Effect of physical aging on the low-frequency vibrational density of states of a glassy polymer

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Abstract

The effects of the physical aging on the vibrational density of states (VDOS) of a polymeric glass is studied. The VDOS of a poly(methyl methacrylate) glass at low-energy (< 15 meV), was determined from inelastic neutron scattering at low-temperature for two different physical thermodynamical states. One sample was annealed during a long time at temperature lower than Tg, and another was quenched from a temperature higher than Tg. It was found that the VDOS around the boson peak, relatively to the one at higher energy, decreases with the annealing at lower temperature than Tg, i.e., with the physical aging.

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I. INTRODUCTION

The effect of the physical aging on the macroscopic thermodynamical properties of glass are well known. On the other hand, the dependence of the structure at the nanometric scale on the physical aging is not yet clarified. It is expected that the possible effects on the nanostructure are very small and hardly observable by the diverse microscopy techniques. It was shown that the properties of vibrations, with energies in the meV spectral range, are dependent on the nanostructure because these vibrations are extended on nanometric lengths. For this reason, it is expected that the experimental study of the characteristics of low-energy vibrations will inform us about the glass nanostructure and its changes by physical aging.

It was earlier suggested that the excess of low-energy Raman scattering, called boson peak and the related excess of vibrational density of states (VDOS) (called also boson peak) is due to an inhomogeneous nanostructure: more cohesive nanodomains are separated by less cohesive zones. From this model, it is expected that the contrast of bonding or of elastic constant between cohesive domains and softer zones weakens with aging, and that, in consequence, the vibrational density of states (VDOS) at low-energy decreases. From previous measurements, it is not clear that the aging induces a decrease of the VDOS at low-energy in the spectral range of the boson peak. Isakov et al. showed, by inelastic neutron scattering, that the low-energy VDOS of the As$_2$S$_3$ glass increases after thermal quenching. This neutron measurement confirmed the increase of the low-temperature specific heat observed by Ahmad et al. after quenching in the same glass. On the other hand, no change of the VDOS was observed after quenching in the polybutadiene glass.

Several experiments aimed to test the effect of thermal treatments on the VDOS have been carried out with the poly(methyl methacrylate) (PMMA) glass. Kanai et al. observed an increase of the inelastic incoherent neutron scattering (INS) intensity at low-energy after quenching from a temperature of 453 K of an annealed sample. However, as it will be shown in the discussion, the conditions of this experiment do not allow to conclude that the rejuvenation (by thermal quenching) and the physical aging (by thermal annealing at a temperature lower than the glass transition temperature, Tg) have opposite effects on the low-energy VDOS. New experiments aiming to test the effect of aging on the low-energy VDOS of PMMA were carried out recently. It was found that the aging by annealing at
363 K, i.e. 10 K below Tg, of a slightly cross-linked PMMA has no effect on the VDOS determined from INS at low temperature, $T = 30 K$. On the other hand, by methanol-assisted aging at room temperature of the same PMMA\textsuperscript{9} a significant decrease of the VDOS in the spectral range of the boson peak was observed\textsuperscript{8}. These observations were in agreement with the Raman ones. A decrease of the Raman boson peak was observed after methanol-assisted aging of the cross-linked PMMA at 300 K, and none after annealing at 363 K. However, the effect of the methanol-assisted aging was much stronger with non cross-linked PMMA\textsuperscript{9}. Probably, the cross-linking makes the nanostructure change much more difficult by annealing.

From the described situation, it is not yet clear that the low-energy VDOS of non cross-linked PMMA decreases by aging, i.e., by annealing at a temperature slightly lower than Tg. A decrease of the Raman boson peak at low-temperature was observed. But the low-energy Raman scattering is proportional to the VDOS and to the light-vibration coupling coefficient C(E), and it is possible that this is the decrease of this coefficient which is responsible for the decrease of the Raman boson peak and not the VDOS. To solve this problem new measurements of inelastic neutron scattering at low-temperature were carried out to determine directly the effect of the physical aging on the VDOS of PMMA. The comparison of the VDOS of an aged PMMA with the one that is rejuvenated by thermal quenching is presented in this paper. The new neutron experimental results with others obtained earlier are discussed to interpret the effect of aging on the glass nanostructure.

II. EXPERIMENTAL

The PMMA plates of clinical grade without any additives were purchased from Goodfellow SARL (reference ME303031). The average molecular weight is close to $10^6$ and the glass transition temperature $T_g$ is about 390 K, as determined by differential scanning calorimetry (DSC). PMMA disks with a diameter of 5 cm and a thickness of about 0.04 cm were cut for heat treatments and inelastic neutron scattering.

