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A review: thermal degradation of polymethyl methacrylate: a metallurgical perspective on fiber and CO_2 laser exposure

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Abstract

This paper presents a thorough examination of the thermal deterioration of polymethyl methacrylate (PMMA) influenced by fiber and CO_2 lasers, investigating their unique metallurgical and thermal effects. The elevated energy density of fiber lasers results in quick and highly targeted heating, enabling speedy material removal and ablation. Nonetheless, this quick heating causes considerable surface roughness, microfractures, and extensive molecular degradation, undermining the material's structural integrity. In contrast, CO_2 lasers, distinguished by their longer wavelength, provide wider and more uniform heat distribution throughout the PMMA surface. This yields a more refined surface finish with enhanced degradation control, however at a reduced processing speed. The review examines the unique thermal distribution patterns generated by each laser type, investigating the development of heat-affected zones (HAZs) and the particular degradation mechanisms occurring inside these zones. The study examines the metallurgical alterations caused in the PMMA structure, focusing on aspects such as chain scission, depolymerization, and the generation of volatile byproducts. Experimental results demonstrate that fiber lasers are optimal for high-velocity material removal procedures where surface finish is not paramount, but CO_2 lasers are favored for applications requiring superior surface precision and less heat damage. These discoveries include substantial industrial ramifications for several industries, including automotive, optical, and medical device manufacture. The analysis closes by examining ways for optimizing laser parameters, including power, pulse length, and scanning speed, to attain a balance among processing efficiency, material integrity, and desired product quality in PMMA manufacturing.

Keywords: *Polymethyl methacrylate (PMMA), thermal degradation, fiber laser, CO_2 laser, metallurgical analysis, laser-induced degradation, heat-affected zone (HAZ), material processing, surface quality.*

1. Introduction

PMMA, known as acrylic or plexiglass, is a clear thermoplastic or added a pigmentation with unique properties that find wide applications within many industries of different structures shown in Figure 1. It possesses excellent optical clarity, high mechanical strength, and good resistance against environmental factors like UV radiation and weathering. For this reason, it is suitable for use in the automotive and aerospace industries, medical devices, buildings, and construction industries, which require durability and transparency [1]. Besides, PMMA is lightweight and easy to mold and process; these features extend the application areas to manufacturing optical lenses, display screens, and even bone cement in orthopedic operations [2]. However, like many polymers, thermal exposure is critical for the performance of PMMA, especially in high-temperature applications like laser processing.

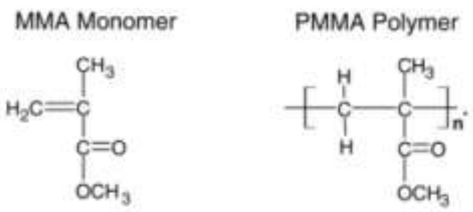

Fig. 1: The chemical structure of the Polymethyl methacrylate [3].

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1.1. Importance of thermal degradation in polymers

For polymer-based product performance, safety, and longevity, heat degradation of polymers, notably PMMA, must be understood. Thermal regulation degrades polymers and permanently alters their mechanical, optical, and chemical characteristics [4]. Thermal breakdown of PMMA may include depolymerization, resulting in volatile methyl methacrylate monomers. Both reactions may discolor, damage polymer structure, and decrease mechanical integrity. This understanding is crucial in aircraft and medical device sectors, where heat exposure may cause catastrophic material breakdown.

In the context of laser exposure, when PMMA is treated under the conditions of concentrated thermal energy, an understanding of the degradation mechanism will be instructive in optimizing various processes such as laser cutting, welding, and 3D printing [6]. With the increasing use of PMMA in additive manufacturing and advanced fabrication techniques, studying its thermal degradation will improve the material's thermal stability and widen its applicability at high temperatures [7].

1.2. Relevance of laser exposure

Material processing is where laser technologies, with the help of fiber and CO_2 lasers, have obtained huge importance due to their ability to deliver energy with high precision and concentration. This allows for effective cutting, engraving, and welding treatments with good efficiency of various materials, including polymers. Processing PMMA by laser provides certain advantages regarding precision, less material waste, and the possibility of complicated processing geometries. Examples of lasers normally used for PMMA include fiber lasers, which are very powerful and efficient, and CO_2 lasers, which perform extremely well in cutting non-metallic materials [8].

However, such intense laser beams greatly induce thermal effects in PMMA. The energy provided by the laser could lead to local thermal decomposition, altering the structure of the polymer molecule and its superficial properties. Due to their higher power density, fiber lasers may lead to considerably faster degradation rates than might be induced by lower power density CO_2 lasers but within an expanded heat-affected zone [5]. From a metallurgical viewpoint, the heat distribution effect on the material at a micro level plays an important role in understanding how laser exposure impacts PMMA regarding structural integrity and functionality.

1.3. The objective of the review

This Review aims to comprehensively review the thermal degradation of PMMA and its specific interest in exposure to concentrated heat from fiber and CO_2 lasers. The thermal degradation mechanisms will be reviewed for PMMA and laser heating-induced metallurgical effects, and several laser types will be compared concerning their thermal and structural effects on the polymer. This Review is focused on the metallurgical and thermal perspectives with the hope that such insights will find further applications in improving the performance and reliability of PMMA-based materials in high-temperature applications, particularly where precision laser processing becomes particularly important.

The Review will discuss the most important findings of research works, analyze the results of experimental and theoretical investigations, and provide recommendations to optimize the thermal stability of PMMA under laser irradiation conditions. This knowledge would allow a deeper understanding of the degradation mechanisms and give useful recommendations to all industries that use lasers to process polymer materials.

2. Review topics

2.1. Thermal degradation mechanisms in polymers

Thermal degradation is one of the most important limiting factors to performance, durability, and safety among polymeric materials in various applications. Thermoregulation can be defined as a non-reversible change in a polymer's chemical structure and physical properties upon exposure to high temperatures. These are manifested by mechanical strength reduction, discoloration, and generating volatile products from degradation processes [9].

