Engineering, Faculty of Process and Environmental Engineering, Lodz University of Technology, Wolczanska 213, 90-924 Lodz, Poland*

http://dx.doi.org/10.5755/j01.ms.18.2.1914

Received 14 September 2011; accepted 17 October 2011

An attempt to replace a wet chemical surface modification of styrene-butadiene elastomers (SBS), improving their adhesion to polyurethane dispersion adhesives, with a clean low-pressure plasma technique was undertaken. Investigations were performed on commercial SBS rubbers. The plasma was generated by an RF discharge (13.56 MHz, plate electrode reactor) in pure argon (Ar). The rubbers surfaces were investigated by 180°-peel tests and scanning electron microscopy (SEM). The presented results indicate that the plasma treatment is a very promising method of improving the adhesion properties of commercial SBS rubbers elastomers and it should replace the wet chemical methods in industry.

Keywords: styrene-butadiene elastomers, polyurethane dispersion adhesives, plasma surface treatment, peel test, scanning electron microscopy.

1. INTRODUCTION

Among various methods, used to improve adhesive properties of polymer surfaces, such as roughening, washing in solvents, ultrasonic cleaning, wet chemical treatment (wet chlorination) [1 – 3], there is one that deserves special attention, due to its wide possibilities of introducing changes to the surface and its 'clean' procedure, which is the surface treatment by cold non-equilibrium plasma [4, 5]. Glow discharge generated in an environment of reduced pressure is the most widely used method of producing such plasma. The surface treatment of polymers can be carried out both in inert gas plasmas (e.g. Ar, He) and chemically reactive plasmas (e.g. O_2, CO_2, N_2O, NH_3). The treatment process by inert plasmas consists in changing the chemical structure of the polymer surface by bombarding it with chemically inert ions, which are the molecules that do not participate in the chemical processes. This operation leads mainly to the preferential etching of the polymer surface by removing certain atoms or their groups and creating a large amount of chemically active centers such as free radicals. Introduction of chemically reactive gas to the plasma causes, in turn, the formation of new functional groups on the surface of modified polymer, such as hydroxyl, carbonyl, amino, halogen groups [6].

The use of plasma treatment provides a very wide range of possibilities for the surface modification of conventional polymers. However, it is necessary to add that despite the extensive research on this subject, the method of plasma surface modification of polymers is not a standard method, in which there would be already established principles of selecting the type and operating conditions of plasma treatment process to achieve the assumed properties of the surface. Chemical reactions on the polymer surface under the influence of plasma are very complex processes, requiring detailed studies to determine the direction of their course and to optimize conditions of treatment for every particular case of selected polymer and the type of plasma. The problem becomes even more complicated in a situation when there are other ingredients added to polymer, as it is the case with rubber compounds.

Even the polymer itself is a copolymer consisting of different polymer blocks, apart from that it is blended with carbon black, silica, zinc oxide, etc. Although such systems (rubbers) have already been the subject of research for some time [7 – 10], we are still far from a thorough knowledge of the molecular structure change mechanisms, and thus – the properties of the rubber surface under the influence of plasma.

For some time, there is a visible interest in the subject of plasma surface modification of polymers to improve their adhesion properties [11 – 13]. Recently much attention has been paid to the use of cold plasma treatment to improve the ability of bonding butadiene-styrene elastomers (SBS) [5, 7, 8, 10, 14 – 17]. However, in large part, these papers concerned the model copolymers, and research on rubber compounds was only preliminary.

In addition, to adequate treatment of rubber surface, selection of a suitable adhesive has significant impact on connection quality of rubber with other material. In the case of rubber compounds formed on a base of SBS copolymers the most commonly used adhesive is the polyurethane solvent adhesive [18]. After applying the glue on the bonding surfaces, prior to contacting them, it

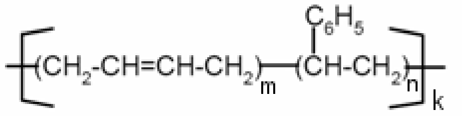
---

*Corresponding author. Tel.: +48-42-6313723; fax.: +48-42-6365663.
E-mail address: *jatyczko@wipos.p.lodz.pl* (J. Tyczkowski)

requires to evaporate the organic solvent. This is the main reason why substitutes for the organic solvent adhesives are intensively searched. The alternative is a polyurethane adhesive in the form of an aqueous emulsion. Aqueous polyurethane dispersions seem to be quite promising replacement for solvent adhesives [19]. One of the major drawbacks, however, is the decline of bond strength observed in some cases after hydrothermal aging, which causes risk of such connections separation during their utilization. Although this problem has already been paid some attention [21], yet it still remains open and requires further studies, particularly in specific cases of polyurethane dispersions use. Generally, our knowledge on the molecular mechanism of bonding with use of polyurethane solvent adhesives is much greater than in the case of the use of aqueous polyurethane emulsions [1, 21].

