LASER TEXTURIZING OF RUBBER SURFACE

***Michał Okraska*[1], Dariusz Bieliński[1], Ewa Korzeniewska[2], Mariusz Tomczyk[2]**

[1] Institute of Polymer and Dye Technology Lodz University of Technology, Stefanowskiego 12/16 90-924 Lodz Poland

[2] Institute of Electrical Engineering Systems, Lodz University of Technology, Stefanowskiego 18/22 90-924 Lodz Poland

Rubber - known for hundreds of years, already used by indigenous people of South America, transformed into vulcanized rubber thanks to Charles Goodyear's experiments from the mid-nineteenth century, has become an inseparable element of the world around us due to its outstanding elastic properties. Thanks to the efforts of generations of chemists, today we have tens of dozens of varieties of elastomers (mainly synthetic ones), which constitute a continuous phase of rubber. Although the work on the rubber has been going on for over 150 years, the elastomeric composites are still being developed. New elastomer matrices, additives, fillers allow the use of rubber for new applications. Modified fillers and nanofillers significantly change the properties of composites, anti-aging agents and biocides added to protect the material from the effects of aging. These treatments have a common feature - they cause changes in the entire volume of the product. But what if we want to change only the surface without affecting the overall bulk properties of a rubber composite?

Modern materials engineering has also found an answer to this question. The basic method of surface modification of materials are still chemical techniques. Due to the well-known mechanisms and processes, they are used in the turnover of many materials. As an example for plastics, hardening by chlorination or hydrophobization can be applied by depositing compounds in baths. [1] These processes have another common feature - they leave a huge amount of waste, which is necessary for disposal or expensive cleaning and recovery. For these reasons many studies are conducted on surface modifications using non-waste techniques. For example, plasma treatment or chemical and physical vapor deposition. [2] Another method is a modification by means of a beam carrying high energy.

Laser texturing is a method of surface modification by selective heating of the material with very high precision. This technique allows to change the morphology of the surface layer without disturbing the material in depth. Its use is simple, cheap and does not generate waste, and the obtained effects are visible to the naked eye. As an example, one can refer to works that resulted in silicon wafers having a structural color or also superhydrophobic metal surfaces. [3,4] The inspiration for many scientists working on laser texturing was nature, which through hundreds of years of evolution has developed surfaces that through their structure have surprising and outstanding properties.

The work presented is focused on the use of laser texturing, used up to now on high stiffness materials, for the processing of elastomeric composites. The scheme of the laser treatment mechanism is illustrated in Fig. 1. Laser beam is absorbed by the material. It is important that the absorption takes place as much as possible in the surface layer of the composite. There is a rapid heating of the surface accompanied by removal or transfer of material from under the beam. In the case of elastomers, the surface is additionally oxidized, and its heating may also result in local crosslinking.

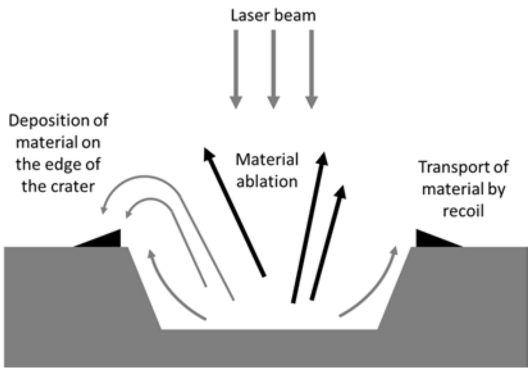

Fig. 1. Scheme of the laser beam operation

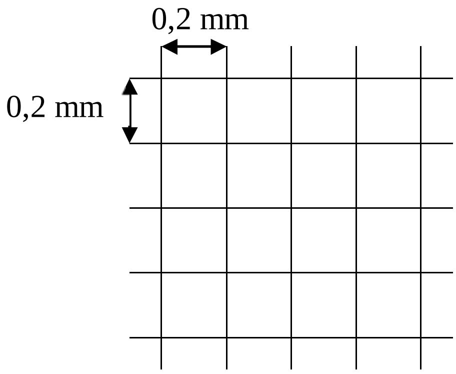

Fig. 2. Texturing grid

The texturing was done on a composite containing a small amount of the pigmenting agent absorbing the near infrared laser beam and cross-linked using a peroxide. The simplification of the material was aimed at eliminating the effects of other additives. The grid on which the moving beam had a pitch of 0.2 mm (Fig. 2) was regulated by the speed and the power.

Figure 3 presents a comparison of SEM images (A), non-contact profilograms (B) and water contact angle (C) for three selected textures made under different conditions on the same composite. In the first row there is a sample of high-energy deposited. One can see the deep etching at the points where the laser falls, and the edge of the remaining protrusion is rounded. The profilometric image clearly shows a significant difference in height between the tanned and raw fields. On the border there is a wide place of varied height, which can be linked to the effect of cross-linking, shrinkage and cracking of the composite. The second line is a sample treated with lower energy. It is characterized by narrow paths of the laser path and clearly sharper edges. From the profilometric image, it can be seen that the edges are clearly higher than the untreated surface, which indicates that the material texture removed from the bottom has been deposited in this place. The last line presents the effects of processing with very low energy. The texture visible in the SEM picture is quite flat, it is also confirmed by the profilogram. Column C of the table illustrates the water contact angle for the textures made. Increasing hydrophobicity by changing surface roughness is a known issue. The implementation of laser pattering of elastomers allowed to increase the hydrophobicity, which is of practical importance.

