Structural Changes in Polymethyl Methacrylate during Laser Machining

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Abstract: The focus of the article is an issue of laser machining of polymethyl methacrylate materials. Specifically, it deals with evaluation of structural changes in polymers as due to the effect of concentrated energy there appears vaporization of the material in the place of cut as well as heat transfer into the material around the place of cut and thus to the heating. As a result of the raised temperature, different structural changes may occur in the material; some high-molecular substances begin to break down into low-molecular substances, and depolymerization or degradation of the material may occur. All these changes may result in a change of the final properties of the product. For experimental machining and subsequent study using the "Fourier Transform Infrared" vibration spectroscopy, PMMA was chosen as it is one of the most feasible polymeric materials in this technology.

Keywords: Laser Technology, Structural Changes, Polymeric Material, Vibration Spectroscopy.

1 Introduction

At material machining, a laser is commonly used as a source of an intense electromagnetic radiation, which is directed to a particular object. The effect of the laser depends on the characteristics of the workpiece material (its physical properties, structure, etc.), the parameters of the laser itself; next, it is also affected by the interaction time between the material and the laser beam. In terms of machining, surface quality assessment and possible changes around the cut, the part of the laser beam that is absorbed by the material is a key aspect with respect to the material. [1].

Polymeric materials are brittle at normal temperatures; with more load and stress they can crack. With increasing temperature, the polymers become more ductile and elastic. Therefore, the properties of these materials are temperature-dependent. In some temperature areas, changes occur faster, or they may occur in fits and starts. These areas are characterized by the transition temperature Tg (glass transition temperature), Tf (flow temperature), which gives us the flow temperature, shows a large increase in deformation and is irreversible (see in Fig. 1). However, changes in the chemical structure of the polymer occur only behind the temperature of Tf, in the areas before the evaporation temperature when the material evaporates. [2].

![Figure 1 The thermomechanical curve of the amorphous polymer](image_url)
Because of the elevated temperature, the polymers begin to soften and, eventually, the kinetic energy of the macromolecule chain can increase until it overcomes the intermolecular forces and the polymer obtains properties that are very close to the properties of the liquid. There may also appear a change in the structure of the polymers by starting some high-molecular substances to break down into low-molecular products. Sometimes monomer cleavage can occur. However, this may happen without changing the chemical composition of a particular polymer. The tendency to depolymerize up to the monomer without changing the chemical composition has also PMMA. The depolymerization process takes place by a chain reaction in which the monomer is released from the ends of the macromolecular chains. [2].

2 Experimental part

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2.1 Polymethylmethacrylate – PMMA

Acrylic PMMA is a transparent, synthetic, highly transparent thermoplastic polymer that is mainly obtained by polymerization of methyl methacrylate. Its chemical formula and is evident from Figure 2.

PMMA transmits light in 92% across the spectrum, reaching up to the UV range. It has excellent mechanical properties, such as water resistance and electrical insulation qualities and is also wholesome. A small surface resistance is considered to be its deficiency as it gets scratched easily. It is applied in more complex machine parts, often in replacing glass - “glazing” of transport means, protective covers of instruments and machines, glasses for watches, office supplies. It is also used in medicine, for example in dentures. [3].
2.2 Sample Preparation
In PMMA samples, the grooves were cut by the EUROLASER LCS XL – 1600 (CO₂ Laser, wavelength 9.3 µm) under various technological conditions (varying power and feed rate, see Table I), marked with digits 1 to 5 (see in Fig. 3). These grooves were then cut through by a band saw to allow access to the place of cut. FTIR measurements were performed in individual grooves. To compare the FTIR results, a base material untreated by the laser beam was set.

Table I Technological parameters

| Cut          | Power [W] | Feed rate [mm/s] |
|--------------|-----------|------------------|
| 1st groove   | 255       | 12               |
| 2nd groove   | 255       | 17               |
| 3rd groove   | 255       | 35               |
| 4th groove   | 255       | 25               |
| 5th groove   | 225       | 45               |

Figure 3 Sample with individual cuts

2.3 Surface Evaluation Using FTIR Infrared Spectroscopy
This is a non-destructive analytical method that allows, based on different interaction of infrared radiation, to identify and structurally characterize organic and inorganic compounds in a given substance. It is generally possible to analyse gaseous, solid and liquid substances. The principle of this method consists in examining the absorption of IR radiation when passing through the material; it changes the rotational vibrational energy state of the molecules, depending on the transformation in the dipole moments of the molecules of the substance. Each atom present in the molecule exhibits vibration around its equilibrium position; the frequency of this vibration is determined not only by the mass of the particles involved, but also by the strength of the bonds.

The frequency of radiation can resonate on certain frequencies with molecular vibrations, so the energy of this radiation can thus be absorbed. Substances that do not absorb IR radiation (for example oxygen, nitrogen, hydrogen, graphite or sulphur) cannot be analysed by this method.