The inelastic neutron spectra were recorded on the time-of-flight instrument IN6 at ILL, Grenoble. The energy resolution is $\delta E = 80 \mu eV$. The momentum transfer range extends from $Q = 0.22 \text{Å}^{-1}$ to $Q = 2.06 \text{Å}^{-1}$. The spectra were taken in the temperature range 2 – 300 K, using an helium cryofurnace. The temperature of 30 K was chosen to obtain the
neutron inelastic scattering by the low-energy harmonic vibrations much higher than the one by anharmonic or relaxational motions\textsuperscript{2}. The scattering cross-sections were obtained after the usual standard calibrations by means of the vanadium runs and the removal of the empty-can contributions. The VDOS for harmonic modes were obtained by taking the average of the spectra given by the different detectors, that is the average over the range from $Q = 0.22 \text{Å}^{-1}$ to $Q = 2.06 \text{Å}^{-1}$. It was calculated through the use of an iterative procedure described elsewhere\textsuperscript{10}. The so-obtained VDOS were corrected by the Debye-Waller factor and the multiphonon contributions.

III. EXPERIMENTAL RESULTS

Two PMMA samples were compared. Sample-1 was heated for 30 minutes at $413 K$, quenched at room temperature, annealed for 30 days at $373 K$ and then 15 days at $363 K$. In the view of the energy landscape, the annealing at two different temperatures was thought to be more efficient for aging: while the higher temperature allows the system to cross over high energy barriers, the lower temperature allows a stabilization into deeper wells. Sample-2 was heated for 30 minutes at $413 K$ and quenched at room temperature on a copper plate. The cooling rate was estimated to be between 50 and 100 K/s. It was controlled, by the observation of the Raman lines, that these thermal treatments, especially the heating at $413 K$, did not induce depolymerization. It was checked that the intensity of the line at $1640 \text{ cm}^{-1}$, that corresponds to the vibration localized on the C=C bond, is zero for both samples. It means that the concentration of MMA monomers is very weak, and that there is no depolymerization\textsuperscript{11} even after heating at $413 K$ for 30 min. As a consequence, Sample-1 was physically aged and Sample-2 was rejuvenated, its thermal history being erased\textsuperscript{1}.

The effect of aging was clearly observed by DSC. A strong endothermal peak appeared for Sample-1, and not for Sample-2, as one can see in Fig. 1. In addition, it was determined, from the DSC curves, that the fictive temperatures were respectively $T_f = 366 K$ and $T_f = 390 K$ for Sample-1 and Sample-2, in agreement with the thermal treatments.

The incoherent scattering functions of both samples, $S(E)$, taken at $T = 30 K$, are compared in Fig. 2. They were determined by taking the average of the spectra given by the different detectors over the range from $Q = 0.22 \text{Å}^{-1}$ to $Q = 2.06 \text{Å}^{-1}$. They are corrected for the elastic peak, that was obtained by measuring the inelastic scattering from the samples.
FIG. 1: DSC curves measured at a heating rate of 20 K/min. Dotted line: reference data for $C_p$ values, Full line: Sample-1 (aged PMMA); Dashed line: Sample-2 (quenched PMMA). The data represented by the dashed line are vertically shifted by -0.5 J/g/K for clarity.

at $T = 2K$. As their shapes are identical from the energy equal to 4 meV, they were normalized by coincidence of the curves from the energy of 4 meV for a better comparison. Considering the experimental error bars due to neutron counting, which are shown on the curves at 1.25 meV, it is clear that $S(E)$ is more intense in the 0.6 – 2 meV spectral range for Sample-2 than for Sample-1.

The VDOS $g(E)$ were deduced from $S(E)$. These VDOS divided by the square of energy, $g(E)/E^2$, are plotted in Figure-3. As expected from $S(E)$ (Figure-2), the boson peak at 1.75 meV is more intense for the rejuvenated Sample-2 than for the aged Sample-1, even if the difference is not huge. Furthermore, it is evident, from Figure-3, that the observed difference originates from the VDOS for harmonic vibration modes and not for anharmonic
FIG. 2: Incoherent neutron scattering function $S(E)$. Full line: quenched PMMA; Dotted line: aged PMMA. The error bars arising from the neutron counting are shown at 1.25 meV on both curves.
ones, because it does not decay monotonously from E=0 to higher energy as expected for anharmonic motions: it is observed (inset of Figure-3) that this difference presents a maximum around E = 1.05 meV. It was detected that it is not the case for a sample slightly depolymerized by heating at 413 K for a much longer time and containing some monomers: even at T = 30K neutron scattering by anharmonic motions due to the presence of monomers was observed, in agreement with previous Raman measurements\textsuperscript{13}. The VDOS were also determined at T = 300K. However, at this temperature, the neutron scattering by anharmonic motions is relatively high for both samples and masks the scattering by harmonic vibrations at low-energy.

