

## PLASMA CHLORINATION OF ELASTOMER SURFACES

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**A b s t r a c t.** An attempt to replace a wet chemical chlorination (with halogenating agents in organic solutions) of the styrene-butadiene elastomer surfaces with a clean plasma technique has been undertaken. Plasma generated by an rf discharge (13.56 MHz, plate electrode reactor) in  $\text{CHCl}_3$  vapor or in a mixture of  $\text{CHCl}_3$  and oxygen was used. The elastomer surfaces were investigated by FTIR spectroscopy, contact angle measurements, and T-peel tests. It has been found that the  $\text{CHCl}_3$  plasma (without  $\text{O}_2$ ) generated at relatively low powers is an effective tool for the surface chlorination. This process, however, is possible only when the appropriate concentration of butadiene blocks there is in the styrene-butadiene block copolymers. For 69 wt. % of butadiene, the peel strengths of the plasma treated (with the discharge power of 10 W) is approx. 56 % higher than that for the material chemically chlorinated and approx. 3 times higher in comparison with the non-treated surface.

**K e y w o r d s:** plasma surface modification, chlorination, polymers, adhesion.

### INTRODUCTION

The plasma treatment enables the realization of various surface modifications by a much more clean, energy-saving and environmentally compatible way in comparison with the classical chemical methods. Today, the ecological condition of the world is an especially important problem and a lot of attention is paid to search for new processes giving guarantee of the environmental protection. In this paper an attempt to replace a wet chemical chlorination of the elastomer surfaces with a clean plasma technique is presented.

The strength and quality of the gluing of elastomers, such as styrene-butadiene rubbers, to other materials (e.g., artificial leather, textiles) are of major importance in the process of making a high quality shoe. It is obvious that the adhesive strength depends in great part on the chemical structure of the elastomer surface and, therefore, can be controlled by various treatments, such as abrasion, washing, and wet chemical modification. One of the common methods is the chemical chlorination of the surfaces by means of active halogen derivatives such as

trichloroisocyanuric acid (TCI) feeding in an organic solvent (e.g. butanone) [1-4]. However, both the vaporizing flammable solvent and educed gaseous chlorine are very toxic and hazardous substances for the environment. Furthermore, it has been established that for synthetic vulcanized styrene-butadiene rubbers, a minimum of 6 h is required to produce an adequate adhesive joint [4]. Recently, it has been suggested that the chlorination of elastomer surfaces could be performed by plasma treatment [5].

Modification of polymer surfaces by implantation of chlorine functionalities by plasma treatment has been already discussed in some papers [6-9]. It has been done with the purpose of an increase in hydrophylicity of the polymer surface. Although different plasmas have been used, such as  $\text{CF}_3\text{Cl}$ ,  $\text{CCl}_4$ ,  $\text{CHCl}_3$ , and different polymers have been treated (polypropylene, polybutadiene), in all these cases, it has been found that chlorine atoms are bonded to the surface structure.

In this paper, preliminary investigations of plasma chlorination processes performed on styrene-butadiene model elastomers are presented. The elastomer surfaces have been characterized by measurements of the peel test, surface energies, and IR spectroscopy.

## EXPERIMENTAL

Thermoplastic elastomer type radial styrene-butadiene block copolymers (Finaprene 435 and Finaprene 507), provided by Atofina S.A. (Belgium), were used in this work. A butadiene-to-styrene ratio was 69 to 31 wt% and 27 to 73 wt% for F435 and F507, respectively. The samples were obtained by injecting the copolymers into a heated mould at 420 K, where plates of 120 mm width and 150 mm length were formed. To further tests, the strips of 10 mm width and 75 mm length cutting from the plates were used.

The plasma treatment was carried out in a parallel plate reactor with a radio frequency (rf, 13.56 MHz) glow discharge. As chlorine precursor, trichloromethane ( $\text{CHCl}_3$ ) was used. This compound was supplied to the reactor as a pure agent or in a mixture with oxygen. The reactive gases were in a flow through the reactor. A typical flow rate of the pure  $\text{CHCl}_3$  was 3.2 sccm whereas for the mixture it was 9.2 and 5.0 sccm for  $\text{CHCl}_3$  and  $\text{O}_2$ , respectively. The oxygen addition was aimed at the prevention against a presumable thin film deposition and also at the further modification of the surface by the formation of hydroxyl, carbonyl, and carboxylic acid groups [10]. An initial pressure in the reactor chamber of approx. 13 Pa was maintained in the whole study. The power of glow discharge was changed from 10 to 80 W. The plasma treatment of the samples lasted 300 s.

