Physica B 466-467 (2015) 50–53

Contents lists available at ScienceDirect

Physica B

journal homepage: www.elsevier.com/locate/physb

Pressure dependence of acoustic anomalies of polydimethylsiloxane studied by Brillouin spectroscopy

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ARTICLE INFO

Article history:
Received 14 March 2015
Received in revised form
26 March 2015
Accepted 27 March 2015
Available online 30 March 2015

Keywords:
High-pressure
Brillouin scattering
PDMS
Sound velocity
Diamond anvil cell

ABSTRACT

The acoustic properties of polydimethylsiloxane elastomer was investigated as a function of pressure by using a multi-pass Fabry–Perot interferometer and a diamond anvil cell. Pressure dependence of the sound velocity, the Brillouin linewidth, and the refractive index was determined up to ~8.7 GPa. Acoustic properties exhibited a crossover behavior at approximately 1 GPa, which was attributed to the complete collapse of the free volume content in this polymer. The refractive index increased from 1.46 at ambient condition to ~1.63 at 8.67 GPa, which reflected the corresponding increase in density.

1. Introduction

Polydimethylsiloxane (PDMS, $CH_3(C_2H_6OSi)_nCH_3$) elastomer is a well-known Si-based polymeric material that has been widely used in various applications [1]. PDMS is viscoelastic, that is, it exhibits elastic behavior in short time window while it shows viscous motion in long time window. Physical properties of elastomers are sensitive to changes of external parameters, such as temperature or pressure. Since polymers are subject to various environmental changes during production, processing and application, it is important to investigate physical properties of amorphous materials under extreme conditions, such as high pressure or wide temperature variation [2,3]. This is the reason why equation of state (EOS) of polymers has been studied by several groups. However, many of previous studies have been carried out at low pressures below 200 MPa by using, for example, a dilatometric method [4]. Only two groups have reported the EOS of PDMS at high pressures up to more than 10 GPa [5,6].

Brillouin light scattering has been used as a powerful tool in the investigation of acoustic properties of polymeric materials [7–10]. The incident photons interact inelastically with thermally-excited acoustic phonons, by which the sound velocity and the acoustic attenuation coefficient can be obtained in the hypersonic frequency range of 10^9–10^{10} Hz. These acoustic properties are sensitive to phase transitions driven by temperature or pressure change. They are also affected by coupling to inter- or intramolecular relaxation processes in polymers. Anomalous changes in the acoustic properties may give us some insights into the microscopic mechanism of the relevant phase transition or vitrification process of amorphous polymers [11].

There have already been many reports on the Brillouin scattering results of PDMS at ambient conditions or as a function of temperature [12–14]. This study aims at reporting the acoustic behaviors of PDMS at high pressures up to ~9 GPa. Two scattering geometries were used to investigate the changes in the sound velocity and the damping behavior in more detail, in particular, at low pressures below 2 GPa where significant change in the effective free volume is expected [15–17]. The pressure dependence of the refractive index of PDMS was also obtained at high pressures.

2. Experimental setup

Sylgard 184 Silicone Elastomer Kit (Dow Corning) was used to prepare PDMS elastomer. The liquid pre-polymer (Part A) was mixed with the curing agent (Part B) with the composition ratio of 10:1 by weight. The solution was placed on a roll mixer for 1 h and it was then poured onto a cleaned glass substrate. The PDMS elastomer was finally fabricated by thermal annealing at 80 °C for 1 h. The Brillouin spectrum was measured by a conventional tandem six pass Fabry–Perot interferometer (TFPI, JRS Co.). For high

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http://dx.doi.org/10.1016/j.physb.2015.03.025
0921-4526/

pressure measurements, a small piece of PDMS was cut and put into the hole of a stainless steel gasket without any pressure medium. The diameter of the gasket hole was 235 μm. A symmetric aperture-type diamond anvil cell (DAC) was used to apply pressure up to −9 GPa. Ruby chips were included in the hole as a pressure marker. The fluorescent *R* lines were measured by using a grating-based spectrometer to obtain the pressure value. The pressure gradient in the DAC was measured by measuring several ruby chips at different positions, and the uncertainty in pressure was about ±0.2 GPa. A forward, symmetric scattering geometry with a scattering angle of 61.3° and 61.6° for the compression and decompression process, respectively, was adopted for the measurement. A circular aperture with a diameter of 15 mm was put in front of the collection lens to reduce the aperture broadening effect. The details of the experimental setup can be found elsewhere [18–20]. The Brillouin scattering experiment was carried out during compression from ambient pressure to 8.7 GPa. However, fine adjustment of the pressure value was not easy during compression, in particular, below 1 GPa. Therefore, as a second run, Brillouin spectrum was measured during decompression from 1.3 GPa to ambient pressure in order to investigate the low-pressure acoustic behaviors in more detail. For this procedure, the pressure was first increased to ~2 GPa and then slowly decreased to 1.3 GPa, and then the decompression experiment started. After the high-pressure measurement, PMDS was investigated at the ambient condition to measure the longitudinal sound velocity and the refractive index, which was 1219 m/s and 1.46, respectively.

3. Results and discussion

Fig. 1(a) and (b) shows the pressure dependence of Brillouin spectra of PDMS measured at the forward, symmetric scattering and backscattering geometry, respectively, while compressing the sample. Brillouin spectra exhibit one doublet corresponding to the longitudinal acoustic (LA) mode. No transverse acoustic (TA) mode was observed over the whole pressure range at both scattering geometries. The Brillouin shift depends on the phonon wavevector, which in turn depends on the scattering angle. This is the reason for the large difference in the Brillouin frequency shift between the two scattering geometries shown in Fig. 1(a) and (b). The location of the LA mode shifts to high frequencies as pressure increases. This change is more substantial at low pressures below 2 GPa. In addition, the linewidth of the LA mode decreases upon compression.