From the molecule viewpoint, the thermal degradation of polymers is a process of chain breaking that, at the end of the process, usually yields small molecules in the form of gases, liquids, or low-molecular-weight compounds. [10] This is caused by the scission of the polymer backbone, initiated either by an oxidation reaction, depolymerization, or chain scission, depending on the type of the polymer and operating conditions. It is common in polymer systems that are exposed to heat in the presence of oxygen, whereby the polymer undergoes a free-radical reaction that often results in the formation of carbonyl compounds and other such oxidative products. Depolymerization involves the breakdown of polymers into their monomer units; this is noted to occur in some thermally sensitive materials, such as the PMMA, which depolymerizes into methyl methacrylate [11].

Another important degradation mechanism involves chain scission, which includes breaking the main chain in the polymer due to heat-induced stress. The degradation leads to a reduction in molecular weight and hence brings down the mechanical and thermal properties of the polymer. In most cases, chain scission is accompanied by crosslinking reactions. Crosslinking exhibits another way of influencing the integrity of polymers through the build-up of a structure of interconnected polymer chains, causing a loss of flexibility or processability in the material [12]. The dominance of crosslinking is higher in the

polymer exposed to repeated thermal cycles, in which the free radicals formed during degradation form a bond between chains.
Those affecting the rate and mechanism of thermal degradation include the chemical structure of the polymer itself, additives it may contain, and environmental ones. A typical example is that polymers with very stable backbone structures, such as aromatics, usually exhibit higher thermal stability than aliphatic polymers. Other additives, including flame retardants or stabilizers, can also inhibit or promote degradation depending on the influence of the susceptibility of the polymer to thermal stress [13]. Other environmental conditions include exposure to oxygen or humidity, which are important factors that decide the degradation pathway.
In the case of PMMA, thermal degradation, which mainly occurs by depolymerization, involves the breakdown of the polymer into its monomeric form, methyl methacrylate, above 200 °C. This happens more effectively when the polymer is subjected to strong heat sources, such as laser radiation, which causes localized heating and initiates the breakdown of the molecular chains. Understanding thermal degradation in polymers is very important, especially in laser applications, when working out the limitations of various materials and optimizing their performance in industrial processes.

2.2. Metallurgical aspects of PMMA degradation

Whereas traditionally, metallurgy has been associated with studying metals, it has much to offer insight into the degradation processes of such varied materials as polymers, like PMMA. Metallurgical principles are quite germane to understanding how thermal and mechanical stresses influence the microstructure and behavior of materials when exposed to elevated temperatures, as in the case of laser-induced degradation. Considering the degradation mechanism of PMMA, the knowledge of metallurgy comes in handy in analyzing the effects of heat distribution, phase changes, and molecular interactions on the structural integrity of the polymer [14].
The thermoplastic polymer PMMA still shows some behavior when obtaining more concentrated heat sources like fiber and CO_2 lasers. Such local heating by lasers can influence its conformation and even lead to its degradation through changes in molecular structure. The metallurgical approach to analyzing the described process embraces the effects of heat on material interactions, changes to the microstructure, and mechanical properties of PMMA through HAZ. This would include phase transformations and grain boundary evolution in metals, while polymers like PMMA, thermal depolymerization, and chain scission would be considered [15]. Heating creates several molecular instabilities that induce chain breakdown, yielding material weakening and thermal degradation.
One of the very crucial metallurgical features in the degradation of PMMA is the analysis of various heating rates and thermal gradients affecting the polymer. Such rapid heating, as produced by fiber lasers, may induce localized stresses within the material, leading to nonuniform degradation and even crack or mechanical failure. The cracks are like the microstructural defects appearing in metals being thermally cycled quickly. This is due to internal stresses developing by differential expansion and contraction. In PMMA, the rapid heating by the laser might well create surface defects, such as pitting or bubbling, as the polymer's molecular chains degrade with volatile byproduct release [16].
Moreover, research on wear and friction in PMMA, particularly when reinforced with additives such as carbon nanotubes, has shown mechanical enhancement of thermal degradation. In a manner analogous to metals, in which the resistance to wear can be altered due to heat-induced phase transformations, PMMA exhibits changes in its friction properties as the material degrades under thermal stress [17]. This interplay between thermal and mechanical wear becomes highly relevant for many applications where PMMA is usually subjected to thermal cycling and mechanical loading, such as in aerospace or automotive components.
The other important factor from the metallurgical point of view is the heat distribution that occurs during the processing of PMMA using the laser. In metals, the melting and consequent solidification caused by the laser result in a heat-affected zone, a fusion zone, and the base material. In polymers like PMMA, no such melting and solidification occur in the classic sense of the word, but the heat causes considerable molecular rearrangements [14]. Depending on their intensiveness and duration, they may cause new chemical bonds or the breaking of already existing ones.
The metallurgical examination of PMMA deterioration also considers additives or coatings used to increase thermal stability. PMMA may be coated with different materials to increase thermal stability or mechanical performance at high temperatures [17]. Like metallurgical coatings on metals, these coatings may prevent disintegration by absorbing and dissipating heat. PMMA is exposed to concentrated heat energy in laser machining and additive manufacturing, making this concept relevant.

2.3. Laser-Induced thermal effects

The interaction of concentrated thermal energy with PMMA due to laser exposure is the introduction of great thermal effects, especially in the case of fiber and CO_2 lasers. Both fiber and CO_2 lasers are well utilized in material processing owing to their high precision and ability to concentrate energy over small areas. In contrast, their differences are huge regarding energy concentration, heat distribution, and the subsequent effects on PMMA while understanding their effect on the thermal degradation of the polymer.

2.4. Energy concentration of fiber and CO_2 lasers

The high-energy-density delivery of fiber lasers is appropriate for applications that require precise material processing; thus, cutting and engraving are some of the preferred applications. The wavelength at which fiber lasers operate is near-infrared, approximately 1.070 nm and such a wavelength allows deeper penetration within the material PMMA. Such a high-energy concentration allows fiber lasers to heat very localized areas rapidly, thus enabling efficient material removal and forming hotspots that can lead to the aggravation of thermal degradation in PMMA [19]. Considering the higher energy density of the fiber laser, molecular breakdown in PMMA occurs much faster. It initiates depolymerization and chain scission more rapidly than lower-energy lasers.