2. EXPERIMENTAL

The study was conducted on commonly used, vulcanized industrial rubber based on styrene-butadiene elastomer (SBS). The general formula of the main chemicals chain of SBS presents Figure 1.



$$-\left[(CH_2\text{-}CH{=}CH\text{-}CH_2)_m\text{-}(\overset{C_6H_5}{\overset{|}{C}}H\text{-}CH_2)_n\right]_k-$$

Fig. 1. The general chemical formula of the main chain of styrene-butadiene elastomer (SBS) used in our investigations

The rubber was supplied by the manufacturer of rubber compounds "Kwarciak" (Poland) Ltd. The detailed composition of the rubber is contained in Table 1.

Table 1. The composition of the investigated rubber made on the basis of styrene-butadiene elastomer

Component	Content [parts of weight]
KER 1502 styrene-butadiene rubber (22 %–25 % styrene)	70
KER N-29 acrylonitrile-butadiene rubber	30
Carbex-330 filler – carbon black	50
Sulfur	2.5
accelerator M 2-mercaptobenzothiazole	1

Samples for peel tests were cut from larger sheets provided by the manufacturer. Dimensions of a single item to be treated were as follows: 14 mm wide, 70 mm long and 4 mm thick.

Plasma treatments were carried out in a two-electrode plasma reactor working at radio frequency (13.56 MHz). Carbon dioxide (CO_2, 99.9 %, Linde Gas Poland), and argon (Ar, 99.9 %, Air Liquid) were used as precursors of the glow discharge. Typical gas flow (Ar, CO_2) through the reactor chamber was 7.5 sccm, and set initial pressure was 13 Pa. Glow discharge power was 50 W. Treatment time ranged from 15 s to 15 min.

In order to determine the surface adhesion of the rubber to dispersive polyurethane adhesive, 180°-peel tests for adhesive-bonded joints were carried out. Such joins were made of the rubber samples before and after plasma modification and standard strips of leather (tanned with dichromate, uncolored). The polyurethane dispersive adhesive “Bonidur US-100” from the Chemical Establishment “Bochem” LLC was spread on each surface to be glued and it was dried for 15 minutes. The dry adhesive layer on the rubber was reactivated at temperature of 353 K and the surfaces were immediately contacted under pressure of 0.4 MPa for 10 s. Then the adhesive joints were conditioned at room conditions for 48 h. The above procedure for the preparation of samples for the peel test is consistent with the European Standard EN 1392:2006. The peel tests were performed using Instron 5566 measuring instrument (tear speed – 1.67×10^{-3} m/s).

To study surface topography and composition of SBS rubbers a scanning electron microscope FEI's Quanta 200 F model with X-Max EDS-Detector (EDX) from Oxford Instruments was used. All measurements in the SEM were carried out under water vapor atmosphere of 100 Pa. Composition of rubbers for about 100 nm penetration depth of electrons beam was studied, using 3.5 keV of electrons energy. However topography micrographs were obtained using 20 keV of electrons energy.

In order to compare the wet chemical treatment and the plasma treatment, samples with chemically chlorinated surface were prepared. The process was carried out by immersing the samples for 30 s in a chlorination solution (2 % trichlorocyanuric acid (TCl) in butanol). Then, the samples were left for 1 h and after this time they were immersed in an aqueous solution of ethanol (25 %) for 30 s to stop the chlorination process. Finally, the samples were dried at room temperature in air for several hours.

