Low-Energy vibrational density of states of plasticized poly(methyl methacrylate)

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Abstract

The low-energy vibrational density of states (VDOS) of hydrogenated or deuterated poly(methyl methacrylate) (PMMA) plasticized by dibutyl phthalate (DBP) is determined by inelastic neutron scattering. From experiment, it is equal to the sum of the ones of the PMMA and DBP components. However, a partition of the total low-energy VDOS among PMMA and DBP was observed. Contrary to Raman scattering, neutron scattering does not show enhancement of the boson peak due to plasticization.
I. INTRODUCTION

Physical studies of plasticized polymers are of interest for attaining optimal properties of the material and revealing the nanostructure, i.e., the distribution of plasticizer molecules in the polymeric glass. Recently an experimental study was carried out on the poly(methyl methacrylate) (PMMA) plasticized with dibutyl phthalate (DBP). Two interesting results were obtained. By small angle X-ray scattering (SAXS) a correlation peak was observed at about 1.5 nm$^{-1}$ in the plasticized sample, while no such peak was detected in the non-plasticized one. This observation shows that the plasticizer is not distributed homogeneously in the polymer and that the zones rich in plasticizer are alternated with the other ones with a low content of plasticizer. Furthermore such arrangement is quasiperiodic with a period close to 4 nm. This inhomogeneity of the plasticized polymer was assumed to be due to the cohesion inhomogeneity of the glassy polymer without plasticizer: "More cohesive are separated by softer interdomain zones". The other interesting experimental result is the increase of the excess of low-frequency Raman scattering (LFRS) or Raman boson peak by plasticization: the boson peak is more intense than the one obtained by adding the LFRS of the two components (PMMA and DBP) according to the composition of the plasticized material. In the frame of the considered interpretation, the intensity of the boson peak is related to the inhomogeneous cohesion: the more contrasted the cohesion at the nanoscale, the more intense the boson peak. The increase of the boson peak is interpreted by the increase of the elastic constant contrast due to the high content of plasticizer in between cohesive domains.

The intensity of LFRS is proportional to the vibrational density of states (VDOS) and to the light-vibration coupling coefficient. The increase of the Raman boson peak may be due to the increase of either the VDOS, the coupling coefficient or both. The excess of VDOS can be observed by inelastic neutron scattering and will be called neutron boson peak. It is why low frequency inelastic neutron scattering (LINS) measurements were carried out on plasticized and non-plasticized PMMA. On the other hand, in order to know the effect of
vibrations of one component on the other, two different plasticized PMMA were compared: the one with hydrogenated PMMA, and the other with deuterated PMMA. Because the incoherent inelastic neutron scattering is much higher for the hydrogenated polymer than for the deuterated one, it will be possible to know the contribution of each component in plasticized PMMA. In this paper the VDOS of different samples will be compared: pure hydrogenated PMMA, pure DBP, plasticized hydrogenated and deuterated PMMA. It will be shown that the plasticization has no effect on the VDOS excess or neutron boson peak, and on the other hand that the low-frequency vibrations of PMMA drag along the motion of the DBP plasticizer.

II. EXPERIMENT

A. Samples

Plasticized or non-plasticized film samples, in the form of the circles of 5 cm diameter and ca. 0.3 mm in thickness, were prepared by casting the solutions of PMMA or PMMA/DBP blends in toluene/dioxane/dichloroetane/acetone mixture onto glass surface. Removing the solvents was carried out under slow evaporation conditions for 24 h at room temperature, with subsequent step-like heating at 80, 100 and 120°C, up to the constant weight of the films. Four samples were compared: pure hydrogenated PMMA (PMMA-H), pure dibutyl phthalate (DBP), hydrogenated PMMA with 23 (mass) % DBP (PMMA-H/DBP), deuterated PMMA with 23 (mass) % DBP (PMMA-D/DBP). The respective glass transition temperatures, as estimated by differential scanning calorimetry (heating rate of 20 K/min), are 390 K for pure PMMA sample 190 K for DBP, and 320 K for the plasticized samples. The number average molecular weight of PMMA-H and PMMA-D is approximately equal to 500 000 g/mol. The percentage of deuteration of PMMA-D is 98%.
B. Neutron scattering

