

Femtosecond Laser Internal Modification of Hot-Extruded Polymethylpentene

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Abstract

This study investigates the application technology of near-ultraviolet femtosecond laser pulse inscription inside polymethylpentene. We discovered that this thermoplastic material exhibits polarization-sensitive characteristics. First, inscription experiments employed a lens with a numerical aperture of 0.05 for focusing. Through analysis of the supercontinuum spectrum, the laser pulse power for stable filamentary inscription was measured to be in the range of 2.2MW - 9.2MW. From this, the nonlinear refractive index of this material was inferred to be $n_2 = 2 \times 10^{-16} \text{ cm}^2/\text{W}$, and the third-order susceptibility $\chi^{(3)}$ was calculated to be $1.1 \times 10^{-14} \text{ esu}$. The stable filamentary processing length ranges from 300 m-1500 m. Subsequently, the experiment utilized a composite objective lens with a numerical aperture of 0.4 to inscribe a Bragg grating with a thickness of $\sim 700 \text{ m}$ and a grating period of 5 m. Through diffraction efficiency testing of the fabricated grating, the maximum refractive index change was inferred to be ~ 0.01 , which represents an order of magnitude improvement over recorded data in literature. Experimental results demonstrate the importance of laser pulse peak intensity for inducing nonlinear absorption, while two-photon absorption constitutes the physical mechanism for mild and controllable modification. This work provides up-to-date references for researchers and for the design and fabrication of optical devices.

Full Text

Internal Modification of Thermal-Extruded Polymethyl Pentene by Femtosecond Laser

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Abstract

This work investigates the application of near-ultraviolet femtosecond laser pulses for internal inscription and modification in polymethyl pentene (PMP) polymeric material. The experiments reveal polarization sensitivity in this thermoplastic material. Using a lens with numerical aperture (NA) of 0.05, we analyze the supercontinuum spectrum and determine that the laser pulse power for stable filamentation processing ranges from 2.2 MW to 9.2 MW. From this, we infer the nonlinear refractive index of PMP at 387 nm to be $n_2^{387} = 2 \times 10^{-16} \text{ cm}^2 \text{ W}^{-1}$, and calculate the third-order susceptibility ⁽³⁾ as $1.1 \times 10^{-14} \text{ esu}$. The stable filamentation processing length varies from 300 μm to 1500 μm . Using a compound objective with NA = 0.4 to focus and inscribe Bragg gratings, we measure the diffraction efficiency to infer a maximum refractive index change of ~ 0.01 , which is one order of magnitude higher than values reported by other research groups. The experimental results demonstrate the critical importance of laser pulse peak intensity for inducing nonlinear absorption, with two-photon absorption identified as the physical mechanism for mild and controllable modification. This work provides up-to-date reference data for researchers and optical device designers.

Keywords: femtosecond laser; polymethyl pentene (PMP); filamentation; supercontinuum

1. Introduction

Polymethyl pentene (PMP) is a lightweight, low-density thermoplastic material with promising optical applications. For high-value parabolic surfaces, thermal extrusion molding can directly form the material, replacing traditional mechanical cutting, grinding, and polishing processes. Additionally, this relatively inexpensive material can substitute for costly glass substrates, thereby enhancing the feasibility of large-scale production. Optical fibers or components fabricated from PMP offer the advantages of chemical inertness and robustness, making it a candidate material for disposable sensor devices in clinical medicine, biology, and chemical applications. The optical properties of PMP are particularly noteworthy. Lytle et al. investigated the optical transmission characteristics of PMP in the 0.4–40 μm range and found that, compared to other polymer materials, PMP exhibits a broad transmission band with good performance even in the far-infrared domain [1]. It is conceivable that femtosecond laser-induced fila-

mentation modification within PMP could enable the fabrication of high-value waveguides or diffractive optical elements while inheriting the excellent optical properties of the bulk material.

While femtosecond laser internal modification techniques for polymer materials such as polymethyl methacrylate (PMMA) are relatively well-established [2-7], studies on PMP remain scarce. PMP is the only crystalline transparent plastic with an extremely low dielectric constant, and these unique characteristics may influence femtosecond laser filamentation effects within the material, presenting many unknown aspects that warrant investigation.