CO_2 lasers, however, operate at 10.6 micrometers, a wavelength highly absorbed by non-metallic materials like PMMA. Greater absorption efficiency promotes more homogeneous thermal energy dissipation along the surface of the polymer. CO_2 lasers will give great results in cutting and engraving PMMA. Their longer wavelength generates heat in a larger area, so the degradation could be slower than fiber lasers since the process may be more controlled [20]. In the case of CO_2 lasers, during exposure, the distribution of heat is much more widespread; localized overheating is less likely to happen, but its corresponding heat-affected zone has increased.

2.5. Heat distribution and its impact on PMMA

The heat distribution around the time of processing with a laser has a great effect on the response of PMMA to focused thermal energy. In such fiber lasers, while the delivery is focused, the HAZ is relatively small but at exceedingly high temperatures. These lead to local thermal stresses that can develop material defects like microcracks or surface pitting in PMMA. These defects occur because of the fast expansion and contraction of the material under intense and concentrated heat, just like what would happen to metals in laser welding conditions [21]. In most instances, localized degradation in PMMA from fiber lasers would generate gaseous byproducts that normally form bubbles or voids in the material. These further compromise the structural integrity of the material.

By contrast, CO_2 lasers spread the heat more evenly over a large area and, thus, minimize the risk of local thermal stress. Their wider heat dispersion allows materials to be treated more smoothly and with minimal surface defects or microcracks. The disadvantage of using a CO_2 laser is that the more gradual heat-up could translate into longer exposure to heat, which, if not properly controlled, could still have significant thermal degradation. Long exposure to heat may cause gradual weakening of the chains in a polymer, hence a reduction of the mechanical strength over time, generally for PMMA [22].

2.6. Comparative effects on PMMA

These are due to differences in energy concentration and the method of heat distribution by fiber and CO_2 lasers. Fiber lasers are more liable to rapid thermal degradation characterized by depolymerization and the release of volatile degradation products because of their high-power density. Because of that, fiber lasers will be more effective in applications requiring high ablation rates in materials, though this results in a long-term compromise on the material's structural integrity [23]. As a result, rapid heating associated with the fiber laser can result in higher surface roughness and greater thermal damage in sensitive or precision applications in PMMA.

On the other hand, in CO_2 lasers, this degradation process is far more gradual and controlled; hence, CO_2 lasers would be more suitable for applications where surface quality needs to be preserved. Due to their low energy concentration, CO_2 lasers develop slower thermal degradation rates. This limits the destruction of the material and thus is ideal for processes requiring smooth finishes, like engraving or cutting intricate designs on PMMA [20]. However, the larger heat-affected zone during CO_2 laser processing may expose a greater volume of material to heat, possibly affecting its long-term thermal stability if a process is not monitored carefully.

The thermal degradation of polymers is a multifaceted process affected by several processes, such as oxidation, depolymerization, chain scission, and crosslinking (Table 1). These processes are influenced by parameters like temperature, oxygen availability, the polymer's chemical composition, and the presence of additives. Laser processing entails further issues concerning energy concentration and thermal dispersion. Fiber lasers, characterized by their elevated energy density, induce quick, localized deterioration, whereas CO_2 lasers, with a longer wavelength, produce more gradual and extensive heating. Comprehending these processes is essential for forecasting polymer behavior under heat stress and refining material selection and production parameters.

Table 1: The thermal degradation mechanisms in polymers

Degradation Mechanism	Description	Contributing Factors	Effects on Polymer	Example
Oxidation	Reaction with oxygen, leading to free radicals and oxidative products (e.g., carbonyl compounds).	Presence of oxygen, high temperatures	Chain scission, discoloration, changes in mechanical properties	Common in polymers exposed to heat in air.
Depolymerization	Breakdown of polymer chains into monomer units.	Thermally sensitive polymers, high temperatures	Reduction in molecular weight, release of monomers (gases or liquids)	PMMA depolymerizing into methyl methacrylate above 200°C.
Chain Scission	Breaking of the main polymer chain due to heat-induced stress.	High temperatures, thermal stress	Reduction in molecular weight, decreased mechanical and thermal properties	Often accompanied by crosslinking.
Crosslinking	Formation of bonds between polymer chains.	Heat, free radicals	Loss of flexibility, reduced processability	More prevalent with repeated thermal cycling.
Laser-Induced Degradation (Fiber Laser)	Rapid, localized heating due to high energy density.	High energy density, short wavelength	Rapid depolymerization, chain scission, microcracks, surface pitting, release of volatile byproducts, smaller HAZ	Precise material processing, cutting, engraving.
Laser-Induced Degradation (CO_2 Laser)	More homogeneous heating due to longer wavelength and greater absorption.	Longer wavelength, greater absorption	Slower degradation, larger HAZ, potential for long-term thermal instability if not controlled.	Cutting and engraving where surface quality is paramount.

2.7. Experimental and theoretical studies on PMMA degradation

Because of the wide use of PMMA in industry, medicine, and science, its response to laser-induced degradation has been widely studied. Thus, several experimental and theoretical works have focused on mechanisms, effects, and optimizations of laser processing in PMMA surfaces. The laser-induced degradation of PMMA is primarily driven by thermal effects, which induce changes in the polymer's chemical structure, surface properties, and mechanical behavior. Several important works that have explored these phenomena describe how changes in laser parameters can influence PMMA degradation and surface modifications; we review those in this section.

2.7.1. Experimental studies on laser-induced PMMA degradation

One recent laser-induced PMMA degradation study employed femtosecond laser irradiation to regulate hydrophobicity on PMMA surfaces. Wang et al. (2020) examined how laser parameters affect PMMA's surface microstructure and hydrophobicity. Femtosecond laser irradiation may create micro and nanostructures on PMMA, which changes its wettability [24]. Thermal deterioration from laser irradiation created surface roughness and increased hydrophobicity. This study demonstrates that regulated laser degradation may optimize PMMA functioning for anti-reflective coatings and self-cleaning surfaces.

