

Laser surface marking on engineering thermoplastic: polyamide

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Abstract. Its style sheet. Marking on polyamide is an important process because this type of material is widely used in many industrial sectors. Also, laser marking is a popular and easily automated method. But materials like polyamide have several properties, such as white color, that make laser marking a complicated process. White color has low laser absorption, so good marking results are difficult to achieve. Different types and parameters of the laser system are used for marking polyamide. To improve the marking results on polyamide, auxiliary materials are often used, which are applied to the polyamide surface. However, the most promising ranges of marking parameters without incorporating auxiliaries on the polyamide surface are still unknown. Successful marking on polyamide requires a deep study of parameters and various conditions.

Keywords: laser marking, polyamide, laser parametrs, laser sources.

I. INTRODUCTION

Research into the impact of laser radiation on materials has been ongoing since the invention of lasers. As technology continues to advance, lasers are widely used for processing various materials [1]. Laser marking is an area of significant interest in laser technology due to its widespread application. Currently, plastics, glass, metals and polymers are the primary focus of scientific investigation concerning the interaction between radiation and materials. There are various models and mechanisms that attempt to explain this interaction, but a comprehensive framework for selecting parameters and explaining material behavior under specific conditions is still lacking [2]. The analysis also seeks to identify the best speed and power levels to use for a specific ablation zone geometry when marking and engraving products, catering to different user needs. Laser marking and engraving has evolved as an appealing method for labeling plastic and polymers consumer goods, offering a

fast and cost-effective way to create various identification products such as barcodes, security information, and codes with flexibility in design [2], [3].

Laser marking is a surface modification technique that changes the surface's optical properties, structural characteristics, and melting or evaporation in the impact zone Fig. 1.



Fig. 1. Different physical processes by interaction of laser beam with the substrate [1]

The aim of this study is to reveal the different possibilities for laser marking of polyamide and how different processing parameters respond to laser irradiation.

II. EFFECTS OF LASER IRRADIATION ON POLYAMIDE PROPERTIES

Some of the most commonly observed effects and changes in surface properties are related to: a) Surface modification; b) Changes in chemical structure; c) Coloring; d) Thermal properties; e) Modification of the microstructure; f) Improved adhesion:

a) Surface modification often results in changes in surface roughness, wettability and adhesion properties. For example, the surface can become more hydrophilic or

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hydrophobic depending on the laser parameters and polymer composition. That is, the laser impact on the surface of polyamide materials leads to significant changes in morphology.

b) Laser interaction with polyamide molecules can cause chemical changes in them. This often results in chain scission, cross-linking, or the formation of new chemical groups. These changes, in turn, lead to a change in the polymer's mechanical properties, such as tensile strength, elongation at break, and impact resistance.

c) Depending on the laser parameters and the composition of the polyamide, laser irradiation can cause changes in the color of the material. This is often due to the formation of chromophoric groups or changes in the molecular structure of the polymer, leading to changes in the absorption and reflection properties of light.

d) The interaction of laser radiation with polyamide materials can affect their thermal characteristics. It caused changes in the crystallinity, melting point and thermal stability of the polymer.

e) Laser interaction with polyamide can affect the mechanical, optical and barrier properties of the material. This effect is a result of microstructural changes in the polyamide matrix. This includes changes in the orientation of polymer chains, crystal structure and morphology.

f) Laser surface treatment can improve the adhesion of polyamide materials to other substrates or coatings. By modifying surface chemistry and morphology, laser irradiation can promote bonding with adhesives, paints, or other functional coatings, improving overall material performance in a variety of applications.

Based on literature reports, three thermal models that describe the interaction of laser radiation with a material have been identified [3-4].