2.1 Filamentation and Supercontinuum Generation in Nonlinear Optics

Femtosecond (fs) pulses can generate nonlinear physical filamentation phenomena (also called “light filaments”) in propagation media. This occurs through alternating Kerr self-focusing and plasma defocusing effects, forming a plasma channel [8]. The onset of self-focusing requires the femtosecond laser’s peak power to exceed a critical threshold [9], given by:

$$P_{cr} = \frac{\pi(0.61)^2\lambda_0}{8n_0n_2} \quad (1)$$

where n_0 is the linear refractive index, n_2 is the nonlinear refractive index, and λ_0 is the vacuum wavelength. Laser beam self-focusing resembles focusing through a positive lens, with the total refractive index expressed as:

$$n = n_0 + n_{2I} \quad (2)$$

The filamentation threshold corresponds to the critical value for self-focusing [10,11]. During self-focusing, as intensity increases, a small number of electrons in the conduction band (seed electrons) generate a weak free-electron plasma through nonlinear multiphoton ionization. The electron density of this plasma increases exponentially along the radial direction of the beam’s transverse mode (typically Gaussian), creating a negative lens effect. Consequently, the increasing electron plasma density causes beam defocusing. Bloembergen established the connection between supercontinuum (SC) generation and filamentation in nonlinear optics, experimentally demonstrating that the supercontinuum arises from self-phase modulation during the alternating focusing and defocusing processes [12]. The spectral broadening from self-phase modulation results from the time-dependent refractive index change $\Delta n/T$. Under stronger illumination, avalanche ionization occurs, producing enhanced effects that generate broader white-light continuum. Notably, self-focusing exhibits material dependence, requiring a bandgap energy $E_g > 2.8$ eV [13]. In most media, the threshold peak power for supercontinuum generation is on the order of megawatts (10^6 W) [14].

2.2 Experimental Setup

The experiments employed a femtosecond laser source (Clark MXR CPA 2010) delivering pulses at $\lambda = 775$ nm with a 1 kHz repetition rate. The single-pulse duration (FWHM) was ~ 170 fs at optimal performance. The output beam had an average power of 1 W, corresponding to 1 mJ per pulse. The main optical path, shown in Figure 1, incorporated a diffractive optical attenuator (DOA) for intensity adjustment. A BBO crystal converted the 775 nm near-infrared light to 387 nm near-ultraviolet light with maximum conversion efficiency of 15%, while rotating the linear polarization direction by 90° . A spatial light modulator, controlled by computer-generated Zernike correction holograms [16], partially compensated for phase errors and wavefront tilt-induced aberrations. A 4f system composed of two positive lenses L1 and L2 housed a fast mechanical shutter (NEWPORT 846 HP, minimum exposure time 1 ms) at the focal plane of L1. A periscope elevated the beam height from 110 mm to 230 mm to accommodate subsequent optics. The PMP sample was mounted on a 3-axis CNC stage (Aerotech). Auxiliary optical paths included a beam sampling path (red dashed box in Figure 1) and a supercontinuum spectral sampling path (black dashed box). In the beam sampling path, a thin-film beam splitter extracted 10% of the optical energy for beam profile measurement using an advanced wide-field beam analyzer (Spiricon), enabling optimization of the laser transverse mode via the spatial light modulator. In the supercontinuum spectral sampling path, the vertically polarized laser beam transmitted through the sample was focused, then attenuated (using dielectric-coated mirrors near Brewster's angle), and coupled into a fiber optic delivery system to an advanced time-gated spectrometer (Andor Shamrock SR 303i). The spectrometer data acquisition was synchronized with the TTL trigger signal from the Pockels Cell driver of the femtosecond laser's chirped pulse amplification system, with a 2 ns delay between the trigger and spectral acquisition. In subsequent experiments, we sampled reflected signals using a mirror; detailed configurations are described in previous work [17].

Figure 1. Schematic of the experimental setup. The red dashed box indicates the beam transverse mode sampling path, and the black dashed box indicates the supercontinuum spectral sampling path.

The PMP raw material used in the experiments was thermal-extruded rod stock, shown in Figure 2(a). The raw material was cold-machined into cylindrical blocks coaxial with the central axis, then cut into rectangular blanks (18 mm $\times$ 20 mm $\times$ 10 mm). The preset beam propagation direction was perpendicular to the cylindrical cross-section. Blanks were hand-polished on front and back surfaces to produce test samples. Polishing was performed on a glass grinding base (THORLABS CTG 913) using a sequence of four abrasive sheets (THORLABS alumina abrasive sheets: 5 μ m, 3 μ m, 1 μ m, and 600 nm) with water assistance. The final polished surface achieved optical-grade roughness. Figure 2(b) shows a macroscopic photograph of a polished sample. During polishing, the material was found to be prone to scratching, causing surface damage as shown in the

microscopic image in Figure 2(c), likely due to bulk removal of polymer chains.

Figure 2. (a) PMP rod, (b) final polished sample, and (c) scratch damage on polished surface.