3. RESULTS AND DISCUSSION

Studies of the SBS rubber surface modified by Ar and CO_2 plasmas were focused on optimizing the plasma process parameters in the direction of maximum improvement of adhesive bonding of these surfaces. Two process parameters have been discussed: the power of glow discharge and duration of plasma treatment. Half of the tested samples were subjected to mechanical roughening before plasma modification. Some roughened and unroughened samples, in turn, were washed with acetone before treatment. Dependences of the peel strength of the adhesive joints versus Ar plasma treatment time for roughened and unroughened samples are shown in Figure 2 and Figure 3, respectively.

As one can see, in the case of not roughened samples without acetone washing, the Ar plasma treatment almost five times improves the peel strength of the joint, in comparison to unmodified samples and three times in comparison to samples modified with the wet chemical treatment. About twofold increase is noticeable already for 5 min time of the plasma treatment. Maximum strength is achieved for 10 min of the modification, followed by its rapid decline.

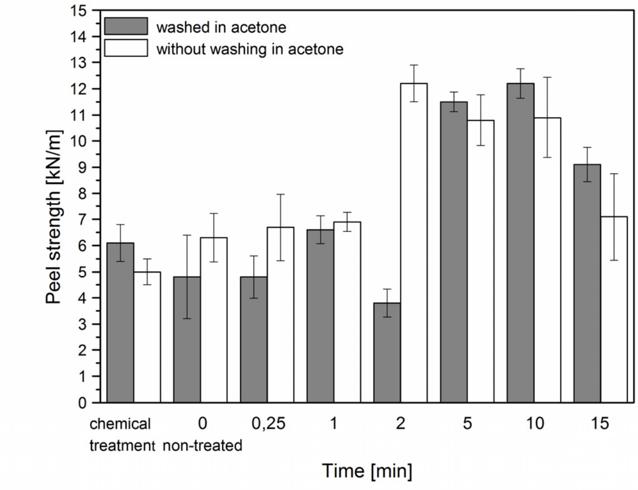


Fig. 2. Joint peel-strength for Ar plasma-modified SBS rubber, roughened, washed and without washing in acetone, as a function of the treatment time (discharge power – 50 W)

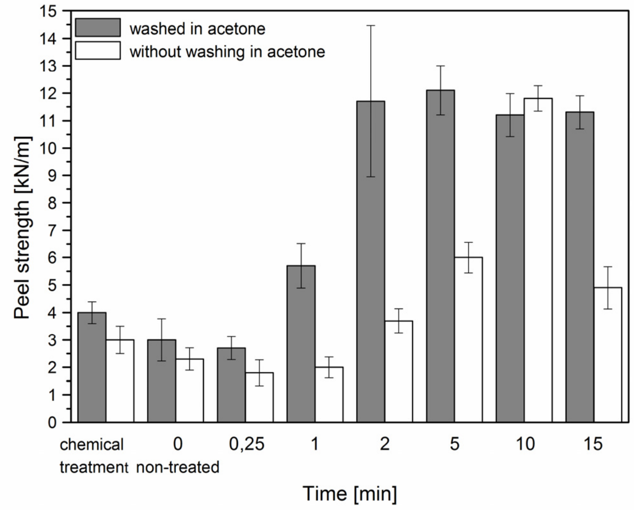


Fig. 3. Joint peel-strength for Ar plasma-modified SBS rubber, not roughened, washed and without washing in acetone, as a function of the treatment time (discharge power – 50 W)

As one can see, in the case of not roughened samples without acetone washing, the Ar plasma treatment almost five times improves the peel strength of the joint, in comparison to unmodified samples and three times in comparison to samples modified with the wet chemical treatment. About twofold increase is noticeable already for 5 min time of the plasma treatment. Maximum strength is achieved for 10 min of the modification, followed by its rapid decline.

An analysis of the joint peel strength for unroughened, washed with acetone, SBS rubber samples modified by Ar plasma also shows the significant improvement in comparison to untreated and wet chlorinated samples. Additionally, slight increase of the peel strength is noticeable for all samples when compared with analogical not roughened samples without washing. Acetone cleans the surface from impurities, which increases the surface energy and leads to increased thermodynamic adhesion. Maximum strength is achieved for 2 min – 10 min of the plasma modification, and for longer treatment it rapid decline. The achieved maximum value is almost four times greater than those obtained for unmodified samples and almost tripled in comparison with samples treated by the wet chlorination.