III. FOR SOME SPECIFIC EXAMPLES OF THE INTERACTION OF LASER RADIATION WITH MATERIAL

For example, when using long pulses (less than 1 ms), the material can be removed through photothermal ablation or evaporation caused by heat, resulting in the destruction of chemical bonds without significant heat input in some instances. Other example, shorter pulses (less than 1 ns) still maintain thermal equilibrium but mainly lead to evaporation. The heating and cooling processes follow specific mathematical functions, and plasma formation leads to gradual crater formation. Or ultra short pulses (less than 1 ps) lead to non-thermal equilibrium, causing direct evaporation and the Coulomb effect. This process removes material without significantly heating nearby areas, and traditional thermal concepts do not apply. Each case has distinct patterns to be considered when processing materials [6-9]. Laser technology offers various methods for marking polymers, such as carbonization, ablation, discoloration, melting. These processes induce changes in the molecular structure, particularly in the position of carbon within the polymer. Under specific wavelengths of laser radiation, the material undergoes energy-induced local alterations in its structure and properties. The selected impact area aims to be minimal yet detectable by the necessary

technical equipment for marking. Utilizing wavelengths, typically within the UV range, the irradiated material undergoes alterations in its optical properties, particularly its transmission coefficient. Even translucent materials with ideal microstructures and no impurities exhibit fundamental light absorption. Upon light absorption in the UV and visible spectrum, the electron shells of molecules become excited, transitioning the molecule from a lower energy state to a higher one. The excitation energy of the electron shell exceeds the energy of its vibrations [6]. As has already been mentioned different techniques such as ablation, oxidation, melting, carbonization, and foaming, as well as effects like discoloration, flowering, and dehydration, can be identified as the primary methods for marking plastic products. For example, some authors used thermoplastic marking Nd:YAG laser-direct marking without additives in their experiments using a fixed mean laser power of 5.5 W, a pulse repetition frequency speed of 20-60 kHz, and a scanning speed of 200-600 mm/s. As a result, various shades of gray and white arose with a slightly rough surface. In another study comparing two lasers: Nd:YAG with a fiber laser found that the duration of exposure for these lasers was similar despite the different laser properties. In addition, already using the solid-state YAG laser, the average power was about 20 W and the pulse repetition rate at 20,000 pulses per second. 60 W power was applied using CO₂ laser. When using fiber lasers for marking, experiments were performed with a short pulse range of 20 ns to 50 ns. While different lasers can be used to label thermoplasts, it is noted that high-energy lasers are commonly used for this purpose. In another article, used fiber lasers with 19.7 W average power, had the following parameters: scanning speed from 100 mm/s to 600 mm/s and marking step from 10 to 45 μm with repetitions from 2 to 12. The results showed that the best contrast was achieved at the marking step of 30-45 μm and the scanning speed of 100 mm/s, markings with gray and yellowish tone were created [10-15]. In polymer production, adding marks at the final stage holds significant value. Many polymer items bear markings for diverse reasons, including adorning or customizing objects, imprinting serial numbers or barcodes for identification, ensuring quality control, and etching logos or product names, serving practical and aesthetic purposes. Typically, the needs involve rapid writing, direct application on the finished product to bypass additional time-consuming and costly measures, as well as limited use of toxic or hazardous substances, ideally relying on uncomplicated and adaptable equipment [16].

IV. LASER MARKING SYSTEMS FOR POLYAMIDE

Laser marking refers to the use of a laser beam to mark or label items and materials. This can involve several methods, including removing material, adding color, annealing, and creating a foaming effect.

Laser marking involves a multifaceted technological procedure, requiring the careful selection of an appropriate laser. When assessing the optimal choice for a particular laser marking system, several important factors must be considered: the mechanism for delivering laser radiation, laser specifications, ease of operation, manufacturer recommendations, service guarantee and

maintenance, as well as cost. It's important to note that the specifications of lasers can vary significantly between different types [17]. Various laser systems can be used in the process of marking - see table 1.

