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Influence of ordering change on the optical and thermal properties of inflation polyethylene films

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Abstract

Changes of thermal diffusivity inside femtosecond laser-structured volumes as small as few percent were reliably determined (with standard deviation less than 1%) with miniaturized sensors. An increase of thermal diffusivity of a crystalline high-density polyethylene (HDPE) inflation films by 10-20% from the measured value in regions not structured by femtosecond laser pulses is considerably larger than that of non-crystalline polymers, 0-3%. The origin of the change of thermal diffusivity are interplay between the laser induced disordering, voids’ formation, compaction, and changes in molecular orientation. It is shown that laser structuring can be used to modify thermal and optical properties. The birefringence and infrared spectroscopy with thermal imaging of CH2 vibrations are confirming inter-relation between structural, optical, and thermal properties of the laser-structured crystalline HDPE inflation films. Birefringence modulation as high as Δn ∼ ±1 × 10−3 is achieved with grating structures.

Key words: thermal diffusivity, femto-second laser structuring, polymers, high density polyethylene

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1. Introduction

Studies of thermal and optical properties of femtosecond (fs) laser-structured amorphous polymers [1] showed that optical properties can be strongly altered by stress-induced (or relaxed) birefringence [2] without detectable carbonization when tightly focused femtosecond laser pulses are used and a low < 103 Hz repetition rate exclude defect and thermal accumulation between pulses [3]. The thermal diffusivity in the fs-laser structured volumes was found affected by air diffused into the voids at the fs-laser irradiated locations. The influence of chemical modifications and structural changes on thermal properties, however, was difficult to separate within thermal diffusivity changes of a few percent. In contrast, crystalline sapphire exhibited strong ∼ 10% changes in thermal diffusivity [4]. For the voids created inside sapphire by single fs-laser pulses, there were no possibility for outside air to enter the voids. Moreover, thermal conductivity of sapphire is orders of magnitude larger than that of air and polymers. Changes in thermal properties can be linked to the order-disorder change at the laser modified-micro volumes or densification. The contribution of the side and back-bone chains on thermal properties of crystalline polymers upon compaction is not well established. It prompted this investigation of thermal properties in fs-laser modified volumes of crystalline polymer hosts. The
Fig. 1. (color online) Setup (a) and thermo-sensor (b) used for measurements of thermo-diffusivity in micro-volumes. Sample (see, (c)) is placed between ITO heater and the sensor which are brought into mechanical and thermal contact with the sample by micro-screws. (c) Shows orientation conventions of the inflation polymer film (c-axis is the plan extrusion direction, called machine direction). We used high density polyethylene (HDPE, see inset in (c)) inflation films of $d = 27 \, \mu m$ thickness; the diameter of sensors was $12.5 \, \mu m$.

advantage to use ultra-short laser pulses is due to reduced probability of chemical modifications as was demonstrated in the case of PMMA [2].

Here we report on a comparative study of thermal diffusivity, infra-red (IR) spectroscopy, and optical imaging of fs-laser structured crystalline high density polyethylene (HDPE). We observed molecular alignment and ordering change induced by fs-laser pulses. Thermal diffusivity is increased up to 20% considerably larger than in amorphous polymers where air diffusion into the laser fabricated voids can explain an increase by a few percent.

2. Samples and methods

The crystalline HDPE films were prepared by the inflation process in Sumitomo Chem. Ltd. The inflation or a bubble blowing method provides 2D extrusion in contrast to the conventional 1D extrusion of the film. The thickness of the films was $27 \, \mu m$. The HDPE is chemically linear polymer with polymer chains oriented by the inflation method. Such 2D-blown films are optically more transparent as compared with the bulk and 1D-extruded HDPE; hence more suitable for optical modifications.

