

Plastic material, and method for processing a plastic material

[01] The invention relates to a method for processing a plastic material, in which the plastic material is processed with a laser.

[02] When ablating material above the vaporisation threshold or during modification of a material below the vaporisation threshold, depending on the type of the plastic material and the processing parameters, in particular in the case of thermosets, de-crosslinking or depolymerisation of the plastic material may occur, which has a negative impact on the properties of the plastic material. This affects mechanical and chemical properties such as strength, elasticity, fatigue strength under cyclic bending stresses, inertness and solubility. Furthermore, the invention relates to a plastic material, in particular an ocular implant or an intraocular lens, which have at least one region in which plastic material has been vaporised or modified using a laser.

[03] Treating plastic materials with a laser in order to remove material and/or to polish the surface is known. An example of this type of processing of a plastic material is shown in DE 10 2017 002 986 B4. There, an intraocular lens is used by way of example to show how material can be ablated with a laser and in addition, how polishing of the surface can also be carried out with the laser.

[04] US 2017/0371180 A1 describes a method for the manufacture of a contact lens, in which an internal cavity in the contact lens is filled with a water-soluble polymer. To this end, a hole is drilled with a laser from the outside of the contact lens to the cavity and the water-soluble material in the cavity is then rendered soluble with UV light. Finally, the hole is closed up again.

[05] However, the present invention not only relates to the treatment of intraocular lenses, ocular implants, methacrylate plastic materials or thermoplastics, but in general to the treatment of plastic material in which the plastic material is processed with a laser.

[06] The laser processing methods for vaporising plastic material or even only for modifying or melting plastic material modify the crosslinking of the molecules in the plastic material. This also modifies the properties of the plastic material at least in the region in which the plastic material has been processed. This is particularly pertinent to the geometry in the case of ablation and in the case of melting. During melting and modification, however, the mechanical and chemical properties are also modified, particularly also the refractive index at the surface or in the volume of the plastic material.

[07] In the context of the invention, the term “plastic material” should be understood to mean a solid object the basic component of which is formed by synthetically or semi-synthetically produced polymers with organic groups. Synthetic plastic materials are produced from monomers by polymerisation (polyaddition, polycondensation, etc).

[08] During the thermal treatment of plastic materials, in particular such as during melting and vaporisation, or indeed in order to modify the refractive index in the material, the degree of crosslinking is reduced. This drops the hardness, the toughness and the melting point, and the solubility increases. This facilitates the processing of the plastic material and this enables a blank, for example, or a blank which has been pre-treated with a laser, to be further processed with a polishing laser.

[09] After polishing the blank with a polishing laser, however, the plastic material still has a lower degree of crosslinking than the untreated blank. This results in the plastic material no longer being as hard and tough as the untreated blank.

[10] Thus, the underlying objective of the invention is to process or post-process plastic materials in a manner such that the disadvantages associated with the de-crosslinking of the plastic material are compensated for or at least minimized.

[11] Fortunately, it has transpired that this problem could be solved with a method with the features of patent claim 1, and also, the underlying problem of the invention is solved with a plastic material as claimed in claim 15.

[12] The concept underlying the invention is that even a variation of the method for ablation, melting or modification of the plastic material, even with the aid of USP lasers with pulse durations of less than 1 ns and pulse energies of 0.1 μJ to 10 μJ , has a deleterious effect on the processed plastic material. Instead of optimising the process method more and more, the underlying concept of the invention is that the plastic material can be irradiated after the laser processing in order to at least partially re-crosslink the plastic material.

[13] Particle beams are suitable for the irradiation. Electron beams, gamma radiation or photon beams, in particular UV photon beams, may be used as the particle beams. The radiation activates the de-crosslinked polymer chain portions in the form of electronic excitation or ionisation, which then lead to increased crosslinking with other polymer chain portions. Tests in which the particle energy and the particle beam power with respect to the incident power per unit area are varied confirm the effect.