Roughening, similarly to washing in acetone, improves values of the peeling forces for samples unmodified and modified in Ar plasma, as well as wet chlorinated ones. An increase of surface roughness, leading to development of contact with the adhesive, significantly affects the growth of mechanical adhesion. For surfaces not treated with plasma, the peel strength increase is almost doubled in comparison to not roughened samples. The Ar plasma treatment, similarly as for not roughened samples influences on an increase of the peel strength, and the maximum values are very similar for these both cases. They are also achieved in a similar duration of treatment (2 min – 10 min). Longer time of the modification causes quite sharp decline in the strength of joints.

In general, the Ar plasma treatment, in power 50 W, gives a few times higher values of the peel strength in comparison to unmodified samples. Regardless of the preparation method of the SBS rubber samples before the plasma treatment (roughened, not roughened, washed in acetone, without washing), similar maximum values of the joint peel strength were achieved. This is a very important result from the point of view of the probable future introduction of this plasma method to industry. It will enable simplification of the current technological process. Mechanical roughening, washing in organic solvents and wet chlorination will be replacing only with the single plasma treatment process. However, further, more detailed studies are necessary.

As far as the Ar plasma treatment mechanism is concerned, it should be noted that the plasma generates radical centers, which create hydroxyl and carbonyl groups after contacted with air. According to our previous investigations [21], in that case the peel strength is proportional to the concentration of these groups, which in turn depends on the time and the power of the glow discharge. Longer plasma treatment causes a decrease in the concentration of the groups, which is manifested as a peel strength maximum. The maximum values of the peel strength observed in the current investigations for the SBS rubber samples can indicate that in this case also the chemical adhesion takes place.

Generally, in the case of samples modified by carbon dioxide (CO_2) plasma, an increase in the peel strength for unroughened and unwashed rubbers was observed (Figure 4) in comparison to unmodified samples and samples subjected to the wet chemical treatment, for all times of the treatment in practice. The exception is time of 15 s. With an increase in the treatment time, the peel strength increases, reaching its maximum for 10 min – 15 min with a value about one-and-a-half times higher than those for untreated samples. The washing of the unroughened SBS samples with acetone, which were then modified by CO_2 plasma (Figure 4), improves the joint strength in comparison to untreated samples and chemically chlorinated ones. Additionally, an increase in the strength values is visible for all samples when compared with analogical samples without washing (Figure 4). Acetone used in the washing process cleans the rubber surface, which increases the surface energy and leads to increased thermodynamic adhesion. The maximum value of the strength is achieved for modification time of about 10 min, and after longer treatment time there is a decrease in this value. Achieved maximum value is over three times higher than those for untreated samples and chemically chlorinated ones.

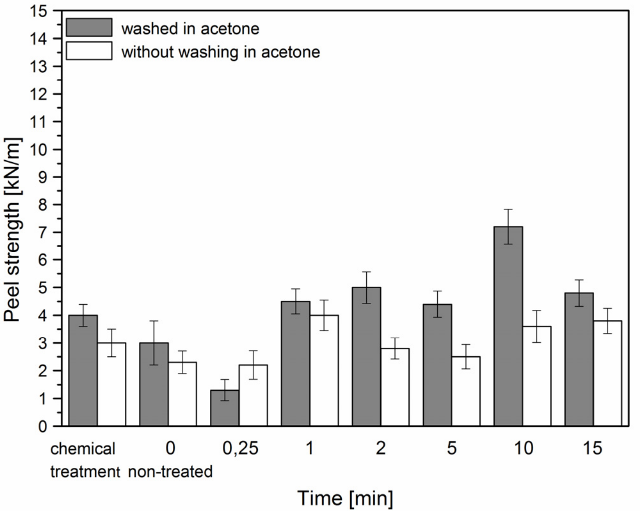


Fig. 4. Joint peel strength for CO_2 plasma-modified SBR, not roughened, washed and without washing in acetone, as a function of modification time (discharge power – 50 W)