IV. DISCUSSION

In this described experiment much care was taken, on the one hand, to make sure that the heat treatments induce only physical aging and not a chemical one like depolymerization, and, on the other hand, to obtain the effect of aging on the VDOS corresponding to harmonic vibration modes. In a previous study of the effect of annealing on the low-energy excitations in PMMA, the conditions of the experiment were different\textsuperscript{7}. Indeed, these authors of this study compared a sample annealed 7 days at T = 363 K to a sample quenched from T = 453 K. It was shown that at this temperature depolymerization occurs and induces an increase of the monomer concentration\textsuperscript{11}. The reversible effect was observed by subsequent annealing at a temperature lower than Tg\textsuperscript{11}. As a consequence, by such a thermal treatment\textsuperscript{7}, this is a partially chemical aging which is obtained instead of a pure physical aging. Furthermore, in this experiment\textsuperscript{7} the inelastic scattering was measured at T = 73 K. At this temperature the scattering by anharmonic or relaxational motions is not negligible\textsuperscript{3}. In these conditions and after observation of the published spectra, it is likely that the difference in the inelastic neutron scattering of annealed and quenched PMMA observed by Kanaya et al. is mainly due to anharmonic motions.

In another glassforming polymer, polybutadiene, no effect of annealing was observed on the VDOS by measuring the inelastic neutron scattering\textsuperscript{6}. It could be suggested that the decrease of the low-energy VDOS by aging is not general for glass-forming polymers. However, the used thermal treatments can explain the non-observation of difference in the VDOS between annealed and quenched polybutadiene. The aged sample was heated for 36
FIG. 3: Vibrational density of states, \( g(E)/E^2 \). Full line: quenched PMMA; Dotted line: aged PMMA. The inset shows the difference curve: \( |g(E)/E^2|_{\text{quenched}} - |g(E)/E^2|_{\text{aged}} \).
h at $T = 169\,K$ (11 K below $T_g$), and the quenched sample was heated for 1 h at 270 K and cooled at 100 K with a rate of 2 K/min. The cooling rate used for this quenching was possibly too slow to avoid an undesired effect of aging during the cooling from 270 K to 100 K.

In a very recent study of a crystallisable silicate material by inelastic neutron scattering, it was observed that the intensity of the boson peak of a hyperquenched ($10^6\,K/s$) sample decreased strongly after annealing at a temperature below $T_g$. The neutron measurements were performed at room temperature, and probably the measured VDOS is partially accounted for anharmonic vibrational modes. A similar behavior was earlier observed with a metallic glass. These results were discussed in the frame of the potential energy landscape model.

A simple explanation of the decrease of the VDOS by aging, in our experiment, could be the increase of sound velocity concomitant with the increase of density, and in consequence a decrease of the Debye VDOS contribution. However, the difference of $g(E)/E^2$ between aged and rejuvenated PMMA is expected to be constant as a function of $E$. It is not the case, this difference has a maximum around 1.05 meV (inset of Figure-3). Instead of having an effect on the Debye VDOS, the aging would change the excess of VDOS responsible for the boson peak. The interpretation of the low-frequency modes in the boson peak is still a matter of debate. Several theoretical models are based on the system dynamics without consideration of the structure, among which the very recent landscape model. Here, we will consider the nanostructural point of view, which is not in contradiction with the dynamical approach and may be relevant to discuss the aging effect. The boson peak was previously interpreted by an inhomogeneous glass elasticity or cohesion at the nanometric scale: more cohesive domains would be separated by softer zones. This view is supported by a recent simulation of the elasticity of small amorphous systems. Previous experimental results are in agreement with quasi-periodic arrangements of the cohesive domains on short distances, so that the boson peak would correspond to a Van Hove singularity associated to the quasi-periodic arrangements. Such interpretation can be compared to the model of Taraskin et al., in which the boson peak is related to the lowest Van Hove singularity of the reference crystalline system pushed down by the effect of disorder-induced level repulsion. In the frame of the inhomogeneous glass nanoelasticity model, the decrease of the low-energy VDOS by aging can originate from a decrease of the contrast in the elasticity at the nano-
metric scale. This would be in agreement with the observations of Isakov et al. about the effect of aging in the $As_2S_3$ glass. These authors determined that the relative effect of aging on the low-energy VDOS was the same as the one on the light-vibration coupling coefficient $C(E)$ in Raman scattering. This coefficient $C(E)$ increases with the amplitude of the dielectric susceptibility fluctuations. The dielectric susceptibility is directly related to the elastic constants by the elasto-optic tensor. Therefore, the dielectric susceptibility contrast at the nanoscale goes like the elastic constant one, and one may conclude that the decrease of $g(E)$ and $C(E)$ have a common origin: the smoothing of the elastic constant contrast at the nanometric scale. The same conclusion can be proposed for PMMA. Unfortunately, it was not possible to perform a quantitative comparison between $g(E)$ and $C(E)$ in the case of PMMA, because the effect of aging on these quantities are relatively much weaker for this glass than for $As_2S_3$.