[14] In contrast to previous approaches, then, in accordance with the invention, a novel method for reducing the de-crosslinking of the plastic material during laser processing is not being proposed, but rather, the de-crosslinking of the plastic material during processing with the laser is accepted and the plastic material is subsequently irradiated in order to at least partially re-crosslink the plastic material. In this manner, the de-crosslinking of the processed blank can be reduced, the plastic material can regain the properties of the blank after it has been processed, and even an increased crosslinking compared with the degree of crosslinking of the blank can be obtained, in order to increase the hardness, the toughness and the melting point and to reduce the solubility.

[15] Thus, the plastic material undergoes a subsequent procedure, with which the reduction in the viscosity generated by previous polishing due to shortening of the polymer chains is turned in the other direction and raised by crosslinking and therefore preferably, the original values for the material as regards hardness, solubility and toughness are largely regained. This may occur outside a lens at its surface, but also inside the material of the lens. Additional crosslinking is appropriate because of the polishing process and the reinstatement of the initial properties, as a rule on the surfaces and in particular the

outer surfaces, and this can be achieved in a particularly advantageous manner with particle beams.

[16] A possible treatment of the plastic material in order to increase the crosslinking would be treatment with crosslinking agents. Crosslinking agents of this type are distinguished by at least two reactive groups. Crosslinkers with two identical reactive groups are described as homobifunctional crosslinkers; on the other hand, those with two different groups are described as heterobifunctional crosslinkers.

[17] The crosslinking of extant polymer chains is known as curing and may be accomplished either via functional groups which are already present in the polymer by appropriate choice of the reaction conditions, or by using multi-functional, low molecular weight substances.

[18] Depending on the degree of crosslinking, the crosslinking of polymers initially generates elastomers and, with increasing crosslinking, also thermosets.

[19] However, in accordance with the invention, a normal crosslinking agent is not employed, but rather, the plastic material is irradiated following the de-crosslinking. The irradiation enables the plastic material which has been treated with a laser beam to then be treated by specific irradiation which is appropriate for increasing the crosslinking.

[20] While in the case of ablation, melting, polishing or modification, irradiation with the laser leads to de-crosslinking of the plastic material, irradiation with other beams or parameters results in a crosslinking of the plastic material.

[21] Thus, the method in accordance with the invention means that a plastic material can be processed up to vaporisation or polishing exclusively by irradiation, and therefore in a contact-free manner, and then, again in a contact-free manner, to regain its hardness or to improve the properties of the material.

[22] These steps of the method may be carried out directly one after the other. They may also be carried out in parallel, wherein the de-crosslinking occurs during the processing of the blank with the laser focussed in the internal region of the blank and/or at

its surface and the irradiation treatment with the particle beam counteracts this de-cross-linking process. In order to be able to process plastic material parts in a continuous process, these may be conveyed on a conveying device through treatment stations such as blank placement, ablation, polishing, crosslinking, final cleaning, final inspection, packaging. However, a stationary blank could be processed and irradiated with one laser. This makes it particularly easy to vary the chronological sequencing of the steps of the method.

[23] The plastic material parts may be heated by the radiation during processing, in order to accelerate the process. However, they may also be heated with separately introduced infrared heating, for example, in particular in order to speed up polishing and/or crosslinking.

[24] In particular, thermosets and thermoplastics which, however, might be crosslinked by the irradiation in a manner such that an elastomer or a thermoset is formed, are suitable for the method in accordance with the invention.

[25] An acrylate or methacrylate is particularly preferred as the plastic material for processing with a laser and then with irradiation for the crosslinking.

[26] The described method is also particularly suitable for the manufacture of implants. The laser processing means that a special implant, and preferably also an implant intended for special surgical treatment, can be manufactured from a blank and this implant can then be hardened again by crosslinking the plastic material. The contact-free treatment of the plastic material means that a plastic material which is suitable for use as an implant can in fact be de-crosslinked and then re-crosslinked, but in the end has similar or identical crosslinking to that of the starting material. This avoids problems which could arise when a plastic material which is authorised for the manufacture of implants is modified by the treatment with the laser and the associated de-crosslinking such that it is no longer suitable for use as an implant.

