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To cite this article: B Antoszewski et al 2017 IOP Conf. Ser.: Mater. Sci. Eng. 233 012036

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Utilization of the UV laser with picosecond pulses for the formation of surface microstructures on elastomeric plastics

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Abstract. Elastomeric plastics belong to a wide range of polymeric materials with special properties. They are used as construction material for seals and other components in many branches of industry and, in particular, in the biomedical industry, mechatronics, electronics and chemical equipment. The micromachining of surfaces of these materials can be used to build micro-flow, insulating, dispensing systems and chemical and biological reactors. The paper presents results of research on the effects of micro-machining of selected elastomeric plastics using a UV laser emitting picosecond pulses. The authors see the prospective application of the developed technology in the sealing technique in particular to shaping the sealing pieces co-operating with the surface of the element. The result of the study is meant to show parameters of the UV laser's performance when producing typical components such as grooves, recesses for optimum ablation in terms of quality and productivity.

1. Introduction
The widespread trend toward miniaturization also applies to elements made of polymers. The wide use of elastomeric plastics results from the special properties of these materials such as deformability, elasticity, chemical stability, weather resistance, good electrical insulation and sometimes biocompatibility and heat resistance. They are used in biomedical, mechatronic, chemical, and electronic industries where, among others, such elements are made as micro-flow systems, surfaces with special adhesive properties, chemical and biological microreactors. Practically, mechanical methods of shaping surface structures of elastomers are ineffective in this case. To meet these needs, laser micromachining having such features as high precision, controlled heat-affected zone (HAZ), automation of the process ensuring treatment repeatability, non-contact machining, minimal range of finishing work are used. Lasers emitting radiation with ultra-short pulses contributing to removing the material without heat effects due to cold ablation are particularly useful here. In the scientific literature more and more articles on laser treatment of elastomeric and generally polymeric plastics appear [1-4]. The laser micromachining of elastomeric plastics is an alternative to lithographic methods. It is one of the direct methods utilizing the most common sources of laser radiation: CO₂ (wavelength 10.6 μm - close to infrared) and Nd-YAG (successive wave harmonics: 1064, 532, 326 and 266 Nm - from near infrared to ultraviolet) including ultrashort pulse lasers.
The constant optimization of production processes results in a continuous increase in requirements for elastomer seals. These requirements can be very different and depend not only on application but also on industry. In general, the suitability of sealing material for a given application is determined by three groups of factors: working temperature, chemical resistance and mechanical properties. Interactions such as working temperature and mechanical properties should also be considered. In addition to the correct material selection, sealing performance can also be determined by issues such as design, construction geometry and physical, chemical and stereoscopic surface properties. In particular, this applies to those parts of the sealing surface on which the sealing at the point of contact of the seal and the surface of the machine element or the housing depend. These are mainly small sealing parts such as sealing lips of different shapes, and cylindrical and flat surfaces. The shaping of surface properties, including adhesive ones, of these parts is essential for processes occurring in the sealing gap. Laser micromachining makes it possible. In many cases it is necessary for PUWO seals of harder materials such as PTFE to use hardened rollers up to 58 - 62 HRC to prevent the fast cutting of a groove under the lip. For dry seals, it is recommended to lubricate the seals with suitable grease or use air lubricants when installing. Due to lack of lubrication the seal may be jammed in the housing. These problems can be solved to a large extent by the use of micro-machining of the elastomeric material at the point of contact of the sealing portion with the surface of the machine element or housing. The shaping of micromachining may be of a different nature. They may be casket-shaped grease reservoirs, groove profiles that form microscopic blades, and assemblies of channels dosing the flow. Such solutions may be used, for example, in the elimination of the stick slip phenomenon and the prospect of using micromachining in combination with the elasticity and dynamics of the seal seems very promising.

With this in mind, the paper explores the potential of micromachining typical materials used for seals.

2. Theoretical basics
As a direct effect of the laser spot on the surface of the material, combustion, melting, sublimation, depolymerization (PMMA), ablation (in particular, desorption), foaming, color change, annealing (metals) occur depending on the type of material and laser beam parameters (wavelength, pulse duration, repetition frequencies, etc.). The classic method of machining directly with the CO$_2$ laser beam has been used for several years now. Unfortunately, it has serious disadvantages: low quality of the obtained structure - high surface roughness strongly dependent on the material used and the minimal spot diameter of 100 µm, which significantly limits the application area. The improved TC & T (Laser Through-Cutting and Pattern Transfer) method of direct CO$_2$ laser machining was developed by Liu and Gong [5]. Thanks to its application, it was possible to obtain micro-channels with a minimum diameter of 30 µm, with smooth surfaces of the bottom and side walls.