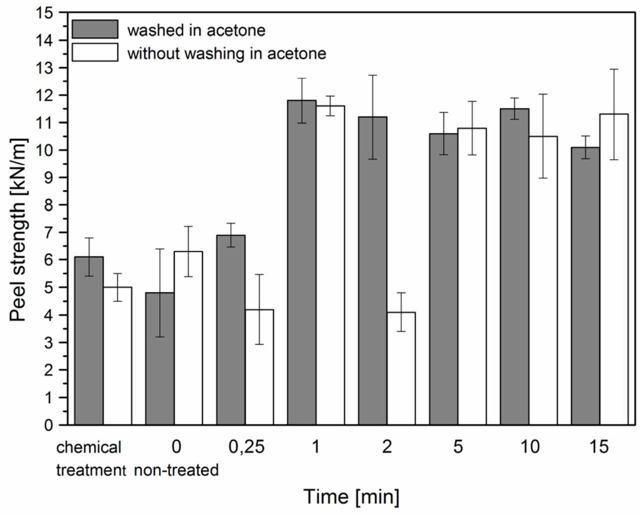
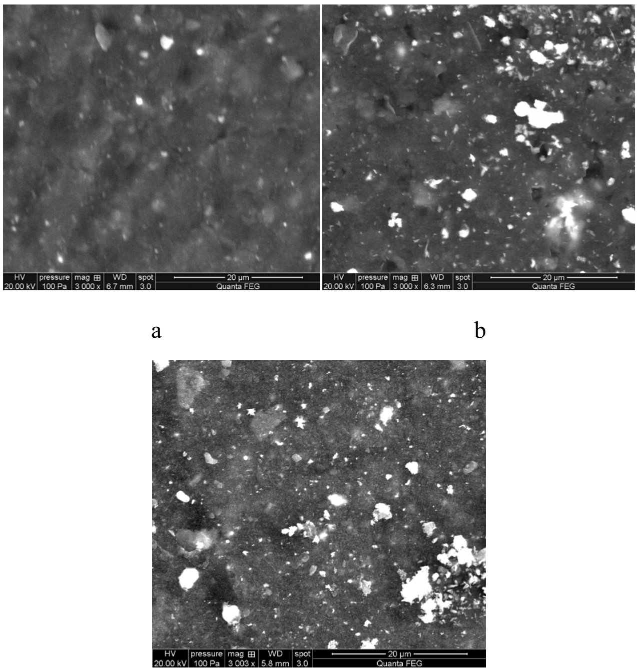


Fig. 5. Joint peel strength for CO_2 plasma-modified SBS rubber, roughened, washed and without washing in acetone, as a function of the treatment time (discharge power – 50 W)

The surface roughening improves values of the peel strength for untreated, chemically chlorinated and modified by CO_2 plasma samples (Figure 5). The increase of surface roughness, and due to this development of contact with the adhesive, influences significantly on mechanical adhesion increase. For samples not modified in plasma, the increase of the peel strength is almost twice bigger, when compared to unroughened samples. The CO_2 plasma treatment of roughened rubbers (Figure 5), similarly as for unroughened and washed in acetone rubbers (Figure 4), influences on increase of the peel strength. The maximum value is in this case much higher than for unroughened rubbers and treated by CO_2 plasma. It is achieved for 5 min – 15 min time of treatment.

Comparing the peel strength values of roughened samples without washing to roughened samples with washing in acetone, their clear improvement is visible, especially for short times of the treatment. As visible on Figure 5, plasma treatment of roughened rubbers, washed in acetone, improves the joint strength for all times of process, in comparison to unmodified samples and samples subjected to wet chemical treatment. Maximum values are similar to values achieved for roughened samples without washing. Additionally, they are much higher than for unroughened rubbers, without washing and washed in acetone (Figure 4). Similarly as in the earlier cases, in the moment of exceeding the maximum, the strength decreases together with increase of process time.



a b

c

Fig. 6. Photo of styrene-butadiene rubber (SBR) samples: a – non-treated surface, b – surface only washed in acetone, c – surface only treated in Ar plasma with power 50 W for 10 min. Magnification 3000×

Treatment in CO_2 plasma with power of 50 W gives several times higher peel strength values in comparison to unmodified samples and samples subjected to wet chemical treatment. Maximum values are achieved for treatment times of 5 min – 10 min. Contact of CO_2 plasma with the rubber surface directly initiates the creation of functional groups, including carbonyl (>C=O) and hydroxyl (–OH) groups. With prolonged exposure to plasma, they are blocked and transformed into inactive oxygen bridges. The density of active groups starts to drop and the surface undergoes crosslinking. The strength of adhesive joints depends largely on the surface density of these functionalities. Their disappearance is observed for treatment times longer than 10 min. The sharp increase in the values of peel strength of joint in the initial stage of modification is a result of the formation of chemical bonds between the surface of SBS rubber and the polyurethane adhesive. The appearance of the maximum strength values of joints reflects the highest density of active groups [22].