Other works by Wang and Song in the year 2022 further developed a hydrophobic prediction model of PMMA surface characteristics. By investigating the interaction between laser parameters, including pulse duration and energy density, the authors could predict what condition the surface of PMMA would be after femtosecond laser processing [25]. The study provided further insight into how laser-induced degradation influences the polymer's surface structure and hydrophobicity. These findings are important in optical devices, where surface properties should be treated carefully to enhance performance and durability.

2.7.2. Theoretical studies on PMMA ablation mechanisms

Another interesting aspect of PMMA degradation is the process of laser ablation, a process in which material is removed from the surface because of heating induced by laser radiation. Li et al. (2024) theoretically and experimentally studied the laser ablation mechanism of PMMA microchannels with one- and multi-pass scans. It turned out from this study that the degradation and ablation efficiency of PMMA was closely related to the number of laser passes and applied power density. Multi-pass laser scanning induced deeper ablation with greater material removal, while single-pass scanning could induce more controlled shallow ablation [26]. This work, therefore, provides an overview of laser parameter optimization involved in the precision microfabrication of PMMA, relying highly on the control of degradation toward the attainment of desired features in the structure.

Regarding this point, Muller et al. studied the nonlinear optical properties of PMMA-based nanocomposites after exposure to laser radiation for potential applications in optical limiting. The authors synthesized and characterized PMMA-based nanocomposites concerning changes in the optical properties due to laser-induced degradation [27]. Experimental findings showed that the laser-induced degradation of PMMA can be employed as a tool, in fact, for preparing materials with enhanced optical properties and, accordingly, broader applicability, for instance, in photonic devices and optical coatings.

Table 2 summarizes key experimental and theoretical studies on laser-induced PMMA degradation. Experimental studies have focused on surface modification using femtosecond lasers, demonstrating the ability to control hydrophobicity and predict surface characteristics based on laser parameters. Other experimental work has shown the potential for laser-induced degradation to enhance the optical properties of PMMA nanocomposites. Theoretical and experimental research on laser ablation has explored the relationship between laser parameters, such as the number of passes and power density, and the resulting ablation depth and material removal. These studies highlight the importance of understanding and controlling laser-induced degradation for various applications, including surface modification, microfabrication, and the development of advanced optical materials.

Table 2: Experimental and theoretical studies on PMMA degradation

Study Type	Focus	Key Findings	Implications/Applications	Authors (Year)
Experimental (Surface Modification)	Effect of femtosecond laser irradiation on PMMA surface microstructure and hydrophobicity.	Laser irradiation creates micro/nanostructures, increasing surface roughness and hydrophobicity.	Optimizing PMMA for anti-reflective coatings and self-cleaning surfaces.	Wang et al. (2020)
Experimental (Predictive Modeling)	Relationship between femtosecond laser parameters (pulse duration, energy density) and PMMA surface characteristics.	Developed a model to predict PMMA surface condition after laser processing.	Enhancing performance and durability of optical devices by controlling surface properties.	Wang and Song (2022)
Theoretical & Experimental (Ablation)	Laser ablation mechanism of PMMA microchannels with single and multi-pass scans.	Multi-pass scans lead to deeper ablation and greater material removal; single-pass scans allow for more controlled, shallow ablation.	Optimizing laser parameters for precision microfabrication of PMMA.	Li et al. (2024)
Experimental (Optical Properties)	Effect of laser-induced degradation on nonlinear optical properties of PMMA-based nanocomposites.	Laser-induced degradation can enhance optical properties.	Expanding applicability of PMMA in photonic devices and optical coatings.	Muller et al.

3. Key findings on laser-induced wettability changes

Another important research direction is studying the effects of laser-induced degradation on PMMA surface wettability. Wang and Song (2021) conducted experiments on the wettability of PMMA surfaces bearing irregular square column structures fabricated with a femtosecond laser. It was presented that laser-induced thermal degradation can be used to control the surface roughness, and thus, the contact angle of the water droplets over the surface was also varied accordingly [28]. These experiments provided a platform to predict changes in the surface properties of PMMA induced by laser processing, potentially suitable for applications requiring precise control of material wettability, such as in microfluidic devices and biomedical implants.

3.1. Comparison of fiber and CO_2 lasers

With laser technologies being used in material processing, especially fiber and CO_2 lasers, specific advantages and disadvantages exist regarding a particular material and its application. PMMA is among those materials for which a choice between fiber and CO_2 lasers shows great differences in thermal degradation, surface quality, and mechanical properties. Whereas both types of lasers work on different principles, their effects are very different regarding thermal behavior, degradation mechanisms, and PMMA performance. In this section, a comparative analysis will be made between the fiber and CO_2 lasers and their respective influences on the thermal degradation of PMMA.

3.2. Wavelength and energy absorption

One of the fundamental differences between fiber and CO_2 lasers is wavelength and energy absorption in PMMA material. Fiber lasers operate at a much shorter wavelength, around 1.070 nm, which lets them concentrate energy in a very small area and produce high power density. PMMA has less absorption at this wavelength, so fiber lasers tend to be more penetrating inside the material, causing localized thermal effects [29].

At some of the localized regions of the PMMA, because of high energy concentration, rapid temperature rise is possible, leading to molecular breakdown through depolymerization and chain scission, which creates faster degradation in the case of fiber laser processing.

On the other hand, CO_2 lasers are of a much longer wavelength at 10.6 µm, where PMMA has extremely high absorption. This high absorption allows the thermal energy in PMMA to be distributed more effectively onto its surface by the CO_2 laser. This results in a wider HAZ with more gradual heating. This minimizes the possibility of overheating in a localized area, yet the overall exposure to thermal energy is higher, and degradation can still be induced for extended processing times [30].

The larger thermal input also influences the superficial finish, with smoother finishes obtained compared to the treatments made with fiber lasers, which normally tend to result in rougher surfaces because of their more aggressive thermal effect.