Figure 3 presents analysis of the polished sample using a simplified polarization dialysis method. By rotating a linear polarizer, pronounced polarization sensitivity was observed as an axial-symmetric petal pattern with a visual glare effect, indicating different lattice arrangements within the petal pattern compared to other regions. This creates anisotropy issues for incident light. For internal processing along horizontal and vertical directions, circularly polarized light should be used, while anisotropy-induced errors must be considered when fabricating PMP optics via single-pass extrusion molding.

Figure 3. Polarization glare effect exhibited by PMP quasi-crystalline material under rotation of a linear polarizer.

3.2 Critical Threshold for Self-Focusing

The optical path configuration is shown in Figure 1 and described in previous work [17]. Experiments used a single-element calcium fluoride positive lens with 50 mm focal length to focus the near-ultraviolet ($\lambda = 387$ nm) laser beam. The spectrometer was configured with a 100 μ m entrance slit for real-time maximum signal acquisition. The sample translation speed was 1 mm/s. As shown in Figure 4, at pulse energy $E_p \sim 0.7$ J/fs, a sharp peak was observed at the central wavelength of 387 nm with bandwidth ~ 2.5 nm (Full Width Half Maximum), corresponding to the 5 nm bandwidth peak observed at 775 nm near-infrared wavelength, consistent with second harmonic generation. The characteristic spectrum from femtosecond pulses matches anti-Stokes broadening. Our region of interest (ROI) was set to 340–370 nm. In Figure 4, the spectral signal for linear polarization is significantly higher than for both circular polarization states, which show minimal difference; this must be considered when evaluating polarization-dependent errors in the experimental optical path.

Figure 4. Anti-Stokes broadening spectra generated by femtosecond pulses with linear, left-circular, and right-circular polarization. The region of interest (ROI) is set to 340–370 nm.

Figure 5 shows scatter plots from ten experimental runs. In regions I and II, spectral signal growth in the ROI is relatively stable, representing weak plasma generation with few photon signals, indicating self-focusing phenomena. In region III, avalanche ionization produces numerous photon signals. Through interpolation, the threshold peak power and pulse energy for self-focusing are determined as $P_{th0} = 2.2 \pm 0.6$ MW and $E_{th0} = 0.4 \pm 0.1$ J, while the avalanche ionization threshold is $P_{th0} = 9.2 \pm 0.6$ MW and $E_{th0} = 1.7 \pm 0.1$ J. Compared with the previously measured $P_{th0} = 1.1$ MW in PMMA [6], this is higher by approximately one order of magnitude but within the same order. In region I, weak plasma formation occurs primarily through

multiphoton absorption [18]. Photon energy plays a crucial role in the order of multiphoton absorption. PMMA has a bandgap of 4.58 eV, representing the minimum excitation energy for electron transition from valence band (VB) to conduction band (CB). PMP's bandgap is ~6.2 eV, requiring two-photon coupling at 387 nm to generate free electrons. Consequently, the self-focusing threshold in PMP is higher than in PMMA. From this we infer the nonlinear refractive index of PMP at 387 nm to be $n_2^{387} = 2 \times 10^{-16} \text{ cm}^2 \text{ W}^{-1}$, and calculate the third-order susceptibility $^{(3)}$ as $1.1 \times 10^{-14} \text{ esu}$. For optimal filamentation processing, operation in region II is recommended, with pulse power selected within the 2.2–9.2 MW range.

Figure 5. Scatter plot of photon counts in the ROI (quantum efficiency ~15) versus pulse energy E_p .

3.3 Single-Element Convex Lens Focusing (NA < 0.1)

Figures 6(a) and 6(b) show filamentation modification using a convex lens with numerical aperture 0.05 (focal length FL = 50 mm) from two perspectives. The laser beam propagation in PMP material is visible as a faint blue channel, with scattered light likely originating from grain boundaries in the quasi-crystalline material. The advantage of using a single-element calcium fluoride lens is that femtosecond laser pulses do not experience pulse duration broadening from group velocity dispersion (GVD) effects [19], and pulse width is a critical parameter for filamentation modification [20]. In ultrafast laser processing, lattice-electron temperature coupling occurs on a ~1 ps timescale. When pulse duration is below 180 fs, optical energy can directly couple into the filamentation region, enabling adiabatic localized modification.

Figure 6. (a) and (b) Refractive index modification processing in PMP. Laser wavelength $\lambda = 387.5 \text{ nm}$, single-element convex lens (focal length $f = 50 \text{ mm}$, NA ~ 0.05), sample translation speed 0.5 mm/s.

Numerical aperture (NA) plays an important role in filamentation, serving as an effective parameter dependent on the focusing optic. For NA > 1, supercontinuum generation cannot occur [21], and optical breakdown is highly probable. The Rayleigh length for Gaussian focusing is:

$$R_L = \frac{\pi n_0 w_0^2}{\lambda}$$

where w_0 is the beam waist. Without filamentation, the processable length of a focused Gaussian beam would be $2R_L = 2 \times \pi n_0 w_0^2 / \lambda = 362 \text{ m}$.