To compare the plasma treatment and the wet chemical modification, the samples were subjected to the "conventional" chlorination. This process was

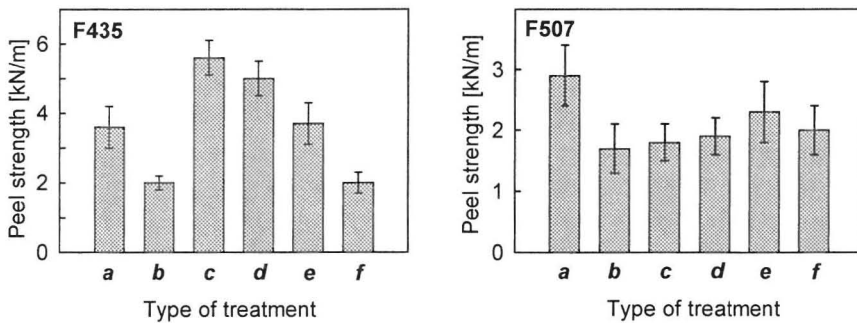
performed by immersion of the samples for 30 s in the chlorination solution (2 wt % of trichloroisocyanuric acid (TCI) in propanone). The chlorination time was 1 h and then the samples were immersed in an aqueous solution of ethanol (25 wt %) for 30 s to stop the chlorination process. Finally, the samples were dried at room temperature in the open air for a few hours.

The sample surfaces were characterized using contact angle measurements (water, glycerine and  $\alpha$ -bromonaphthalene, 298 K) and Fourier transform infrared (FTIR) spectroscopy. A NRL model 100 Contact Angle Goniometer (Rame-Hart) equipped with a digital camera and a programmable system to calculate the surface free energy was utilized for the contact angle records. FTIR spectra were recorded using a Bio-Rad model 175C spectrometer equipped with an IRS microscopy system (Harrick Scientific), working in a reflection mode. Signal accumulation from 20 scans was taken with the resolution of  $4\text{ cm}^{-1}$ .

To determine the adhesion strength of the elastomer surfaces, T-peel tests were carried out. Adhesive joints were made using the elastomer samples with the surface mechanically roughed before the modifying treatments and strips of a standard leather (box cow, chrome tanned, non pigmented). The one-component solvent-born polyurethane adhesive, based on heksandiol, was spread on each adherend and dried for 15 minutes. The dry adhesive film on the elastomer was reactivated at 353 K and the surfaces were placed in contact immediately under a pressure of 0.4 MPa for 10 sec. Then, the adhesive joints were conditioned for 48 h at room conditions. The T-peel strength measurements were performed using an Instron 5566 test instrument (peeling rate =  $1.67 \times 10^{-3}$  m/s).

## RESULTS AND DISCUSSION

Figure 1 presents results of the T-peel test for the F435 and F507 elastomers. The samples were treated by plasma generated in the pure  $\text{CHCl}_3$  vapor as well as in the mixture of  $\text{CHCl}_3$  and oxygen. The results are shown for two extreme values of the applied power, namely 10 W and 80 W. For comparison, T-peel test results for non-treated samples and chemically modified by TCI are also shown in the figure.



**Fig. 1.** Measurements of the T-peel strength for F435 and F507 elastomers after various types of the surface treatment: *a* – TCl treated; *b* – non-treated; *c* – plasma  $\text{CHCl}_3$ , 10W; *d* – plasma  $\text{CHCl}_3$ , 80W; *e* – plasma  $\text{CHCl}_3/\text{O}_2$ , 10W; *f* – plasma  $\text{CHCl}_3/\text{O}_2$ , 80W.

As one can see, the plasma treatment can evidently improve the peel strength compared to the untreated surface in the case of the F435 elastomer. When the pure  $\text{CHCl}_3$  vapor is used, the peel strength is also higher (approx. 56%) than that for the samples treated by TCl. The use of oxygen in the reactive mixture deteriorates the adhesion properties of the treated surfaces, although the low power supplied to the plasma reactor gives the peel strength of a similar value to that measured for the TCl treated samples. It is striking that for the low discharge power, the better peel strength of adhesive joints is obtained. We observe such a behavior both for the plasma treatment by pure  $\text{CHCl}_3$  and also when the  $\text{CHCl}_3/\text{O}_2$  mixture is used.