Brillouin spectra were fitted by the Voigt function in order to derive the Brillouin frequency shift (ν_B) and the full width at half maximum (FWHM, Γ_B) of the LA mode at each pressure. Fig. 2 (a) and (b) shows the pressure dependences of ν_B and Γ_B of PDMS measured during compression and decompression. ν_B is linearly proportional to the longitudinal sound velocity, while Γ_B is related to the acoustic attenuation of this mode. The LA mode frequency increases significantly as pressure increases from ambient pressure to ~1 GPa. The change in ν_B amounts to ~4.7 and ~14.5 GHz for the forward, symmetric scattering and the backscattering geometry, respectively. The rate of the frequency change becomes smaller beyond ~1 GPa. During the compression from 1 GPa to 8.7 GPa, the corresponding change in ν_B is ~5.1 and ~20 GHz for the forward, symmetric scattering and backscattering geometry, respectively. The substantial increase in the mode frequency upon compression to ~1 GPa is accompanied by significant reduction of Γ_B as shown in Fig. 2(b). If we look at the linewidth obtained at the backscattering geometry in Fig. 2(b), Γ_B first increases from 1.68 GHz at ambient pressure to a maximum of 1.92 GHz at ~0.1 GPa, and then reduces to ~0.5 GHz upon increasing pressure from ambient one to ~1 GPa. Γ_B maintains nearly the same value

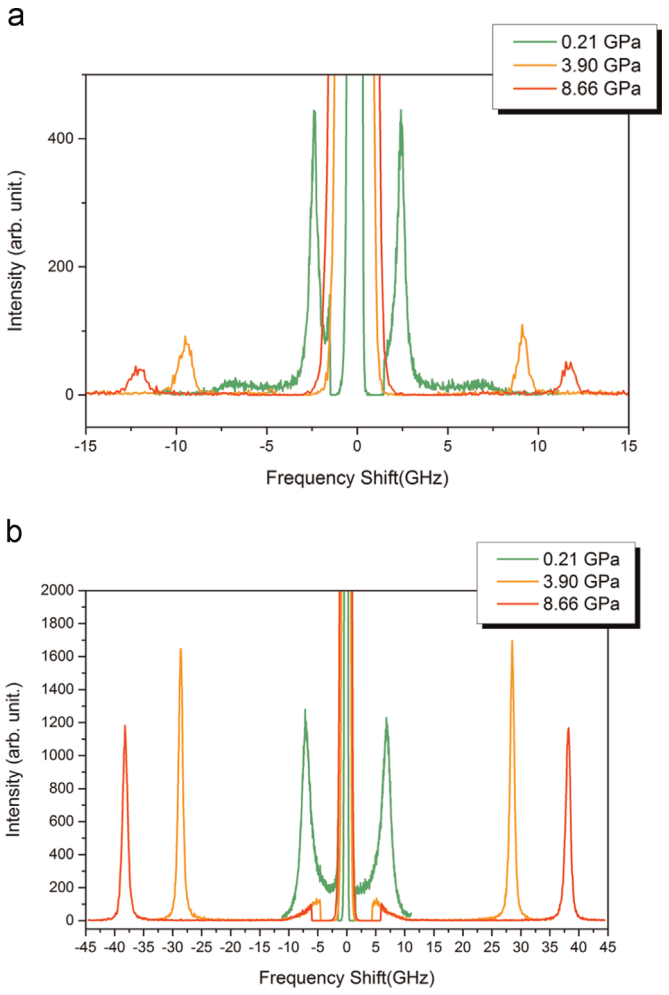

Fig. 1. Brillouin spectra of PDMS measured at (a) the forward, symmetric scattering and (b) the backscattering geometry.

beyond ~1 GPa as shown in Fig. 2(b). The linewidth data obtained at the forward, symmetric scattering geometry shows nearly the same pressure dependence, although the magnitude is different due to the difference in the phonon wavevector between the two scattering geometries.

The longitudinal sound velocity of PDMS can be obtained by using the frequency shift measured at the forward, symmetric geometry [6,20]. The pressure dependence of the sound velocity is shown in Fig. 3(a), along with the results reported by Stevens et al. [6] Both measurements exhibit nearly the same pressure dependence. The sound velocity increases rapidly upon compression in the low-pressure range below 1 GPa, beyond which it grows rather slowly. It reaches at about 6230 m/s at the highest pressure of 8.67 GPa. The noticeable difference in the sound velocity between the compression and the decompression processes may in part be ascribed to the uncertainty of ±0.2 GPa in the determination of pressure values. However, we cannot exclude the possibility that the macroscopic properties may exhibit a hysteretic behavior at low pressures due to the viscoelastic property of PDMS or to some unknown microscopic origin. Fig. 3(b) shows the attenuation coefficient of the LA mode. It decreases rapidly upon compression at low pressures below 1 GPa and maintains an almost the same value at high pressures.

The results of Figs. 2 and 3 indicate that low-pressure acoustic behaviors of PDMS are distinct from high-pressure properties. The remarkable changes in ν_B and Γ_B at low pressures clearly indicate that PDMS is very soft and viscoelastic in this low-pressure range