TABLE 1 CLASSIFICATION OF LASER MARKING SYSTEMS TYPES FOR POLYMER/POLYAMIDE MATERIALS [18]

Laser Marking System Type	Description
CO ₂ Laser Marking Systems	Utilize a carbon dioxide laser to mark polymer materials. CO ₂ lasers are suitable for marking a wide range of polymers, including polyamides. They typically operate in the infrared wavelength range and are known for their high power and precision. CO ₂ lasers can produce high-quality marks with minimal thermal damage to the surrounding material.
Fiber Laser Marking Systems	Employ a fiber laser source to mark polymer materials. Fiber lasers offer high beam quality, excellent focusability, and efficient energy conversion. They are capable of producing fine, high-contrast marks on polyamide surfaces. Fiber lasers are particularly suitable for marking applications that require high-speed processing and precision.
Diode-Pumped Solid-State (DPSS) Laser Marking Systems	Use a diode-pumped solid-state laser to mark polymer materials. DPSS lasers offer a compact and efficient laser solution with high beam quality and reliability. They are often used for marking polymers due to their versatility, precision, and ability to produce permanent marks with minimal heat-affected zones.
UV Laser Marking Systems	Employ ultraviolet (UV) lasers to mark polymer materials. UV lasers operate at shorter wavelengths compared to other laser types, allowing for precise and high-resolution marking on polyamide surfaces. UV laser marking systems are suitable for applications requiring fine details, such as micro-marking or marking on sensitive materials.
Green Laser Marking Systems	Utilize green lasers to mark polymer materials. Green lasers offer a compromise between the infrared CO ₂ lasers and UV lasers, providing good beam quality and absorption characteristics for marking polyamides. Green laser marking systems are suitable for a wide range of marking applications, including high-contrast marking and color change marking on polymer.
Hybrid Laser Marking Systems	Combine multiple laser sources or wavelengths within a single marking system. Hybrid laser marking systems offer versatility and flexibility, allowing users to switch between different laser types or wavelengths depending on the specific marking requirements of polyamide materials. They can accommodate a wide range of marking applications, from surface engraving to color marking and barcode printing.

Practical considerations play a role in selecting the right laser, but the most critical factor is its wavelength. Lasers are available across a range of wavelengths.

Common lasers for marking include the following: CO₂ gas laser (used for thermosetting polymers), xenon chloride (XeCl) excimer gas laser with a 308 nm wavelength, Nd:YAG solid-state laser, ytterbium fiber laser with a wavelength of 1060 nm, frequency-doubled Nd:YVO₄, 532 nm wavelength (visible, green), frequency-tripled Nd:YVO₄ or Nd:YAG solid-state laser with a 355 nm wavelength (UV). UV lasers have gained rapid popularity lately. [17-19].

The use of lasers to mark polymers has become increasingly popular in the past ten years. This method is quick, affordable, and adaptable, enabling the creation of permanent and durable marks. The process involves directing a laser (typically a focused Nd-YAG pulsed laser emitting at 1064 nm) onto the polymer's surface to achieve the marking [16]. The main aim of laser marking is to alter the visual contrast. This can be achieved in two ways: by changing the color or by changing the reflections. Virtually all types of lasers can be utilized for marking. Small spots of this kind are commonly employed in machine-readable systems. The use of such a small spot diameter for eye-readable codes is feasible if multiple lines are used to increase the width. However, adding more lines also increases the resulting marking time. To reduce processing time and increase the spot size, special long-focus lenses or telescopes are utilized. The type of image being marked, its design and quality, the type of item, operational requirements, and the material being used should determine the type of laser and the laser beam positioning systems to be employed. Typically is employed with galvano mirrors systems Fig. 2. [20].

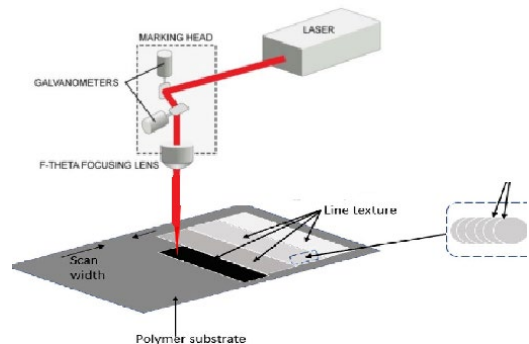


Fig. 2. Laser marking schematic image [20]

The focal length is crucial in deciding the size of the focused area, marking field, minimum line width, and power density on the workpiece. The combination of the scanner and the marking software dictates the scanning speed. Control systems and software for various laser marking setups vary significantly. The control system may involve workpiece feeding, beam activation/deactivation control, and interfaces for computers, laser sources, stages, and protection/alarm systems. The marking software should be simple to integrate into the consumer system and offer user-friendly interaction [17]. The characteristics of laser marking on materials, like surface texture, contrast in marking, and the coloration of the surface, are interconnected with the operational settings of the laser beam. This includes factors such as the speed of scanning, electrical current, the size of the beam spot, and the width of the line. These parameters

can be adjusted conveniently to ensure that the material's surface receives adequate localized heat from the laser while minimizing any undesired damage. Nevertheless, many plastics either have a light color, are transparent to laser beams, or exhibit minimal surface alterations following laser exposure [21].