3.3. Heat-Affected Zone (HAZ) and material damage

The HAZ in materials is represented by the area that undergoes any alternation induced by heat development upon laser processing. The high-density energy of fiber lasers creates smaller HAZs, though they are known to produce higher peak temperatures. This results in fast thermal degradations characterized by crack, bubble, and surface roughness formation due to speedy expansion and contraction under heat stress [31]. The small HAZ saves the area from degrading, but the severity in that area is much more serious than CO_2 lasers.

However, whereas CO_2 lasers cause larger HAZs owing to wider thermal energy absorption by PMMA, this heating is way slower and more uniform. This method reduces the chance of cracks and surface flaws because less severe stress builds up but increases susceptibility to gradual degradation in material strength since it is exposed to more prolonged heating. In contrast, the destruction of the local area is not as heavy, but it influences a larger volume of material and, therefore, can lead to long-term stability deterioration inside the polymer structure [29]. This makes CO_2 lasers more suitable for applications with surface smoothness and precision requirements, but fiber lasers should be preferable for deeper material penetration and high-speed processing.

3.4. Surface finish and quality

The surface quality after laser processing strongly depends on the laser used. Due to their higher energy density and localized heating, fiber lasers tend to give rougher surfaces with more pronounced thermal degradation. A very fast temperature increases leads to vaporization and thermal cracking of PMMA; hence, further post-processing may be required on these surfaces to achieve the required smoothness. Moreover, the most disadvantageous feature of fiber lasers is that they can create surface pitting in applications that require high optical clarity or smooth finishes.

Laser type substantially affects surface quality following laser processing. Fiber lasers provide rougher surfaces with more thermal deterioration due to increased energy density and targeted heating. Fast temperature rises cause PMMA evaporation and thermal cracking; therefore, these surfaces may need post-processing to achieve smoothness [32]. The biggest drawback of fiber lasers is that they may cause surface pitting in applications that need excellent optical purity or smooth surfaces.

PMMA surfaces are smoother with CO_2 lasers due to broader, homogenous heat dispersion. CO_2 lasers are good for engraving since their thermal deterioration process is slower, preventing large faults or fractures. This tradeoff is because the slower degradation process may fail in high-speed material removal, particularly for deep cuts with extensive details [30].

3.5. Speed and efficiency

Regarding material removal and processing speed, fiber lasers can offer shorter processing times due to the higher energy density. That will allow the fiber laser to ablate PMMA at higher speeds, which makes it suitable for high-speed applications in cutting and drilling. However, faster removal also means increased thermal degradation and poorer surface quality. Generally, industrial applications allow using fiber lasers when speed and throughput are more important than surface aesthetics.

The energy density is, however, lower for CO_2 lasers, which makes the material removal process slower. This finally allows for finer control over the degradation process. Since the removal rate is slower, CO_2 lasers would be more effective in applications requiring precision with minimum damage to the material, such as engraving and surface texturing [32]. The reduced degradation rate allows removing the material in a controlled way to retain the integrity of the surface. This reduces further finishing processes.

4. Review results

4.1. Observed metallurgical changes in PMMA

Although a polymeric material is normally studied within a different framework from metals, there are significant metallurgical changes in PMMA following laser exposure. Conversely, the application of metallurgical principles in studying the microstructural and physical changes has been quite useful, especially in laser processing contexts. The study focused on the response of PMMA subjected to both fiber and CO_2 laser irradiation; under such conditions, it was observed that thermal degradation-induced changes come with serious structural changes to the material, at least at a molecular level.

Amongst the several observations, generating microstructural defects like surface cracks, pitting, and voids due to rapid heating and cooling cycles during laser processing holds a front position. Fiber lasers generate unusually high energy concentrations over a tiny area, thus inducing localized thermal stresses leading to crack generation and surface roughening [29]. Such defects are like the microstructural changes in metals under severe thermal cycling when their rapid expansion and contraction lead to stress-induced cracks. The mechanical integrity of PMMA is decreased with the appearance of these cracks, affecting suitability for applications where structural stability is an issue.

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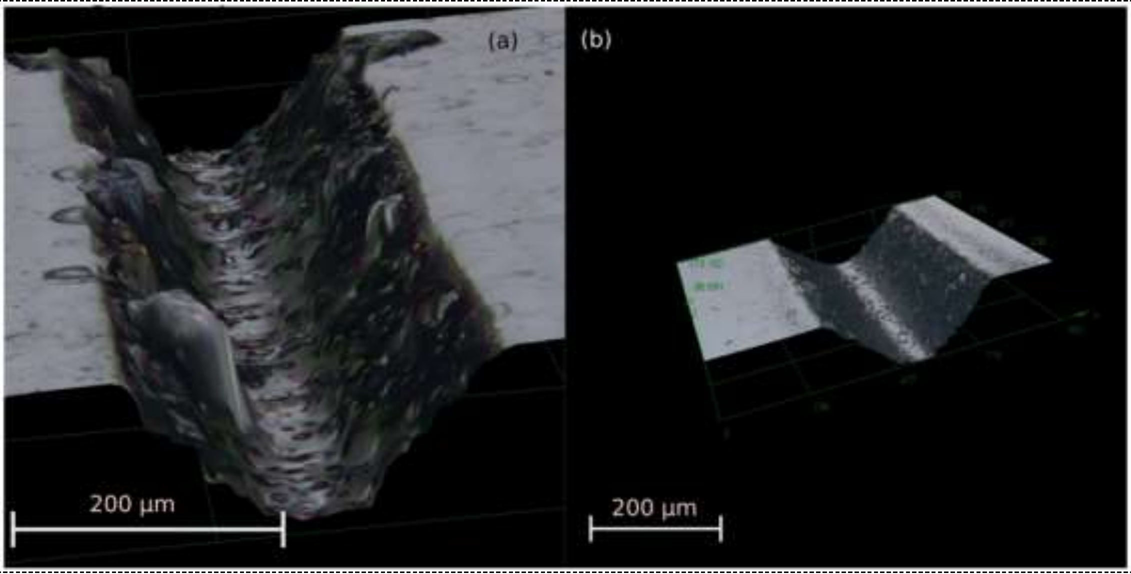

Fig. 2: An enlarged microscopic image of a 200 µm depth microchannel fabricated using (a) multi-pass processing and (b) defocused processing [31].