Micro-scale fabrication inside HDPE film was carried out with $0.5 - 2 \, \mu m$ pitch, by 30-100 nJ pulses of 800 nm wavelength and 150 fs duration. The objective lens of numerical aperture $NA = 1.42$ was used. Entire thickness of the film was filled with alternating layers [4] to maximize the modified volume. Two types of structures were recorded: (i) the lateral ($c, b$) and axial ($a$) spacings were $2 \times 2 \times 2.5 \, \mu m^3$ with a half lateral period alternating in each layer (the opal-like structure) and (ii) $0.5 \times 2 \times 2.5 \, \mu m^3$ and $2 \times 0.5 \times 2.5 \, \mu m^3$ grating type structures aligned in to perpendicular directions. The optical birefringence was measured by Abrio polariscope. The thermal diffusivity was determined using a micro-scale thermo-electric sensor by the thermal wave (TW) [5,6] method. Figure 1(a,b) shows setup of the TW measurements.

The differential polarization dependent IR absorption spectroscopy and imaging of fs-laser structured regions was used to determine molecular alignment changes; details will be reported elsewhere. To quantify orientation changes the Herman’s function $f = (3 \cos^2(\theta) - 1)/2$ has been calculated at the peaks specific for the CH$_2$ rocking and bending absorption bands at ~ 720, 1460 cm$^{-1}$, respectively; here $\theta$ is the angle with a chosen direction. When $f = 1$ the polymer chains are aligned to the chosen direction and are random at $f = 0$. The crystallinity of the film was determined from the ratio of the 730 to 720 cm$^{-1}$ Raman modes [7–9] and was ~ 82%.

3. Results and discussion

The inflation processing is widely used in production of polymer films, in which melt is forced out off nozzle forming a bubble; the obtained plain film
The flow field direction defines the ordering in the polymer [10]. It is known that HDPE crystallizes forming alignment along c- and the a-axis orientations at high stress [9,11,7]. When the inflation film formation is applied to polymers which tend to crystallize, one would expect optical, mechanical, and thermal properties affected by the interplay of the imposed ordering by stress and spontaneous ordering due to crystallization.

is stretched in two directions along c and b-axes (Fig. 1). The flow field direction defines the ordering in the polymer [10]. It is known that HDPE crystallizes forming alignment along c- and the a-axis orientations at high stress [9,11,7]. When the inflation film formation is applied to polymers which tend to crystallize, one would expect optical, mechanical, and thermal properties affected by the interplay of the imposed ordering by stress and spontaneous ordering due to crystallization.

Molecular ordering influences thermal and optical properties of polymers. We used fs-laser structuring to modify polymer on the scale of ~1 – 2 µm with tightly focused laser pulses (Fig. 2). Different contrast at different orientation of the cross-polarized Nicol prisms ((a) vs. (b)) signifies changes of refractive index which is different for the gratings recorded with π/2-shifted orientation (Fig. 2). At the used conditions voids were formed at the irradiation side with shock-compressed shells as it was used to make empty-core channels in PMMA [12]. The polymers are modified on a micro-scale and ultra-fast thermal quenching is favorable to “freeze” molecular orientation and to reduce probability of chemical modifications.

Polariscope measurements were carried out to quantify the birefringence and distribution of the azimuthal axis as we reported earlier in laser structured regions of sapphire [4]. Figure 3 summarizes the results for the regions A1 and A2. A strong modulation of birefringence, ∆n, was observed. The structure A2, where the grating planes are perpendicular to the polymer c-axis (machine direction) shows significant reduction of the birefringence (b). This is consistent with the randomization of the
polymeric ordering initially imposed by inflation-extrusion. Birefringence of the film is proportional to the orientational order along c-axis, \( O_c \), and reciprocal to that along a-axis, \( O_a \): \( \Delta n \propto \frac{O_a}{O_c} \). When the grating is recorded along the c-axis (region A1 in Fig. 2) the birefringence is enhanced, most probably, due to imposed ordering along the scan direction of the laser beam. It is known that thermal expansion of polymer main chain (c-axis) is smaller than that of a- and b-axes. The grating type structure along c-axis minimize the volume change with lower thermal expansion coefficient [13] and the higher thermal conductivity along c-axis.

