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STUDYING THE POLYMERIZATION OF 2-(HYDROXYETHYL) METHACRYLATE USING LASER ULTRASONICS TECHNIQUES

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ABSTRACT

Biocompatible polymerized 2-(hydroxyethyl) methacrylate (pHEMA) is a very popular material for medical applications. Despite different studies, realised recently, there are still many questions to be answered concerning the polymerisation processes of HEMA upon compression, which does not require an initiator [1]. For this reason, the application of non-destructive contactless laser ultrasonic techniques to the evaluation of HEMA properties looks very promising. In this work, we present the measurements of longitudinal sound velocity in HEMA in a diamond anvil cell (DAC), using well known sub-nanosecond experimental set-up. First results obtained using picosecond ultrasonics are also presented. These results are compared then for a validation.

1. MEASUREMENTS IN HEMA USING SUBNANOSECOND EXPERIMENTAL SET-UP

First, experiments with HEMA monomer (mHEMA) in diamond anvil cell (DAC) were performed using subnanosecond laser ultrasonic pump-probe set-up [2]. This technique is based on the application of ~1 ns pulsed Nd:YAG laser working on 1.065 μm wavelength for the excitation of ultrasound pulses detected by a beam of 0.532 μm continuous laser, focused at known distance relative to the excitation beam. Both beams have a diameter of ~5 μm on the surface of material under the study. The photo of the high-pressure volume in a DAC, filled by mHEMA is shown in Fig. 1A. mHEMA and Fe opto-acoustic micro-generator are introduced in ~200 μm hole, drilled in the gasket. Typical signals in mHEMA at 2.75 GPa are shown in Fig. 1B.

The upper curve corresponds to the distance of 10.48 μm between the pump and probe beams. Then, the distance d has been increased with a constant step of 5.25 μm . Typical signals show the following ultrasonic pulses: skimming longitudinal wave in HEMA (SL) propagating along the interface with Fe, skimming transversal wave in HEMA (ST) along the interface, and mixed acoustic wave (SL-TT), skimming longitudinal wave in HEMA (SL) converted at certain distance to transversal wave in volume of HEMA (TT).

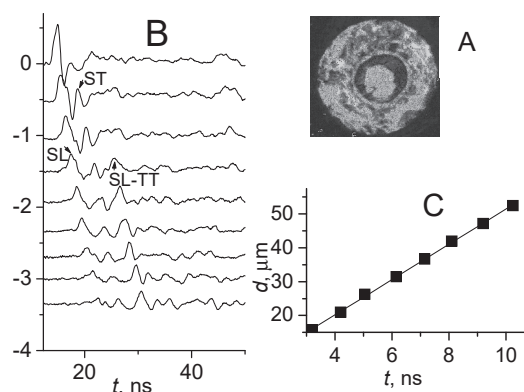


Fig. 1 **A**: Microscope image of the high-pressure volume in a DAC with mHEMA and Fe generator; **B**: Optoacoustic signals in mHEMA at 2.75 GPa **C**: Curves, used for the evaluation of sound velocity (squares – experimental points, black line – a linear fit) (B)

Then, we have used the arrival times of the pulses, corresponding to the SL wave in mHEMA to determine its sound velocity. For each position of the pump beam d , the arrival time t was determined to obtain the points traced in Fig. 1C. The linear fit to these points provided the sound velocity in HEMA. To obtain pHEMA, we compressed mHEMA to 11.5 GPa and then decompressed immediately to ~0.5 GPa. After 10 minutes at this pressure, the pressure was reduced to 0 GPa. This procedure led to the increase of the sound velocity, from 1.5 km/s in mHEMA to 3.0 km/s in pHEMA. The measurements by Raman spectrometry confirmed the polymerisation of HEMA. The obtained values of longitudinal sound velocities in pHEMA and mHEMA are shown in Fig. 3. The results concerning ST wave in HEMA will be analysed in the future.