Rapid heating and cooling cycles during laser processing cause microstructural flaws such as surface cracks, pitting, and voids. Fiber lasers create significant energy concentration in a small region, and localized thermal strains cause cracks and surface roughening. Microstructural changes in metals during intense temperature cycling cause stress-induced fractures during fast expansion and contraction. Cracks reduce PMMA's mechanical integrity, making it unsuitable for structurally unstable applications [30].

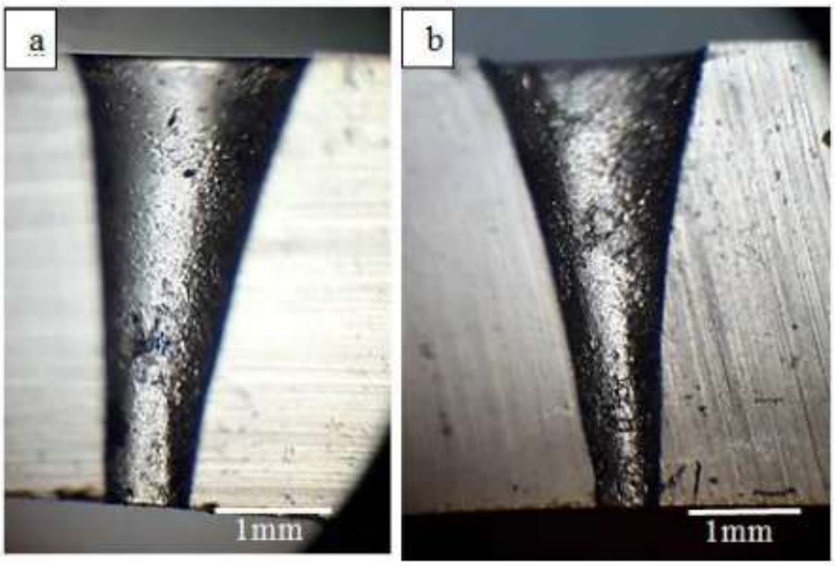

Fig. 3: Hole cross section at 707(W/cm2) power density: (a) 0.2 s exposure time and (b) 0.4s exposure time [30].

The hydrometallurgical changes in PMMA after exposure to the laser underline that the parameters of the laser should be controlled with extreme care to lessen the defects on its surface and the degradation of molecules. Both fiber and CO_2 lasers induce significant structural changes in PMMA; however, the nature and extent of such changes would also depend upon the laser type and exposure conditions.

4.2. Thermal distribution and degradation patterns

The thermal energy distribution during laser processing is a critical factor that dictates the degradation pattern. In the laser processing of PMMA, fiber, and CO_2 lasers have different heat application modes, resulting in different material degradation profiles. This knowledge of thermal energy distribution on both the surface and subsurface layers of the material becomes imperative for predicting and controlling the degradation process in PMMA.

4.3. Fiber laser thermal distribution

Because of their high energy density, fiber lasers deliver concentrated heat, which increases the temperature in a very small area. Therefore, this concentrated energy results in rapid temperature increases that promote immediate thermal degradation by depolymerization and chain scission. Heat is delivered into an extremely small volume of material; the temperature gradients are sharp between the zone reached by the laser and the rest of the material. Therefore, these gradients assist in developing HAZs that show intense material damage in the irradiated area. The degradation of PMMA caused by a fiber laser is characterized by the fast vaporization of the ablated polymer, creating bubbles, pits, and voids [29].

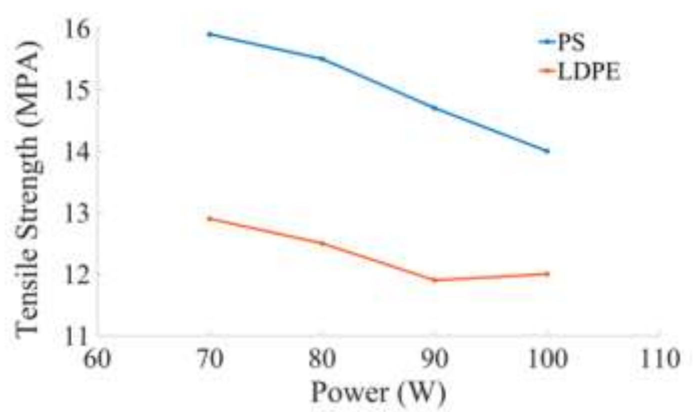

Fig. 4: Parametric trend to indicate the effect of the power on tensile strength break for PS and LDPE [29].

It is one of the patterns well recognized in the degradation of fiber lasers through distinct zones comprising a central ablation area where the material is removed and a heat-affecting zone where thermal damage extends radially from the ablation site. PMMA often undergoes its molecular breakdown within such a heat-affecting zone, leading to discoloration, reduced mechanical strength, and surface roughness [30]. Besides that, these effects are significantly enhanced in the case of the processing with fiber lasers due to high thermal gradients, which makes it difficult to achieve smooth and consistent surface finishes without additional post-processing. The rapid heating-cooling cycle may induce residual stresses in the material, further complicating its thermal stability and longevity.

4.4. CO_2 laser thermal distribution

In contrast, the CO_2 laser provides a more uniform heat distribution with its longer wavelength highly absorbed by PMMA. The consequence is that heat will spread over a larger area, reducing localized heating intensity and hence giving control to the degradation process. The slower heating rate causes more gradual depolymerization of the PMMA molecular chains to yield smooth surface finishes and fewer microstructural defects. On the other hand, the broader heat distribution signifies that a greater amount of material volume is exposed to thermal energy that could deteriorate gradually with the increase in time, especially if the laser exposure is long [31].

Wide heat-affected zone with reduced severity of material damage characterizes the degradation patterns produced by CO_2 lasers. The gradual heating prevents the formation of large cracks or pits, but the overall thermal exposure can still result in a loss of tensile strength and flexibility of the material. The extended heat distribution influences the polymer's optical properties, as the material is usually rendered less transparent after long CO_2 laser exposure. This is due to the reorganization of the polymer chains, which also form subsurface defects that scatter light and reduce clarity.