Laser methods of surface treatment of polymeric materials [1,2] using radiation to generate thermal effects consist in melting micro areas of the surface with a thickness of several micrometers, in increasing the surface roughness and removing its fragments, and if the process is carried out in the presence of oxygen, oxidation on the surface also occurs. This method is suitable for polyamides, polyesters and aramid materials, or for polyolefines and PTFE if ultraviolet absorbers are introduced to them because the absorption coefficient of laser radiation by the surface of the polymeric material determines the effectiveness of this technology.

Laser radiation is used for very fine processing of small surfaces of complex geometrical form, e.g. in electronics, or in the manufacture of medical devices where they are additionally provided with sterilization. Laser radiation affects the improvement of wetting and free surface energy values by the implementation of polar functional groups, mainly in the oxidation process, the degree of the polymer crosslinking, and the type of the geometrical structure of the surface without changing the core properties.

When polycarbonate, polytetrafluorurate or polystyrene are processed, the use of the laser radiation wavelength less than 308 nm is required, which is provided by an ArF excimer laser. If the radiation energy lower or higher, respectively, than the ablation threshold of the mentioned polymeric materials
is used, an improvement in hydrophilic or hydrophobic properties is provided, which is accompanied by an increase in roughness [2, 6].

3. Theoretical basics
Laser ablation is the process by which the chemical bonds of macromolecules of polymeric material are destroyed by laser light. There are two mechanisms of ablation which can occur separately or simultaneously: photochemical and photothermal. The thermal ablation of a polymer occurs as a result of the excitation of molecules into the high energy state by laser radiation. This results in generation and, at a later stage, in heat accumulation and an increase in material temperature. The thermal ablation occurs after exceeding the temperature value of the material called the threshold ablation temperature (T_D). The energy initiating the thermal ablation is expressed by the following relation:

$$E_{th}^j = c_v \frac{(T_D-T_R)}{\alpha(1-R)}$$

where:
- T_R - initial temperature of polymer material,
- c_v - specific heat of polymeric material,
- α - radiation absorption coefficient,
- R - reflectivity factor of laser radiation.

The mechanism of photochemical ablation consists in the photolytic breaking of chemical bonds, especially C-H bonds. Ablation achieves its full degree of development when a large number of (n) chemical bonds simultaneously break as a result of a laser pulse. The value of the energy that initiates ablation (the threshold value of ablation energy) describes the dependence:

$$E_{th}^j = n \frac{h \nu}{\phi \alpha (1-R)}$$

where:
- ϕ - quantum yield of breaking bonds (value from 0-1 range),
- hν - photon energy.

4. Experimental
Experimental research was carried out on a test bench existing at the Center for Laser Technology of Metals of the Świętokrzyski University of Technology.

A test bench is a laser machine for micro-machining. The test bench layout is shown in Figure 1.

**Figure 1.** TruMicro5325c laser test bench layout.

The characteristics of the basic units of the laser machine for micromachining are as follows:
- Laser TruMicro 5235c - type of laser: pulsed diode impulse laser disk with 3 harmonic generation,
- wavelength: 343 nm,
- average power: 5W,
- minimum pulse duration: 6.2ps,
- 400kHz pulse frequency with the possibility of dividing by natural numbers from 1 to 10000,
- maximum pulse energy: 12.6μJ,
- mod: TM_{00},
- M^2 =1.3,
- maximum fluency: 4.8 J/cm^2.
Scanner IntelliSCAN 14 - biaxial scanner (XY) for ultraviolet light 343 nm, - aperture: 14 mm, - standard F-Theta lens with focal length: \( f = 160 \) mm, - Rayleigh length - 0.76 mm, - spot diameter - 18.2 \( \mu m \).