2. MEASUREMENTS IN HEMA USING PICOSECOND ULTRASONICS

Then, to improve precision of the sound velocity determination, we have performed several test experiments with HEMA in a DAC, using classical picosecond ultrasonic pump-probe (800 and 400 nm)

set-up with a delay line [3]. The Brillouin scattering oscillations, obtained in picosecond ultrasonic experiment in mHEMA at 0 GPa and at 2.75 GPa are shown in Fig. 2A (1) and (2), respectively. Then, HEMA was polymerised, using the procedure described in Part 1. The result of picosecond ultrasonic experiment in polymerised HEMA at 0 GPa, obtained after the compression procedure described in Part 1, is shown in Fig. 2A (3) and the corresponding FFT spectra in Fig. 2B. Using the equation for the frequency of Brillouin oscillations $f_B = 2n \cdot v / \lambda$, the values of sound velocities were evaluated. It is worth noting, that the evolution of n with pressure is not known both for mHEMA and pHEMA. Taking the value of $n=1.5$ at 0 GPa, the sound velocity has been obtained as 1.5 km/s and 3.0 km/s for mHEMA and pHEMA, respectively. The sound velocity in mHEMA at 2.75 GPa was found to be 5.4 km/s, assuming the same value of the refractive index as at $P=0$ GPa.

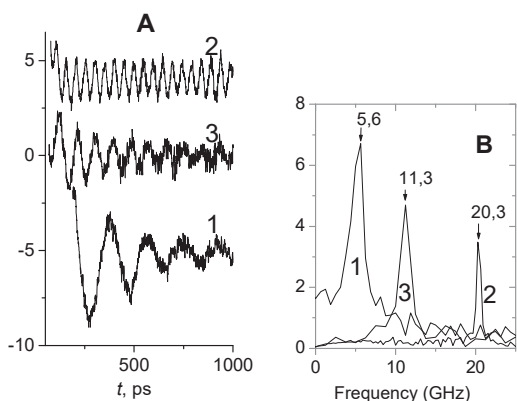


Fig. 2 A: Brillouin oscillations in mHEMA at 0 GPa (1), at 2.75 GPa (2) and in pHEMA at 0 GPa (3); B: The corresponding FFT spectra.

3. CONCLUSION

The summary of results obtained for pHEMA and mHEMA using the above described two techniques is shown in Fig. 3. The values of sound velocity obtained in mHEMA by subnanosecond and picosecond techniques have good agreement at the pressure of 2.75 GPa. It is important, that subnanosecond ultrasonics dealing with skimming waves allows to determine sound velocity without an additional measurement of the refractive index. This fact could be used in the future for the development of the technique of measurement of refractive index of transparent materials in DAC from the frequency of Brillouin oscillation, if sound velocity is already determined from the results of subnanosecond ultrasonics.

We are planning in future to perform 3D imaging of HEMA compressed in a DAC. To make it possible in a reasonable time, we will apply an ultrafast laser technique based on an asynchronous optical sampling (ASOPS).

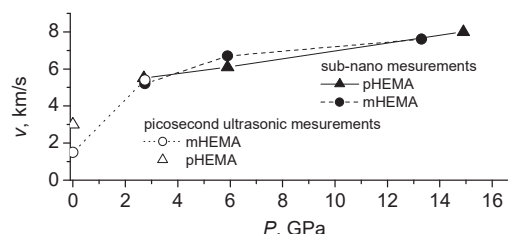


Fig. 3 The summary of results for the evaluation of longitudinal sound velocity using subnanosecond ultrasonic technique: solid circles – mHEMA; solid triangles – pHEMA. Using picosecond ultrasonic measurements: open circles – mHEMA; open triangles – pHEMA.

The maps of the Brillouin frequencies obtained using the picosecond ultrasonic technique could significantly extend our knowledge about the earlier recognised two different states of mHEMA above and below 6.5 GPa [1], which cannot be distinguished by any other technique because the solidified mHEMA is amorphous. Moreover, it should potentially allow following in time the 3D spatial spreading of the polymerization starting from nucleuses. In perspective, the 3D imaging of the transient processes at high pressures with nanometers depth resolution could be possible.

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