V. MATERIAL POLYAMIDE

Thermoplastics are the main polymers used for marking, engraving, and welding processes (Figure 2). In etching, the laser beam eliminates a portion of the original material. This leaves a noticeable indentation. During ablation, the laser eliminates a layer of coating, revealing the underlying base material in the mark. Through annealing and color transformation processes, the laser heats the workpiece, changing its color while maintaining a smooth surface. In foaming, reactions in the plastic material cause the formation of gas bubbles, resulting in a raised or textured mark [22].

Polymers are actively used in a number of engineering applications, therefore the study of laser marking processes on these materials is extremely important. One of the three most important groups of factors affecting laser marking processes are the properties of polymers. Structurally, they are mainly made up of linear, branched or cross-linked chains, and the forces of attraction between the polymer chains determine the characteristic properties of the polymer Fig. 3. [18]

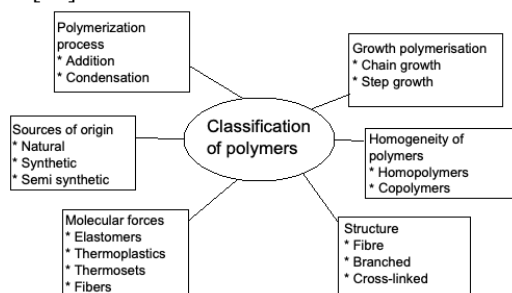


Fig. 3. Polymer classification (adopted from [18])

Understanding the material behavior during marking requires continuous information about the physical properties under specific sets of marking parameters. Obtaining such information is challenging because the material's structure (amorphous, partially crystalline, or fully crystalline) depends on the heating-cooling cycles. Additionally, the temperature range during marking can lead changes in structure through heating and cooling [23]. Depending on the characteristics of the polymer and the intensity of the laser, various processes can occur. The marking occurs as a result of the polymer surface undergoing carbonization at high laser power. At lower power levels, foaming or melting may be observed. Most commonly used polymers are suitable for this marking method. However, for an effective process, the polymer must have strong absorption at the laser wavelength. Materials such as inherently possess some level of photosensitivity at 1064 nm and can be easily carbonized at high temperatures, allowing them to be marked without the use of additives. Nevertheless, even for these

polymers, additives are typically included to enhance the required photosensitivity for achieving a writing speed suitable for practical applications. Certain polymers are transparent in the near-infrared range (1000–1100 nm). In such cases, additives are necessary [24-25]. Increasingly, thermoplasts are added to the marking paint, pigments. Inorganic pigments, such as color effect pigments, are often added to plastic resins as additives for laser marking applications. The well-distributed pigment particles within the plastic resin matrix absorb the incoming laser radiation and transfer the resulting heat to the surrounding polymer molecules of the resin. High pulse power and short interaction time are commonly used for laser beam marking. This thermal influence leads to carbonized black marking or light marking (foaming) depending on the polymer type. Due to their specific dispersion as particles, inorganic pigments are held in place by the macromolecular structure, hindering migration, unlike organic dyes [26]. When choosing a laser marking system for a specific application and material, for example polyamide, several factors need to be taken into account, including power density, thermal properties such as thermal conductivity, heat capacity, melting point, and heat of vaporization, as well as reflectivity, including material factors, wavelength, and temperature [29].