Using electron scanning microscopy (SEM), examination of the surface topography of SBS rubber samples was performed. The micrographs were obtained for three types of unroughened samples: without any treatment, untreated with plasma but washed in acetone, and treated in Ar plasma for 10 min at power of 50 W (for this type of plasma and treatment parameters, the peel strength value was very high).

For the raw surface (without any treatment), numerous slight depressions (darker areas) and elevations (brighter areas) are visible (Figure 6, a). Their average size varies from a few to several μm. After acetone washing, there is sudden increase of roughness (Figure 6, b). Number of hills and hollows is growing rapidly with a decrease in their size (on average, they are from a few tenths to a few μm). The Ar plasma treatment also causes development of the rubber surface (Figure 6, c), as in the case of the washing with acetone (Figure 6, b). In addition, the nanoroughness rapidly increases. Its average size is a few hundred nm. This means that Ar plasma consumes and purifies the surface of loosely adherent layers, causing the formation of large quantities of nanoroughness. By increasing the number of depressions, into which the adhesive may penetrate, the role of mechanical adhesion is increasing in creating the adhesive-polymer joints strength. The increase in surface roughness can also affect the increase in density of functional groups.

Using the EDX method, the surface elemental composition of SBS rubber samples was determined. The investigations were performed on the samples without any treatment, washed with acetone, and modified by Ar plasma for 10 min (50 W). Mass content of carbon in all samples is similar and ranges from 81.88 % for untreated rubbers to 83.65 % for plasma treated rubbers. However, the amount of oxygen decreases from 14.82 % for samples not treated to 10.29 % for the samples treated with the plasma. This means that the plasma cleans the surface of strongly adsorbed water molecules, which cannot be achieved by washing with acetone. Increase of the mass content of other elements, such as Si, S, Zn, Mo after the plasma treatment, indicates the etching effect that removes organic compounds and pollutions from the surface uncovering the rubber bulk.

4. CONCLUSIONS

The obtained results show that plasma treatment of commercial rubber of SBS type, conducted in plasma generated in CO_2 and Ar, for the proper process parameters, causes a drastic increase in the peel strength of joints created with the use of polyurethane dispersion adhesives. This increase can exceed several times the value of the joint strength for the rubber not treated in plasmas. Particularly high values are obtained using argon plasma. The results indicate the possibility of using low-temperature plasma as a clean method of activating the surface of SBS rubber in the process of bonding with the polyurethane dispersion adhesives. This is a new, important result, crucial from the point of view of seeking environmentally friendly technology in the area of adhesive-bonding SBS rubbers.

Acknowledgments

This work was supported by the Polish Ministry of Science and High Education, which funded the project N N507 612938. The authors thank to MSc. Mariusz Domański for the technical assistance.

REFERENCES

1. **Patrie, E. M.** Handbook of Adhesives and Sealants, McGraw-Hill, New York, 2000.

2. **Salamone, J. C. (Ed.).** Polymeric Materials Encyclopedia, CRC, Boca Raton, 1996.

3. **Martin-Martinez, J. M., Fernández-Garcia, J. C., Huerta, F., Orgilés-Barceló, A. C.** Effect of Different Surface Modifications on the Adhesion of Vulcanized Styrene-butadiene Rubber *Rubber Chemistry & Technology* 64 1991: pp: 510 – 521.

4. **Strobel, M., Lyons, C. S., Mittal, K. L.** (Eds) Plasma Surface Modification of Polymers – Relevance to Adhesion, VSP, Utrecht, 1994.

5. **Tyczkowski, J., Krawczyk, I., Woźniak, B.** Plasma Surface Modification of Styrene-butadiene Elastomers for Improved Adhesion In: **d'Agostino, R., Favia, P., Oehr, C., Werheimer, M. E.** (Eds) Plasma Processes and Polymers, Wiley-VCH, Weinheim, 2005: pp. 233 – 252. http://dx.doi.org/10.1002/3527605584.ch18

6. **Inagaki, N.** Plasma Surface Modification and Plasma Polymerization. Basel: Technomic, 1996.