[27] Good results have been obtained using the method for an ocular implant and in particular for an intraocular lens.

[28] Processing the plastic material with an ultrashort pulse laser (USP laser) is particularly suitable for the inventive processing of a plastic material, because here, a particularly precise modification to the plastic material can be obtained, extending from a partial modification to the material properties via a vaporisation of regions of the material up to subsequent polishing by melting material on the surface of the plastic material.

[29] In order to be able to manufacture specific plastic objects for use as a mechanical component or as an implant, for example, advantageously, during processing, a portion of the plastic material is vaporised with the laser or the refractive index is modified in the interior of the blank. In addition, during processing, the plastic material may be polished with the laser, during which specific regions of the material are ablated or, in addition, liquefaction and therefore an increased surface tension effect is obtained with a view to smoothing in order to prevent microscopic structuring on the surface.

[30] A simple processing of the plastic material is obtained when the plastic material is processed with the laser on the surface of the plastic material. Even processing the surface of the plastic material, however, also necessarily results in processing regions of the plastic material which lie beneath the surface in the interior of the plastic material.

[31] In addition to processing of this type near the surface, the laser beam may also be used for specific processing of the plastic material in the interior of the plastic material. This in particular involves regions of the plastic material which are at least 0.2 mm from the surface of the plastic material.

[32] By coordinating the de-crosslinking with the laser and the crosslinking with the irradiation, specific predefined material properties may be set up on a region of the surface or in a region of the volume of the blank.

[33] On the same point, an increase in the de-crosslinking may be compensated for by an increase in the crosslinking, or the desired material properties are set up by the combination of a defined de-crosslinking and a defined crosslinking.

[34] The defined combination of material properties may, however, also be used to provide de-crosslinking and crosslinking to different extents at different points, surface regions or volumetric regions. This means that the blank gains different material properties depending on which region of the blank is under consideration.

[35] As an example, the blank may have outer surface regions which are particularly hardened by the irradiation, and internal regions which are less intensively hardened by the irradiation.

[36] In this manner, for example in the case of a lens, in the path of a beam of light passing through the lens, the refractive index in one region may be increased and it could be reduced or increased in another region in order to balance out the change caused by processing of the blank or to obtain a specific refractive index.

[37] As is the case with lasers, the total duration, pulse duration and intensity can be varied, and so these parameters may also be used to vary the effects of the irradiation on the properties of the material in the irradiated region.

[38] In order to irradiate the plastic material after de-crosslinking in order to obtain at least partial re-crosslinking of the plastic material, an irradiation with photons is proposed.

[39] An irradiation of the plastic material with electrons, beta radiation or gamma radiation has also been shown to be advantageous, however.

[40] The treatment of plastic materials with high energy electron beams, beta radiation or gamma radiation endows the plastic material employed with the thermal, mechanical and chemical properties of high-performance plastic materials. This means that inexpensive commodity plastics may also be used for the method. Radiation crosslinking may be carried out here following shaping, as the last processing step in the process chain. The particular processing, in particular the hardness of the surface obtained thereby, means that the plastic material parts can also be packed loose in pallet cages or cardboard boxes. Because an exact dose of radiation is applied, the crosslinking can be precisely controlled.

The material properties can be precisely defined in advance and be achieved by pinpoint-accurate irradiation. Shielding will even enable the degree of crosslinking inside a shaped part to be varied. In this manner, a plastic material part may have different hardnesses.

[41] In contrast to chemical crosslinking processes, radiation crosslinking takes place at low temperatures; this facilitates processing.

[42] Particularly good results have been obtained with the crosslinking of polyethylene (PE), polyamide (PA), polybutylene terephthalate (PBT) and polyvinyl chloride (PVC). In addition, the method in accordance with the invention is suitable for thermoplastic elastomers (TPE) and polypropylene (PP), but also for thermosets such as methacrylates and polymethacrylates.