TABLE 2 CLASSIFICATION PHYSICAL PROPERTIES OF POLYMERS INFLUENCED BY LASER IRRADIATION DURING LSM[29]

Polymer	Glass-transition temp, T _g (°C)	Melting point (°C)	Ultimate tensile strength (MPa)	Yield tensile strength (MPa)	Thermal conductivity (W/mK)	Specific heat capacity
PTFE	-97	330	33.6	11.6	0.27	1.4
PP (isostatic)	+100	160	13.8-460	12-43	0.11-0.44	1.92
PS	90-95	240	44.9	43.9	0.14	2.1
PMMA (atactic)	+105	270	75.0	75.4	0.2085	1.46
Nylon 6,6	+57	250	73.1	45-63.6	0.26	2.2
LDPE	-20	110	11	10.8	0.3	2.2
HDPE	-90	120-140	30.5-35	26-33	0.48	1.9
PP (atactic)	-18	160	36.8	30.7	0.11	2.0
PC	+150	288-316	64	62	0.2	1.2
PE	+69	260	51.8		0.05	1.87
PVC	+87	100-260	1.38	55	0.190	0.84-1.17
PSU	+190	332-371	72	74.9	0.22	1.2
PEEK	+140	+340	110	98.8	0.25	2
PVDF	-37.6	160	42.8	44-48	0.19	1.5

High molecular weight polyamides have become incredibly important in practical applications, particularly in the production of nylon fibers. One of the most commonly used polyamides in this context is the one created through the condensation of hexamethylene

diamine and adipic acid, known as "66 polymer". In the abbreviated naming system for polyamides created from diamines and dibasic acids, two numbers are used to signify the number of carbon atoms in the diamine and dibasic acid, respectively. For instance, the polymer created from hexamethylene diamine and sebacic acid ($\text{HOOC}(\text{CH}_2)_8\text{COOH}$) is named "6,10". The focus is on the high tensile strength of the fibers, which closely resemble natural silk, and the high melting points of the polyamides in comparison to polyethylene (for example, 66 nylon melts at 250°C , but while polyethylene melts at 115°C). It is presumed that these characteristics are somehow linked to forces between the polar groups in the molecules. It's expected that there are hydrogen bonds between the $\text{C}=\text{O}$ groups of one molecule and the NH groups of its neighboring molecules. Furthermore, polyamides are of interest due to their connection to proteins: the grouping $-\text{CO}-\text{NH}-$ is present in both types of substances [27]. But there are other types of polyamide. For instance, one part is polylaulactam, a material with a high molecular weight. It is known as polyamide 12 (PA 12) and is used in various industrial applications. The other part in each belongs to a group of segmented polymers with the following chemical structure Fig. 4.

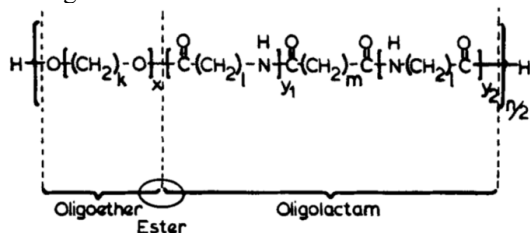


Fig.4. Chemical structure of polyamide (PA12) [27]

A single unit of the structure is made up of a relatively short chain of a type of nylon. This component has the ability to form crystals and is known as the hard section due to its high melting point. The other component comprises a short chain of tetrahydrofuran molecules (with an average molecular weight of 1000 g/mole). This part is considered the soft section because it has a low glass transition temperature and contains a low level of crystalline structure. The hard and soft sections are connected together through an ester linkage facilitated by a dicarboxylic acid [28], [29].

VI. CONCLUSIONS

Today, various lasers are used to label plastics. They can include fiber lasers, solid state lasers, and gas lasers. However, in most cases, 1064 nm fiber lasers are used for marking thermoplastics. The main parameters affecting the results of the natural marking process are contrast, the structure of the material, and the color of the material. These parameters depend on the settings of the laser system. When marking, it is important to know not only the parameters of the laser system but also the physical characteristics of the labeled material. For example, a thermoplastic material like polyamide has a white color, which complicates the marking process. A "gold

standard" for polyamide labeling has still not been found, as dyes are often used in the labeling process to facilitate it. However, these additives can alter the physical structures and properties of polyamide.

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