The maximum thermal diffusivity change measured by setup shown in Fig. 1 was in the laser structured region B2 recorded by 100 nJ pulses. This pattern is an opal-like where the layers are alternating along the a-axis with a half lateral period shift; the periods were 2 \( \times 2 \times 2 \), \( \times 2 \), \( \times 50 \) \( \mu m^3 \) for the axes \( c-b-a \), respectively. Thermal diffusivity of unstructured HDPE inflation film is determined: \( (1.16 \pm 0.01) \times 10^{-7} \) m\(^2\)s\(^{-1}\). This value is consistent with the values of thermal diffusivity in different density and crystallinity films of HDPE [7]. Thermal diffusivity is decreasing as HDPE is changed from the bulk material into 1D films drawn by extrusion and, gets even smaller, in the 2D inflation films discussed here [14,15,7].

Figure 4 shows the normalized thermal diffusivity of regions structured by opal- and grating-like patterns. The scattering of data in Fig. 4 for the repeated measurements can be explained by slight differences in thermal contact due to surface roughness.

The polarized IR spectrum is correlated with the side chains CH\(_2\) rocking/bending orientation. The IR peak corresponding to molecular vibrations can be used to identify changes in the molecular orientation. An IR dichroism was observed in the region B2 (Fig. 5). It was found that fs-laser pulse irradiation with energy power > 65 nJ deformed orientation along the a- and b-axes confirmed by IR spectrum and imaging for the vibrations at 720-730 cm\(^{-1}\) and 1460-1470 cm\(^{-1}\) (Fig. 5), corresponding to the rocking and bending modes, respectively. Crystallinity of the film is proportional to the intensity ratio of 730- to 720 cm\(^{-1}\) modes [8]. Since small integral crystallinity changes were observed in the laser structured regions, < 3\%, (Fig. 5(b)), we can conclude that the main cause of the observed large birefringence alterations in the laser structured regions are due to the orientation (and densification) changes rather than those of crystallinity as discussed next.

Polarization dependence of the vibrational spectra were used for determination of the Hermans orientation function. A reduction up to 60\% in orientation for the 720 cm\(^{-1}\) was observed in the region B2, whereas for the A2 region (fabricated at 60 nJ; IR dichroism is present), the orientation function is unchanged with small changes of thermal diffusivity (Fig. 4). Correlation between the increase of the micro-scale thermal diffusivity (region B2) and reduction of orientation function of IR spectrum for side chains (CH\(_2\) rocking and bending) indicates that thermal diffusivity is influenced by the orientation relaxation.

Decrease of the CH\(_2\) side chain orientation along b-axis, which is correlated with the thermal diffusivity (Fig. 5), can also occur due to melting. When fs-laser irradiation is used at the irradiance larger than that of the void formation threshold > 50 nJ/pulse for the employed focusing, the shock-amorphisation and melting are expected. Due to ultra-fast thermal quenching, the amorphous phase can be “frozen” and retrieved to the ambient conditions. Creation of amorphous regions, which are more optically transparent, favors the establishment of a high birefringence contrast since \( \Delta n \propto \frac{O_a}{O_c} \) as discussed above.

The half-height birefringence variation, \( \Delta n \), and the Hermans orientation functions at 720 cm\(^{-1}\) are compared in Fig. 6. It is apparent that disorder (\( f \Rightarrow 0 \)) introduced the largest changes in the crystalline HDPE matrix. However, the disorder has caused an increase of thermal diffusivity. This can be explained by compaction and density increase due to change in molecular orientation [16–19], which favors an increase of thermal diffusivity [20].

4. Conclusions

It is demonstrated that thermal diffusivity through thin films of crystalline polymers can be measured with high fidelity. The value of thermal diffusivity of the inflation HDPE is \( (1.16 \pm 0.01) \times 10^{-7} \) m\(^2\)s\(^{-1}\) measured with a \( \sim 10 \) \( \mu m \)-diameter sensor. Femtosecond-laser structuring can be used to increase thermal diffusivity by \( \sim 20 \% \) mainly due to disordering revealed by IR absorption. The correlation between the increase of the micro-scale thermal diffusivity and the reduce of the orientation function of IR spectrum of side chains, CH\(_2\) rocking and bending, indicates that thermal diffusivity is influenced by the orientation relaxation.
in the polymer. Birefringence modulation as high as $\Delta n \sim \pm 1 \times 10^{-3}$ can be recorded with laser irradiation sites relaxing the main polymer orientation and/or inducing local change in ordering on a micro-scale. Possibility to increase and decrease local birefringence is prospective for number of optical applications.

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