[43] The invention therefore also concerns a plastic material, in particular an ocular implant or an intraocular lens which has at least one region in which the plastic material has been processed with a laser, and in this regard, de-crosslinking of the plastic material occurs with the laser and the plastic material is post-treated in at least one region in order to re-crosslink the plastic material. An example of processing of this type with a laser is the vaporisation of a portion of the plastic material, or in fact polishing of the plastic material by modifying the surface of the plastic material.

[44] Particularly preferred plastic materials are polished after the vaporisation of a portion of the plastic material and they are post-treated in order to crosslink the plastic material once again.

[45] The term “plastic material” as used in the context of this invention should be understood to mean any plastic materials as raw materials, as shaped parts or any plastic material parts such as mechanical elements or implants, or in fact also plastic surfaces or regions of plastic material inside another component.

[46] An exemplary embodiment in accordance with the invention describes the manufacture of an intraocular lens. This lens is manufactured from a blank for which initially, an ablation of material is carried out using an ablative laser. In this regard, a region of the

blank in which the laser impinges on the blank is vaporised. This ablation of material of 0.01 to 10 μm /pulse is obtained with a laser with a pulse energy of 0.1 μJ to 10 μJ . The pulse duration of the USP laser in this regard is less than 1 ns and the laser wavelength is preferably between 193 nm and 370 nm. Advantageously, the focal diameter is between 5 and 5 μm .

[47] The blank consisting of an acrylate is then initially shaped by vaporisation of regions of the surface so that it reaches almost the prescribed final shape. Next, the blank is processed further with a polishing laser.

[48] Because this leads to a de-crosslinking in the processing regions, the blank is then treated in at least these regions with an electron beam, with beta radiation or with gamma radiation. The treatment duration is such that the processed surface at least regains the degree of crosslinking of the blank or may even have a higher degree of crosslinking at least in parts.

[49] This makes it possible to manufacture plastic material parts and also in particular medical implants with a particularly hard and solvent-resistant, and therefore bio-resistant, surface.

[50] The combination of a de-crosslinking method using a laser and a crosslinking method by means of a treatment with radiation means that the plastic material part can also be manufactured with different densities. Thus, for example, an intraocular lens manufactured by the method may have a harder, i.e. more crosslinked, layer of plastic material on the surface than in the interior, for protection purposes. Crosslinking gradients could be obtained in a cross section through a plastic material part and because of the prescribed crosslinking, the refractive index in the interior or even inside the lens can be specifically varied.

[51] This enables a beam of light passing through the plastic material object to be influenced not only by means of the material properties and shaping at the surface of the plastic material object and in particular the lens, but also by the pre-set material density

in the plastic material and in particular also by a density gradient inside the plastic material.

[52] In a preferred exemplary embodiment, a plastic material blank is modified during the laser processing and then is irradiated in a manner such that afterwards, the plastic material once again has the material properties of the plastic material blank.

[53] The methods described in DE 10 2017 002 986 A1 are particularly advantageous having regard to processing the plastic material with a laser.

[54] An exemplary embodiment is illustrated in the figure and will be described below.

[55] The single figure diagrammatically shows a side view of a processing unit.

[56] The conveyor belt shown in Figure 1 conveys lenses 2 (only generically numbered) past a plurality of processing stations. By way of example only, an IR emitter 3, which heats the lens 2, is shown as the first processing station. The next processing station is a laser 4 which specifically modifies the shape of the lens. Next, there is a processing station with a laser 5, which polishes the surface of the lens. The fourth station is an emitter 6 for high energy electron beams, beta radiation or gamma radiation. The last station is a packing station 7 at which the lens 3 is packaged in a sterile manner.

[57] As an alternative, the lenses could also be in stationary positions and various processing stations are guided past the lenses. In addition, a combination of these two operational modes could be implemented.