Figure 7 shows the filamentation modification results. The maximum filament length achieved was $1530 \text{ m} \gg 2R_L$ (~362 m), while the minimum length approached $2R_L$. Filament lengths ranged from 300 m to 1500 m. The laser beam originated from the right side, with the starting point clearly located before the geometric focus, moving closer to the source with increasing energy—

consistent with previous studies [22]. This demonstrates that the filamentation mechanism enables longer processing lengths. The filament length follows a power-law relationship with pulse energy with exponent ~ 0.53 , approaching the theoretical value of 0.5 from Zverev and Pashkov's work [15]. Focusing with $NA < 0.1$ is suitable for inscribing waveguides and other optical elements.

Figure 7. Microscopic side view of filament modification morphology. Filament length follows a power-law relationship with pulse energy with exponent ~ 0.53 .

3.4 Compound Objective Focusing ($NA \sim 0.4$)

High-NA objective focusing is suitable for precision optical device inscription. Figure 8(a) shows internal modification using a specialized compound objective with $NA \sim 0.4$ (THORLABS LMU-20X-NUV). The optical element features anti-reflection (AR) dielectric coatings on the entrance face to enhance UV transmission, measured at 99%. For high-NA applications, optical breakdown effects must be considered. Breakdown does not produce filamentation but directly damages the material, creating voids and carbonization. Note that such microscope objectives consist of multiple optical materials, and positive group velocity dispersion (GVD) can cause pulse broadening [20]. Filamentation is a third-order nonlinear effect where pulse duration is a critical factor. Figure 8(b) shows a side-view microscopic image of a volume Bragg grating (VBG) approximately 690 μm thick and 3 mm wide, with line density 200 lines/mm and grating period $\Lambda = 5 \mu\text{m}$. Using a 532 nm laser at Bragg incidence, the first-order diffraction efficiency was measured as $\pm 1 \sim 39.8\%$. Figure 8(c) demonstrates the diffraction effect, and Table 1 lists measured background and diffraction order intensities. The first-order diffraction efficiency matches Kogelnik's theoretical model [24]:

$$\eta_{\pm 1} = \sin^2 \left(\frac{\pi \Delta n L}{\lambda \cos \theta_B} \right)$$

where L is grating thickness, λ is probe wavelength, and θ_B is Bragg angle. However, due to the pulse duration ($\tau = 180 \text{ fs}$), material breakdown occurred, limiting the observed diffraction efficiency by scattering. This result infers a refractive index change $\Delta n \sim 0.01$, one order of magnitude higher than that achieved with low-NA lens inscription.

Figure 8. (a) Internal inscription using near-UV compound objective with $NA \sim 0.4$; (b) Side-view microscopic photograph of a $\sim 690 \mu\text{m}$ thick volume Bragg grating; (c) First-order diffraction test using 532 nm laser at Bragg incidence.

Table 1. Volume Bragg grating diffraction efficiency test measurements

Parameter	Value
Background light (mW)	-

Parameter	Value
Diffraction efficiency ()	39.8%
Order 1 (+) (mW)	39.0%
Order 0 (+) (mW)	40.5%
Order 1 (-) (mW)	-
Δn	~ 0.01

4. Summary

The PMP raw material used in experiments exhibits polarization-sensitive glare effects. For 180 fs pulse duration, the measured thresholds for self-focusing are $P_{\text{th}0} = 2.2 \pm 0.6$ MW and $E_{\text{th}0} = 0.4 \pm 0.1$ J, while avalanche ionization thresholds are $P_{\text{th}0} = 9.2 \pm 0.6$ MW and $E_{\text{th}0} = 1.7 \pm 0.1$ J. From these measurements, we infer the nonlinear refractive index of PMP at 387 nm to be $n_2^{387} = 2 \times 10^{-16}$ cm²W⁻¹, and calculate the third-order susceptibility ⁽³⁾ as 1.1×10^{-14} esu. The 387 nm photons in PMP generate free electrons through two-photon coupling, forming weak plasma.

Using a lens with NA ~ 0.05 for filamentation modification, the maximum filament length ranges from 300 μ m to 1500 μ m. For a Bragg grating inscribed with a compound objective (NA ~ 0.4), testing with a 532 nm laser on a 690 μ m thick grating with 5 μ m period yielded a first-order diffraction efficiency $\pm_1 = 39.8\%$. This result infers a refractive index change $\Delta n \sim 0.01$, one order of magnitude higher than that achieved with low-NA lens inscription.

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