7. **Pastor-Blas, M. M., Martin-Martinez, J. M., Dillard, J. G.** Surface Characterization of synthetic Vulcanized Rubber Treated with Oxygen Plasma *Surface and Interface Analysis* 26 1998: pp. 385 – 399.

8. **Ortiz-Magan, A. B., Pastor-Blas, M. M., Ferrandiz-Gomez, T. P., Morant-Zacares, C., Martin-Martinez, J. M.** Surface Modifications Produced by N_2 and O_2 RF Plasma Treatment on a Synthetic Vulcanized Styrene-Butadiene Rubber *Plasmas and Polymers* 6 2001: pp. 81 – 105. http://dx.doi.org/10.1023/A:1011352903775

9. **Park, S. J., Cho, K. S., Ryu, S. K.** Filler-elastomer Interactions: Influence of Oxygen Plasma Treatment on Surface and Mechanical Properties of Carbon Black / Rubber Composites *Carbon* 41 2003: pp. 1437 – 1442.

10. **Ortiz-Magan, A. B., Pastor-Blas, M. M.** Migration of Processing Oils of Thermoplastic Rubber Treated with RF Plasma *Plasma Chemistry and Plasma Processing* 2008: pp. 391 – 404. http://dx.doi.org/10.1007/s11090-008-9127-1

11. **Liston, E. M., Martinu, L., Wertheimer, M. R.** Plasma Surface Modification of Polymers for Improved Adhesion: a Critical Review In: **Strobel, M., Lyons, C. S., Mittal, K. L.** (Eds) Plasma Surface Modification of Polymers – Relevance to Adhesion, VSP, Utrecht, 1994: pp. 3 – 39.

12. **Friedrich, J., Kühn, G., Mix, R., Unger, W.** Formation of Plasma Polymer Layers with Functional Groups of Different Type and Density at Polymer Surfaces and their Interaction with Al Atom *Plasma Processes and Polymers* 1 2004: pp. 28 – 50.
13. **Cognar, J.** Some Recent Progress in Adhesion Technology and Science *Comptes Rendus Chimie* 9 2006: pp. 13 – 24.
14. **Ortiz-Magan, A. B., Pastor-Blas, M. M., Martın-Martınez, J. M.** Different Performance of Ar, O_2 and CO_2 RF Plasmas in the Adhesion of Thermoplastic Rubber to Polyurethane Adhesive. In: **d'Agostino, R., Favia, P., Oehr, C., Werheimer, M. E.** (Eds) Plasma Processes and Polymers. Weinheim: Wiley-VCH, 2005: pp. 177 – 192. http://dx.doi.org/10.1002/3527605584.ch14
15. **Tyczkowski, J., Krawczyk, I., Woźniak, B.** Plasma Chlorination of Elastomer Surfaces *Acta Agrophysica* 8 2002: pp. 231 – 238.
16. **Tyczkowski, J., Krawczyk, I., Woźniak, B.** Modification of Styrene–butadiene Rubber Surfaces by Plasma Chlorination *Surface and Coatings Technology* 174/175 2003: pp. 849 – 853.
17. **Krawczyk, I., Tyczkowski, J., Woźniak, B.** Improvement of Adhesive-bonding of Elastomers by Plasma Surface Modification *Polish Journal of Applied Chemistry* 49 2005: pp. 61 – 70.
18. **Dollhausen, M., Warrach, W.** Polyurethane Adhesives Technology *Adhesives Age* 25 1982: pp. 28 – 32.
19. **Julia, J.** Water Based PUR Dispersion for Adhesives and Coatings *Sympozjum UTECH-94 REF* 44 1994: pp. 1 – 8.
20. **Dormisch, J.** Polyisocyanate Crosslinkers for Agueous Polyurethane Dispersions *Adhesives Age* 2 1996: pp. 16 – 21.
21. **Wirpsza, Z.** Polyurethanes – Chemistry, Technology and Applications. E. Horwood, New York, 1993.
22. **Tyczkowski, J., Krawczyk-Kłys, I., Kuberski, S., Makowski, P.** Chemical Nature of Adhesion: Plasma Modified Styrene-butadiene Elastomer and Polyurethane Adhesive Joint *European Polymer Journal* 46 2010: pp.767 – 773.

Presented at the 13-th International Conference-School
"Advanced Materials and Technologies"
(August 27–31, 2011, Palanga, Lithuania)