XYZ coordinate table - XYZ movement range: 200 mm, 200mm, 275 mm, - bearing capacity: 70kg spread evenly distributed load, 10kg for the Z axis, unevenly distributed load, - repeatability of positioning: +/- 0.0001 mm, - resolution of measurement of displacement: 0.5 micrometer, - max speed: 500mm/s.

Experimental

Three materials used in the construction of seals with distinctly different properties were selected for the study. NBR nitrile rubber is the most popular material for general purpose seals. PEBAX is used for precision seals in laboratory and medical equipment. Polamid PA6 is characterized by its high stiffness, high temperature resistance and durability. It is used, among other things, for flat seals and support rings.

| Name of the material | Density of the material \( \text{kg/cm}^3 \) | \(^{6}\text{Shor hardness} \) |
|----------------------|----------------------------------|-------------------|
| NBR nitrile rubber   | 1.1                              | 50                |
| Poliamid PA6         | 1.13                             | 74 (skala D)      |
| PEBAX                | 0.59                             | 54                |

The purpose of the conducted research was to determine the possibility of micro-surface machining of selected elastomer plastics for shaping structures useful in sealing technology.

The attempt consisted in making longitudinal micro recesses on the materials tested with a maximum laser power of 400 kHz and variable scan speeds of 1000, 2000, 3000, 4000 and 5000 mm / s. The treatment marks were identified by analyses done using HIROX microscopy.

An exemplary 3D view of the cut and section profile is shown in Figures 2 and 3. HIROX microscope software allows you to determine the depth and width of the groove as well as its cross-sectional area. Knowing the scan speed and material density, the machining efficiency was determined. A summary of the measurement results is shown in Table 2.

![Figure 2](image-url)
Figure 3. Profile of groove section in NBR at 1000 mm / s. mm/s.

Table 2. Summary of research results.

| Scan speed [mm/s] | NBR   | PA 6   | PEBAX |
|------------------|-------|--------|-------|
| 1000             | Depth [μm] | 16.861 | 11.545 | 24.004 |
|                  | Width [μm] | 51.936 | 39.906 | 58.956 |
|                  | Machining efficiency [g/s] x 10^6 | 349.277 | 224.353 | 369.026 |
| 2000             | Depth [μm] | 7.883  | 5.441  | 11.495 |
|                  | Width [μm] | 53.551 | 25.494 | 37.438 |
|                  | Machining efficiency [g/s] x 10^6 | 294.382 | 126.985 | 163.947 |
| 3000             | Depth [μm] | 4.617  | 2.970  | 8.446  |
|                  | Width [μm] | 40.756 | 15.926 | 36.593 |
|                  | Machining efficiency [g/s] x 10^6 | 219.453 | 113.943 | 208.920 |
| 4000             | Depth [μm] | 4.503  | 6.823  |
|                  | Width [μm] | 41.897 | 38.194 |
|                  | Machining efficiency [g/s] x 10^6 | 291.540 | 240.625 |
| 5000             | Depth [μm] | 3.955  | 2.803  |
|                  | Width [μm] | 37.555 | 24.074 |
|                  | Machining efficiency [g/s] x 10^6 | 271.277 | 107.391 |

5. Analysis of results
Surveys and observations have shown that a laser emitting UV radiation at 343 nm in picosecond pulses can be recommended as a tool for the micromachining of elastomeric materials and, in particular, NBR, PA6 and PEBAX. The micromachining of recesses is efficient and precise and the workpiece does not lose its elasticity. At the site of the treatment and its surroundings, no charring and other signs of overheating were observed. These recesses retain their characteristic dimensions with a +/- 15% deviation along the entire length of the groove, which demonstrates the high repeatability and accuracy of the machining. The estimated removal efficiency of the material is in the range of 369.026 10^-6 g / s to 107.391 10^-6 g / s and was the highest for PEBAX. The hardest material to work
was PA6 which is the material of the highest density and hardness of the tested materials. As the scanning speed increases when the recesses are made, the process yield and depth of grooves are reduced. The greatest changes in depth occur when passing from 1000 mm / s to 2000 mm / s. Detailed microscopic examinations are required to evaluate structural changes at the work site. The conducted research confirms the possibility of applying the developed technology to shaping the surface parts of the seals cooperating with the surface of the machine element or the sealing housing. This opens new prospects for improving the performance of seals such as reducing friction and damage probability, improving lubrication conditions, and increasing durability.

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