4.5. Performance and degradation efficiency of fiber vs. CO_2 lasers

There are large differences in performance and degradation efficiency when fiber and CO_2 lasers apply to PMMA due to their operating principles, wavelengths, and thermal effects. Each type of laser has pros and cons concerning processing speed, energy efficiency, precision, and the degree of degradation they impart to PMMA.

4.6. Fiber laser performance and degradation efficiency

Operating at a shorter wavelength of about 1.070 nm, the fiber lasers must focus much more energy in a much smaller area than that achievable by carbon dioxide lasers; hence, they provide high energy density. Moreover, this results in heating, which is highly localized, and capable of treating PMMA much faster. This is one of the reasons why fiber lasers prove highly efficient in tasks related to removing materials, such as cutting, drilling, and engraving. The fast heating causes effective ablation, which is very useful in those high-precision applications where time is of the essence. However, this efficiency comes at the price of more serious thermal degradation [29].
Because the energy is concentrated, fiber lasers give rise to steep temperature gradients; hence, the loci of molecular breakdown in PMMA are confined. Its main degradation mechanism is depolymerization, where the polymer chains break down into smaller volatile compounds. This results in a fast degradation process characterized by the increase of bubbles, cracks, and voids because of the rapid vaporization of the material. Degradation in fiber lasers is very effective; it results in a higher degree of surface roughness and the possibility of structural damage, especially in areas needing precision in sensitive areas [30].

4.7. CO_2 laser performance and degradation efficiency

PMMA absorbs greater heat at 10.6 µm, resulting in a more uniform heat distribution. Though slower than fiber lasers, CO_2 lasers frequently surpass them in surface quality. Progressive heating ensures regulated breakdown without quick depolymerization. CO_2 lasers are appropriate for applications requiring high surface accuracy with little material damage because they reduce surface flaws and smooth the finish [6].

Fig. 5: The microscope pictures the strongest and weakest joints [6].

Since CO_2 lasers ablate material slower than fiber lasers, their degradation efficiency is lower. HAZ fractures and microstructural flaws are rare because Thermal Shocks are less targeted. When PMMA mechanical integrity is important, slower degradation processes minimize residual stresses, making CO_2 lasers better.

4.8. Key comparisons

4.8.1. Speed and precision

Fiber lasers are quicker and more effective in high-material-removal applications but cause greater heat damage. CO_2 lasers process slowly but provide better surfaces with less heat damage.

4.8.2. Surface quality

CO_2 lasers treat flat surfaces better than fiber lasers. Thus, CO_2 lasers are superior for optical components and healthcare equipment surface aesthetics and functionality.

4.8.3. Degradation efficiency

Fiber lasers erode PMMA faster but may harm its structure. CO_2 lasers deteriorate evenly and smoothly but slowly.

4.9. Implications for industrial applications

The results show a significant difference in the efficiency and performance of fiber and CO_2 lasers because of degradation. The difference in performance and efficiency between fiber and CO_2 lasers is important to industries that depend on PMMA and laser processing. Proper laser type for any application is found by balancing the need between speed, precision, surface quality, and material integrity.

4.10. High-speed processing and cutting applications

Industries such as automotive, aerospace, and manufacturing employ fiber lasers for high-speed material removal. Fiber lasers will be suitable for cutting PMMA parts where precision is required without major concerns about the surface finish. The production of PMMA parts used in automotive light systems stands to benefit from this method because such parts can easily and efficiently be cut into very complex shapes. However, the enhanced thermal degradation must be steered by the critical choice of laser parameters like power density and pulse duration to keep the surface defects minimum and the structural stability intact [29].