On the other hand, in the case of the F507 elastomer, the used plasma treatment gives the peel strength of the same or only a bit higher value in comparison with the non-treated samples, but evidently lower than that obtained after the wet chemical process. Comparing the results for F435 and F507, one should take into account differences in the chemical constitution of these copolymers. The former copolymer contains 69 wt % of butadiene in the structure whereas only 27 wt % of this monomer is incorporated into the latter material. The role of the surface chlorination consists in the chemical bonding of chlorine atoms to the surface and then their participation in the crosslinking between the surface and the adhesive. The efficiency of this process depends on what positions in the copolymer chains are substituted with chlorine atoms. By analogy with polychloroprene [11], it should be expected that  $\beta$  carbon atoms in 1,2 addition configuration of the monomer units in the polybutadiene blocks, substituted with chlorine atoms, are especially active crosslinking sites. Thus, if the higher concentration of the polybutadiene blocks in a given styrene–butadiene block elastomer is, the greater peel strength of adhesive joints created by the surface chlorination should be. This is consistent with the results presented above.

For better characterization of the surface properties of the elastomers under discussion, measurements of the contact angles were carried out. The calculated surface free energy  $\gamma_s$  and its components (the dispersion  $\gamma_s^d$  and polar  $\gamma_s^p$  component) for both types of elastomers after various treatments are shown in Table I. Generally, these results reveal the lack of any distinct correlation between the free surface energy and the peel strength. For example, in the case of F435 the surface energy for the sample subjected to the  $\text{CHCl}_3$  plasma action with the power of 10 W is very similar to that for the non-treated sample, although the peel strength is 2.8 times higher in the former case. On the other hand, the highest values of  $\gamma_s$  and its polar component  $\gamma_s^p$  is observed for the  $\text{CHCl}_3/\text{O}_2$  plasma treatment with the power of 80 W, but the peel strength of such samples is practically the same as that for the non-treated samples.

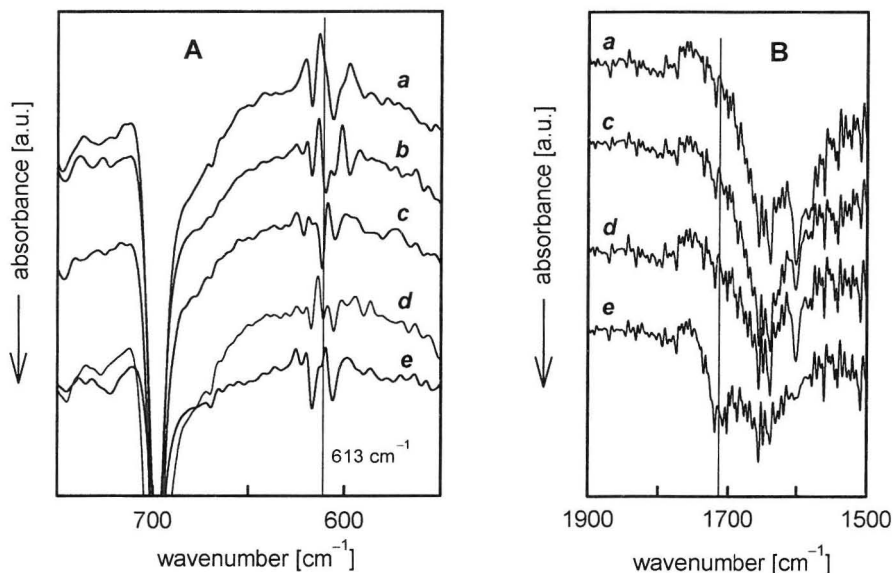
**Table I.** Surface energies of the styrene-butadiene elastomers after various plasma treatments.

Type of treatment	Elastomer F435			Elastomer F507		
	$\gamma_s$	$\gamma_s^d$	$\gamma_s^p$	$\gamma_s$	$\gamma_s^d$	$\gamma_s^p$
non-treated	32.5	30.7	1.8	33.3	31.7	1.6
plasma $\text{CHCl}_3$ 10W	31.5	29.0	2.5	35.3	32.1	3.2
plasma $\text{CHCl}_3$ 80W	33.2	28.2	5.0	40.6	37.6	3.0
plasma $\text{CHCl}_3/\text{O}_2$ 10W	35.8	32.3	3.5	42.0	35.2	6.8
plasma $\text{CHCl}_3/\text{O}_2$ 80W	41.7	23.7	18.0	42.4	36.5	5.9

These observations show that the dominant mechanism of the adhesion strength improvement by the used plasma treatments consists in the creation of active sites in the elastomer surface by chlorine atoms and the process of the thermodynamic adhesion (connected with the surface free energy [3]) is unimportant in this case.