The effects obtained in the course of previous work are very revolving. So far, the effectiveness of using iron oxide as a coloring agent allowing effective modification has been confirmed. Hydrophobicity has also been shown to increase with an increase of laser beam energy, although the material undergoes oxidation during texturing, which should result in the opposite effect. Contact angle for water increase from 99° for non-modified to 128° for sample shown in Fig 3 row 1. It is planned to develop the research in many directions, such as the use of various elastomer matrices, coloring agents, mesh designs and expanding the research on textures.

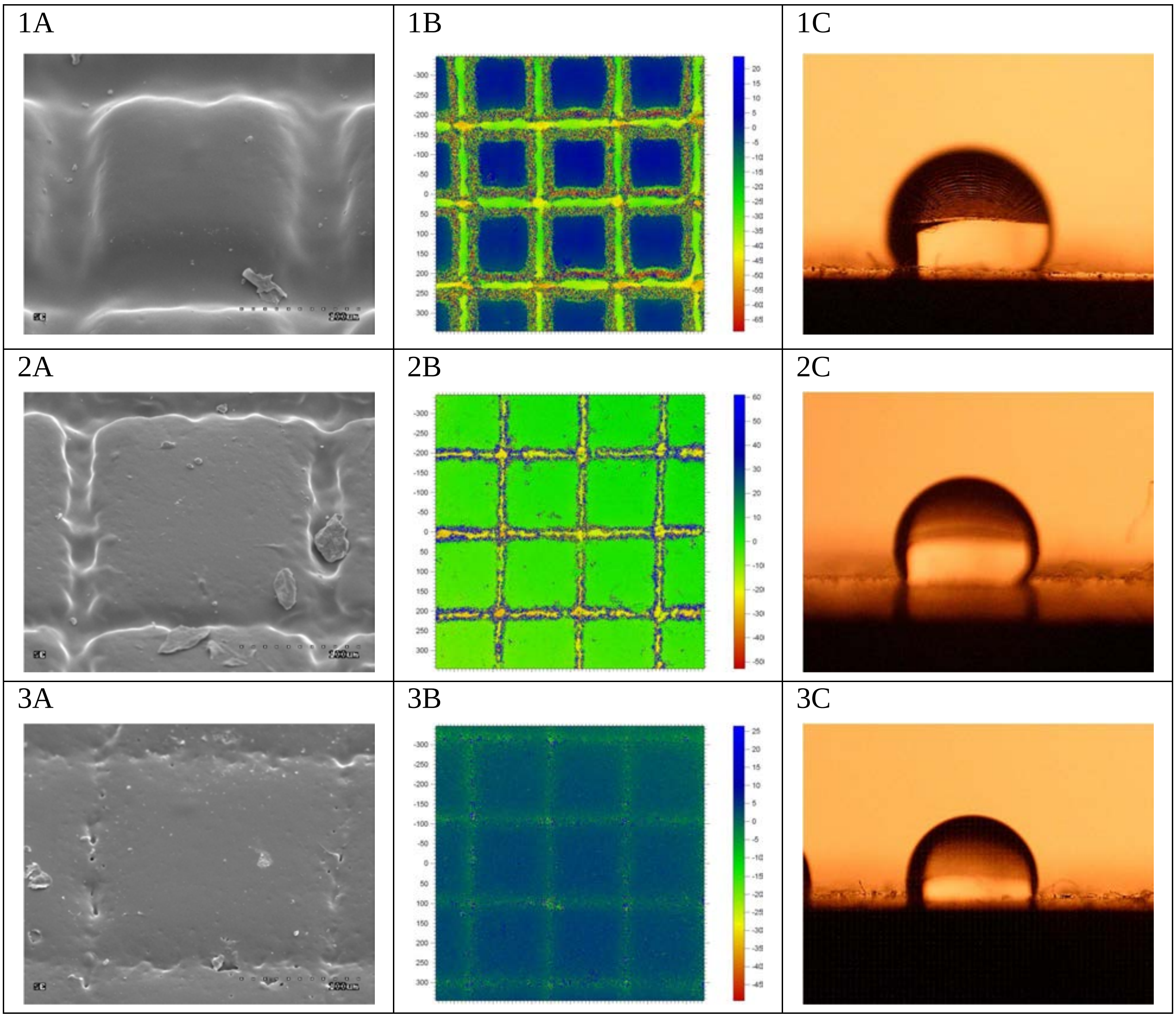

Fig 3. Comparison SEM (column A) profilograms (column B) and contact angel for water (column C) for texture pattering in different condition.

[1] VAN AMERONGEN, G. J.; KONINGSBERGER, C.; SALOMON, G. Chlorination of natural rubber. I. Preparation and properties of chlorinated rubber. Journal of Polymer Science Part A: Polymer Chemistry, 1950, 5.6: 639-652.

[2] FRANCE, Richard M.; SHORT, Robert D. Plasma treatment of polymers effects of energy transfer from an argon plasma on the surface chemistry of poly (styrene), low density poly (ethylene), poly (propylene) and poly (ethylene terephthalate). Journal of the Chemical Society, Faraday Transactions, 1997, 93.17: 3173-3178.

[3] VOROBYEV, A. Y.; GUO, Chunlei. Antireflection effect of femtosecond laser-induced periodic surface structures on silicon. Optics express, 2011, 19.105: A1031-A1036.

[4] WU, Bo, et al. Superhydrophobic surfaces fabricated by microstructuring of stainless steel using a femtosecond laser. Applied Surface Science, 2009, 256.1: 61-66.