[58] The irradiation which serves for crosslinking may be carried out with electron beams. In this regard, an electron energy of $E = 150 \text{ keV} - 300 \text{ keV}$, in the limiting case also up to 1.5 MeV , may be used. The mean power of the electron beam is then, for example, $P = 1\text{-}5 \text{ kW}$.

[59] A favourable dose may be $PD = 50\text{-}500 \text{ kGy}$ (kilo-Gray). This dose may also be provided in several successively applied doses. To this end, the emitter could pass over

the workpiece a number of times so that finally, the desired total dose for obtaining the desired crosslinking has been applied.

[60] In practice, the irradiated surface A was 2 x 20 cm. This resulted in intensities I of $0.5 \text{ kW/cm}^2 - 3 \text{ kW/cm}^2$. A suitable forward speed for the aforementioned surfaces was $V = 3 - 10 \text{ cm/s}$.

[61] In order to obtain an appropriate intensity per unit area, the data could be scaled up or down.

[62] In the case of stationary irradiation, appropriate intensities, irradiation durations and dose levels are calculated.

[63] The methods described in DE 10 2017 002 986 A1 are values for normal processing of a plastic material blank with a laser. In this regard, de-crosslinking occurs which then ought to be compensated for. On the other hand, by a pre-specified combination of de-crosslinking and crosslinking, the material properties of the plastic material blank are modified specifically at its surface and optionally also in its internal volume.

[64] The special processing which is described in DE 10 2017 002 986 B4 also describes the process step of de-crosslinking for the exemplary embodiment, which is followed by the process step of crosslinking described in this application.

Patent claims:

1. A method for processing the plastic material of a plastic material object, in which the plastic material is processed with a laser and at least partially modified, wherein the plastic material is de-crosslinked and then irradiated in order to at least partially regain a crosslinking of the plastic material, *characterized in that* during processing of the plastic material with the laser, plastic material is ablated in a processing region, at the same time or subsequently the processing region is polished with the laser or with another laser and the plastic material is irradiated in this polished processing region.
2. The method as claimed in claim 1, *characterized in that* the processing region is on the outer surface of the plastic material object.
3. The method as claimed in one of the preceding claims, *characterized in that* the plastic material is a thermoplastic or a thermoset.
4. The method as claimed in one of the preceding claims, *characterized in that* the plastic material is an acrylate and preferably a methacrylate.
5. The method as claimed in one of the preceding claims, *characterized in that* the plastic material is an ocular implant.
6. The method as claimed in one of the preceding claims, *characterized in that* the plastic material is an aid to vision such as, in particular, an intraocular lens or a contact lens.
7. The method as claimed in one of the preceding claims, *characterized in that* the laser is a USP laser.
8. The method as claimed in one of the preceding claims, *characterized in that* a portion of the plastic material is vaporised with the laser during the processing.

9. The method as claimed in one of the preceding claims, *characterized in that* the plastic material is polished with the laser during or after the processing.
10. The method as claimed in one of the preceding claims, *characterized in that* the plastic material is processed with the laser at the surface of the plastic material.
11. The method as claimed in one of the preceding claims, *characterized in that* the plastic material is also processed with the laser at least in the interior of the plastic material.
12. The method as claimed in one of the preceding claims, *characterized in that* the plastic material is irradiated with particle beams, in particular electron beams.
13. The method as claimed in one of the preceding claims, *characterized in that* the plastic material is irradiated with photons.
14. The method as claimed in one of the preceding claims, *characterized in that* the plastic material is irradiated with beta radiation or gamma radiation.
15. The method as claimed in one of the preceding claims, *characterized in that* a plastic material blank is modified during the laser processing and is then irradiated in a manner such that afterwards, the plastic material again has the material properties of the plastic material blank.
16. A plastic material, in particular an ocular implant or intraocular lens, which has at least one region in which the plastic material has been processed with a laser and therefore at least partially modified, *characterized in that* this region has been post-treated in order to crosslink the plastic material again, wherein in this region, the plastic material has been polished after vaporisation of a portion of the plastic material.