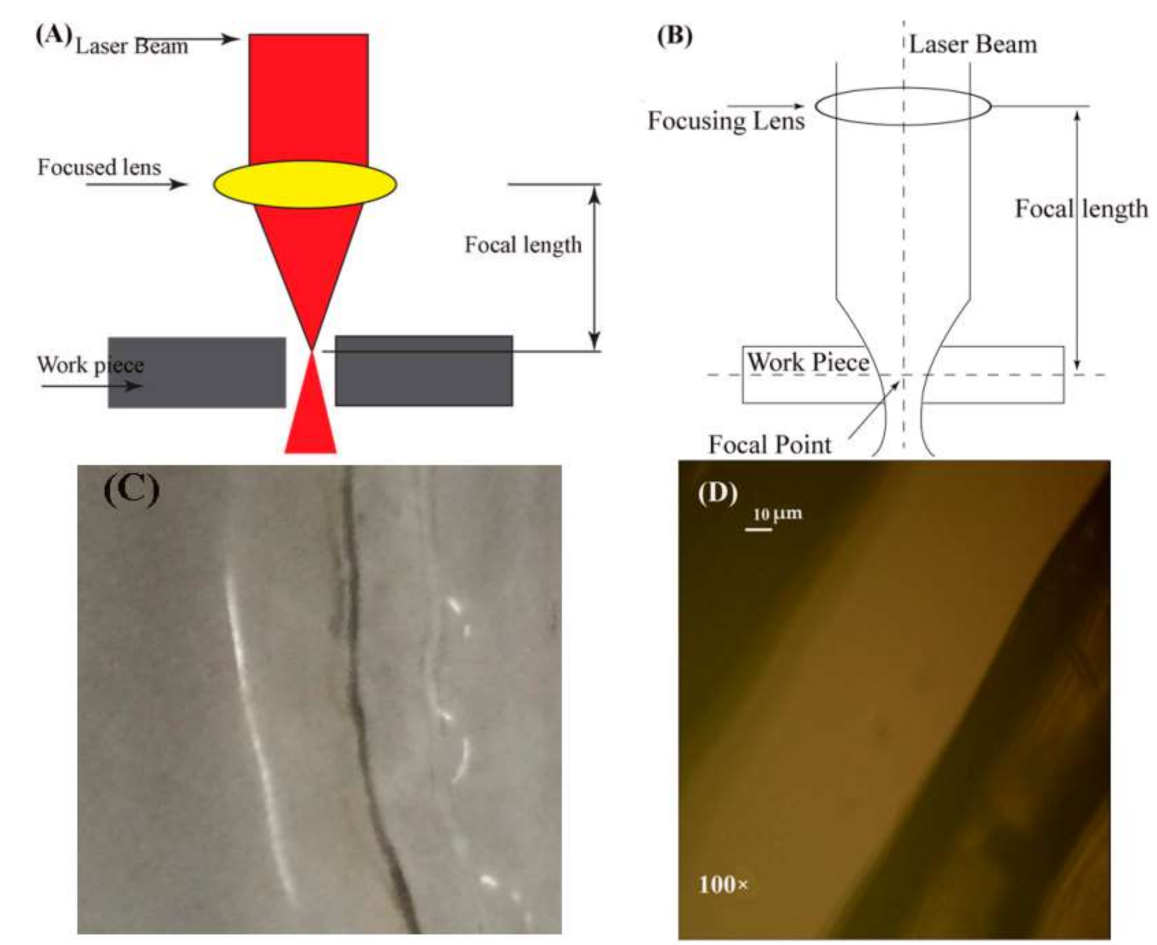

Fig. 6: (A and B) schematic demonstration of focal point positions and standoff distances when cutting in a laser, (C) Physical examination; and (D) microsopic examination of the cut part at the higher standoff distances [29].

4.11. Precision applications and surface-sensitive industries

CO_2 lasers work harmoniously with industries relying heavily on surface quality and precision. Applications involving optics, display manufacturing, and medical devices frequently require PMMA to maintain optical clarity and smooth surface properties. For example, during the manufacturing process for optical lenses or display screens, it would be appropriate for CO_2 lasers to act with the required precision, ensuring minimal surface roughness and thermal damage for the material properties to retain their optical characteristics [30]. Besides these, CO_2 lasers find their application in the manufacturing of medical devices, particularly those in which PMMA is a standard material used for prosthetics and dental appliances. Extensive post-processing may not be necessary with the smoother surface finish provided by a CO_2 laser; hence, it saves time and reduces costs.

4.12. Tradeoffs in additive manufacturing and microfabrication

Fiber lasers are paramount in additive manufacturing and microfabrication industries, much like CO_2 lasers. Generally, fiber lasers are used in micro-drilling and engraving of PMMA owing to their high precision and quick degradation efficiency. This makes it priceless during the production of microfluidic devices, given that the technology allows for finer channel creation faster. However, surface roughness and structural damage risk necessitate some post-processing steps to ensure device functionality.

Conversely, where complex designs on PMMA require smooth surfaces and tight tolerance, such as in the fabrication of microchannels for lab-on-a-chip devices, CO_2 lasers are preferred. The slower degradation process of CO_2 lasers ensures that the material has maintained its structural integrity, an essential property to ensure functionality at those very small-scale components.

4.13. Long-Term material stability and durability

For industries where the longevity and stability of the PMMA parts are imperative, again, the advantages of CO_2 lasers lie in the aspect of a more controlled thermal degradation process. Since the smoothing of the surface finish and reduced thermal stress in the materials contribute to its longer service life, applications in construction, signage, and large-format displays can take advantage of the processes utilizing CO_2 lasers. Slower processing time does not matter when it concerns these three applications since they do not require speed but rather durability and surface aesthetics.
The tradeoffs in choosing between fiber or CO_2 lasers in this industrial application domain about PMMA are speed, surface quality, and degradation efficiency. The fiber laser turns out best for applications that require high speeds in the ablation of material, while CO_2 lasers ensure high precision of the surface quality, which is good enough for industries dealing in optical and medical areas. It permits the identification of the influence of each type of laser on PMMA degradation, thus enabling industries to optimize the balance between efficiency and material integrity illustrated in table 3.

Table 3: Comparative Table of Laser Effects on PMMA

Comparison criteria	Fiber laser	Co_2 laser
Wavelength	~1,070 nm (near-infrared)	~10.6 µm (infrared)
Energy distribution	Highly localized; high energy density	Broader and more uniform distribution
Thermal degradation mechanism	Rapid depolymerization; chain scission	Gradual depolymerization; less severe
Heat-affected zone (haz)	Small but intense, with steep gradients	Larger but more uniform and controlled
Surface finish	Rough, with pitting, cracks, and voids	Smooth, with minimal surface defects
Processing speed	Faster material removal (high-speed cutting)	Slower but allows precision and control
Structural damage	Greater localized damage; mechanical stress	Minimal structural damage over a large area
Applications	High-speed cutting, engraving	Surface-sensitive industries, engraving

5. Conclusion

This paper examined the metallurgical and thermal deterioration of PMMA under concentrated heat energy from fiber and CO_2 lasers. Fiber and CO_2 lasers were compared for energy concentration, heat dispersion, and impacts on PMMA structural and surface characteristics. Fiber lasers remove material quickly and penetrate deeper, but they cause heat deterioration, surface roughness, fissures, and molecular disintegration. Though longer to process, CO_2 lasers can manage heat distribution, producing cleaner surface finishes with fewer material flaws. Metallurgical research shows that laser-induced thermal stress alters PMMA microstructure and mechanical characteristics. Fiber lasers caused more localized yet severe damage, whereas CO_2 lasers caused more progressive deterioration. These results may affect industrial applications where speed, accuracy, surface quality, and material lifespan must be considered when choosing between fiber and CO_2 lasers. However, fiber lasers will become increasingly significant for high-speed cutting or engraving in the automotive and aerospace industries, where speed is crucial. Optics, medical devices, and microfabrication benefit from CO_2 lasers' accuracy and beauty. CO_2 lasers may also manage PMMA's structural integrity over time in applications that demand long-term endurance and little post-processing. The Review emphasizes PMMA degradation processes and material responses with various lasers. Industries may optimize PMMA processing by using carefully chosen parameters for individual application demands, improving product efficiency and quality. Laser technologies and new methods should be developed and refined to reduce heat deterioration and maximize laser-based material processing advantages.

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