Investigations of FTIR spectra supply valuable arguments to support the crucial role of the plasma chlorination process in the adhesive-bonded joint formation in the case of the elastomers under discussion. Two regions, namely  $500\text{--}800\text{ cm}^{-1}$  and  $1500\text{--}1900\text{ cm}^{-1}$ , were taken under account in this paper. Fig. 2 (A and B) presents adequate spectra for F435 after various treatments. In the first region, the band at  $613\text{ cm}^{-1}$ , which is attributed to C–Cl stretching vibration [9], is analyzed. It is readily noticeable that the higher intensity of the  $613\text{ cm}^{-1}$  band (and in consequence, the higher density of C–Cl groups) is related to the higher adhesion strength (Fig. 1, F435). On the other hand, the creation of C=O groups in the sample treated by  $\text{CHCl}_3/\text{O}_2$  plasma at 80 W (Fig. 2B, spectrum *e*), which is revealed by bands at the region of around  $1700\text{ cm}^{-1}$ , does not cause any changes in the adhesion strength, although the surface free energy grows evidently (Table I). It should be also noticed that the  $613\text{ cm}^{-1}$  band is not observed in any F507 samples

after the used plasma treatments. This is in a good coincidence with the peel strength (Fig. 1, F507).



**Fig. 2.** FTIR spectra of F435 samples in the C–Cl (A) and C=O (B) regions: *a*) non-treated; *b*) treated by  $\text{CHCl}_3$  plasma at 10W; *c*) treated by  $\text{CHCl}_3$  plasma at 80W; *d*) treated by  $\text{CHCl}_3/\text{O}_2$  plasma at 10W; *e*) treated by  $\text{CHCl}_3/\text{O}_2$  plasma at 80W.

## CONCLUSIONS

The presented investigations clearly indicate that the plasma chlorination is a very promising method to improve the adhesion properties of styrene–butadiene elastomers. It has been found that the pure  $\text{CHCl}_3$  plasma generated at relatively low powers supplied to the reactor is an effective tool for the surface chlorination. This process, however, is possible only when the appropriate concentration of butadiene blocks there is in the styrene–butadiene block copolymers. For 69 wt. % of butadiene, the effect of chlorination is clearly visible whereas for 27 wt. %, it is not observed. In the former case the plasma chlorination can give the peel strength, which is measured for the joints between the treated elastomer surface and the polyurethane adhesive, with value of approx. 56 % higher than that for the surface chemically treated by TCI, and approx. 3 times higher in comparison with the non-treated surface. The plasma chlorination consists in the attachment of chlorine atoms to the surface structure and the creation of C–Cl groups. This is confirmed by FTIR studies. It is suggested, however, that only certain of these groups

(probably located at the 1,2 addition configuration of the monomer units in the polybutadiene blocks) are active centers for the crosslinking between the surface and the adhesive. It should be also emphasized that the adhesion strength improvement has a typical chemical character and changes in the surface free energy are rather unimportant in this case.

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## PLAZMOWE CHLOROWANIE POWIERZCHNI ELASTOMERÓW

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**S t r e s z c z e n i e.** Podjęto próbę zastąpienia mokrego chemicznego chlorowania powierzchni elastomeru styrenowo-butadienowego przez chlorowanie w parach  $\text{CHCl}_3$  i tlenu, z wykorzystaniem rf (13.56 MHz) plazmy generowanej w elektrodowym reaktorze. Powierzchnie elastomerów scharakteryzowano wykonując badania absorpcji w podczerwieni (FTIR), pomiary kąta zwilżania oraz testy zrywania. Ustalono, że plazma generowana bez tlenu i przy relatywnie niskiej mocy jest efektywnym narzędziem do chlorowania powierzchni badanych elastomerów.

**S ł o w a k l u c z o w e :** plazmowa modyfikacja powierzchni, chlorowanie, polimery, przyczepność.