The result of the measurement is a graphical representation of the energy dependence expressed as absorbance at the wavelength of the incident radiation. The absorption intensity is usually described as a percentage, with IR unit being the so-called reciprocal centimetre (cm⁻¹). It is true that each substance under
investigation has a unique spectrum. [4].

FTIR spectroscopy enables to distinguish the molecular structure of the materials based on their various absorption in the infrared range of electromagnetic radiation. For FTIR, a Germanium crystal was used in the form of a tip touching the measured surface under constant pressure. The measured area was 100 μm x 100 μm.

Measurements were performed at 25 °C, atmospheric pressure 1016.4 hPa and humidity 45 %.

3 Results and Evaluation

The curves have a characteristic geometry of PMMA. The dark blue colour shows the curve for the groove 1 (Edge_1), the green curve belongs to the groove No. 2 (Edge_2), the orange is the groove No. 3 (Edge_3), the light blue includes the groove No. 4 (Edge_4) and the red is the 5th groove. The X axis shows the wavelength in cm$^{-1}$ while the Y axis represents the absorption (see in Fig. 4).

When comparing the geometry of the curves 1-5, it can be stated that in terms of qualitative material changes of the machined surface, these changes were not proven by FTIR. All samples (grooves 1 to 5) have almost the same infrared spectra. Thus, based on the results, it can be concluded that changes of the technological parameters (the power and feed rate), do not affect the molecular bond in the examined material.

![Figure 4](image-url) Qualitative comparison of IR spectra of individual laser-irradiated surfaces

In addition, a qualitative comparison of IR spectra of surfaces irradiated and non-irradiated (depicted by black curve) by laser beam was performed, as you can see in Figure 5. In FTIR spectra, there can be noted some significant changes on the stretches marked by vertical lines. In the area of about 3000 cm$^{-1}$, it can be seen that the non-irradiated surface (black curve) has the highest absorption intensity at the wavelength of 2920 cm$^{-1}$. Furthermore, a stretch at 2850 cm$^{-1}$ is also visible. These stretches are associated with valence vibrations of CH$_2$ groups, both asymmetric (2920 cm$^{-1}$) and symmetric (2850 cm$^{-1}$). Stretches at wavelengths of 2990 cm$^{-1}$ and 2950 cm$^{-1}$ are linked by asymmetric and symmetric vibrations of CH$_3$ groups. It can be seen that with the irradiation of the surface, the stretch intensity decreases to 2920 cm$^{-1}$, almost disappears, and then only appears as a stretch edge of 2950 cm$^{-1}$. The 2850 cm$^{-1}$ stretch almost completely vanishes with the surface irradiation.

This phenomenon can be attributed to the material degradation and chain shortening with surface irradiation, resulting in a decrease of CH$_2$ groups in the spectrum and an increase of terminal CH$_3$ groups. Another observable phenomenon is that the 1475 cm$^{-1}$ wavelength, which belongs to the deformation vibrations of CH$_3$ groups, has only a very little noticeable edge in the non-irradiated surface spectrum. On the
other hand, irradiated surfaces show a totally differentiated (though intensely small) stretch. This could confirm the consideration of the CH$_3$ moieties in the material and the possible degradation of the -CH$_2$- groups. The 1720 cm$^{-1}$ stretch is typical for esters (bond - (CO) -O-). It is a valency vibration. Furthermore, in the region of about 1100 cm$^{-1}$ there is a stretch for the deformation vibration of this bond.

Thus, it can be stated that structural changes in the material caused by laser radiation have been demonstrated using vibrational spectroscopy - FTIR spectroscopy.

![Figure 5 Qualitative comparison of IR spectra of individual laser cut surfaces with non-irradiated surface](image)

**4 Conclusion**

Nowadays, the laser technology is an indispensable part in a wide range of industries, including engineering, medicine, research and others. In spite of all its advantages, however, it concerns a high-energy source of radiation; thus, the heat-affected zone at the cutting area occurs during machining. The size of this area varies, depending on many factors, such as laser wavelength, technological parameters, and the thermal conductivity of the workpiece plays a big role here. Although plastics belong among materials with a low thermal conductivity, there is also a very high temperature at the cutting point for a short time, and the heat spreads into the internal volumes of the material. As mentioned above, due to the raised temperature, various undesirable changes may happen in the material, even if they occur only in close proximity to the cutting point. [4], [5], [6].

The PMMA was selected for experimental machining and subsequent study using the Fourier Transform Infra Red Vibration Spectroscopy. A qualitative comparison of the IR spectra of surfaces was performed, on which a laser beam with a non-irradiated surface was applied. There are some significant changes in the FTIR spectra of the irradiated sample on the vertical lines, which suggests.
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