The results obtained by the inelastic neutron scattering study presented in this paper must be compared to other previous ones. Same measurements were carried out with PMMA slightly cross-linked by trimethyl-1,1,1-propane trimethacrylate (TRIM). With this cross-linked PMMA, no effect of aging was observed on the low-energy Raman scattering by harmonic vibration modes. It is believed that it is due the presence in the zones between domains of cross-links which reinforce the linking of a domain with its next-neighbors and, then, precludes the decrease of the contrast between soft zones and cohesive domains with aging. Methanol-assisted aging of PMMA at room temperature was also studied. PMMA plates was soaked for more than one month in methanol at room temperature and then dried. By mechanical relaxation measurement, it was shown that the effect of this treatment corresponds to an aging at room temperature accelerated by the presence of methanol. This can be explained by a preferential location of the methanol in the softest zones, which makes easier the molecular segmental motions.

It may be noticed that the tendency towards a more homogeneous structure by aging was deduced from elastic light scattering by Takahara et al. in the case of PMMA. These authors determined the correlation length and the amplitude of density fluctuations at the scale of 200 nm. They found that the values of these two fluctuation characteristics decreased after an aging at $T = 353 K$ for less than 10 hours. These conclusions are not exactly comparable to the ones suggested in this paper. In the present work, the explored length scale is 10 times smaller, and deals with the fluctuations of elastic constant, and not with
The density ones.

The effect of aging or rejuvenation by thermal treatments on the low-energy vibrations, is now compared to that of a plastic deformation. It is well-known that a plastic deformation rejuvenates a glass. The effect of plastic deformation by shearing on the low-energy vibrations was investigated by Raman scattering in the case of PMMA and polycarbonate (BPA-PC) glasses. An increase of the Raman scattering intensity in the region of the boson peak was observed. This increase of Raman intensity can be attributed, at least partially, to an increase of VDOS. Furthermore, as a confirmation, no increase of low-energy Raman scattering was observed after plastic deformation of the cross-linked PMMA, like after thermal quenching. These results confirm the effect of aging (and rejuvenation) on the low-energy VDOS and on the glass nanostructure, consistently with the proposed interpretation.

It is noted that the experimental results and their interpretation are in agreement with, on the one hand, the view of a vitrifying liquid, that was deduced by Stillinger from the potential energy landscape, "as a patchwork of relatively strongly bonded molecular domains separated by irregular walls of weakened bonds"; and, on the other hand, with the recent numerical simulation of aging and rejuvenation, which shows that the aging induced a pronounced decrease in the system pressure, and that local compression and expansion of rearranging clusters of atoms appear as the shear deformation proceeds and, therefore, erases the aging. This description is not far from the one involving the arrangement of more cohesive domains separated by less cohesive zones as proposed earlier, the contrast between cohesive domains and softer zones decreasing with aging, and inversely increasing with rejuvenation, as suggested in this discussion.

Finally, it is remarked that the observed decrease of the VDOS with aging confirms qualitatively the very recent predictions deduced from the energy landscape model.

V. CONCLUSION

The inelastic neutron scattering experiment described in this paper shows clearly a lower harmonic vibration density of states for aged poly(methyl methacrylate) than for thermally quenched (rejuvenated) one. Much care was taken to avoid chemical effects by thermal treatment. The neutron measurements were carried out at low-temperature to obtain the scattering by harmonic vibrations. The effect of thermal quenching is compared to the
one of a plastic shearing observed earlier. The rejuvenations obtained by both thermal and mechanical treatments are characterized by an increase of the low-energy vibrational density of states. These effects on the vibrational density of states are in agreement with the model of an inhomogeneous cohesion in the polymeric glasses at the nanometric scale, and with the energy landscape deductions. It would be interesting to establish a relation between the glass nanostructure or the nanoelasticity and the profile of the energy landscape.

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