The inelastic neutron spectra were recorded on the time-of-flight instrument IN6 at the ILL, Grenoble. The wavelength of the incident neutrons was equal to 5.12 Å resulting in an elastic resolution (FWHM) of 80 µeV, and an elastic momentum transfer range extending from $Q = 0.22 \, \text{Å}^{-1}$ to $Q = 2.06 \, \text{Å}^{-1}$. The spectra were recorded at three different temperatures, at 4 K for the determination of resolution, 30 K and 300 K, using a helium cryofurnace. The temperature of 30 K was chosen to obtain the neutron inelastic scattering by the low-frequency harmonic vibrations without the scattering by anharmonic or relaxational motions negligible at this temperature [3]. The scattering cross-sections were obtained after the usual standard calibrations by means of the vanadium runs and the removal of the empty cans contributions. The VDOS for harmonic modes were obtained by taking the average of the spectra given by the different detectors, i.e., the average over the range from $Q = 0.22 \, \text{Å}^{-1}$ to $Q = 2.06 \, \text{Å}^{-1}$. Because the first sharp peak of PMMA in the static structure factor is at $Q = 0.95 \, \text{Å}^{-1}$, a value that is lower than the upper limit of the experimental Q-range, the incoherent approximation was applied by using the total neutron scattering bound cross-section ($\text{coherent} + \text{incoherent}$). The VDOS were calculated through the use of an iterative procedure described elsewhere [4]. The so-obtained VDOS were corrected by the Debye-Waller factor and for the multiphonon contributions.

III. EXPERIMENTAL RESULTS

The VDOS divided by the square of energy, $G(E)/E^2$, are plotted in Figure 1. This type of plot is conventional for comparison with the Debye regime. It was not possible to obtain the absolute VDOS. However, as the shapes of the $G(E)/E^2$ curves for the different samples were observed to be identical at the energies higher than 4 meV, a normalization was obtained by coincidence of the curves from an energy of 4 meV. Obviously this normalization does not allow to compare the total VDOS of the different samples, but it makes possible
the comparison of the boson peaks, which appear around 2 meV.

The boson peak appears at an energy slightly lower than 2 meV for pure PMMA-H, as observed before [3], and higher for pure DBP (Figure 1). The relative intensity at low energy is higher for pure PMMA than for pure DBP, and decreases with plasticization. However, although the LINS of PMMA-D is expected to be very low, in view of its relatively weak neutron bound cross-section [3], $G(E)/E^2$ of PMMA-D/DBP and of PMMA-H/DBP are not very different. On the other hand, it is noted that the slope of $G(E)$ or $G(E)/E^2$, on the low-energy side of the boson peak is the steepest for the pure DBP.

IV. INTERPRETATION

A. Model

From a simple glance of the curves in Figure 1, one expects that the plasticization does not increase the boson peak relatively to the one obtained from the addition of the VDOS of respectively the PMMA and DBP components. It is confirmed by Figure 2. As it can be observed, $G(E)/E^2$ of PMMA-H/DBP is very well fitted by adding the VDOS of respectively PMMA-H and DBP in the following proportion:

$$G_{PMMA-H/DBP}(E) = aG_{PMMA-H}(E) + bG_{DBP}(E)$$  \hspace{1cm} (4.1)

The low-energy VDOS of the plasticized glassy polymer obeys the general addition law:

$$g(E) = \sum_i C_ig_i(E)$$  \hspace{1cm} (4.2)

where $g(E)$ and $g_i(E)$ are the absolute VDOS, and the coefficient $C_i$ the (mass) concentration of the component $i$. In our PMMA-H/DBP, for instance, $C_i$ is 0.77 and 0.23 for respectively PMMA-H and DBP. The coefficients $a$ and $b$ in (4.1) are proportional to 0.77 and 0.23 respectively. The good fit in Figure 2 demonstrates that the plasticization does not enhance the neutron boson peak or the low-energy VDOS like it does for the Raman boson peak [1].
In order to try to fit in a similar manner $G(E)/E^2$ of PMMA-D/DBP, it was taken into account that the observed VDOS, $G_i(E)$, depends on the total neutron bound cross-sections of the different atoms in the molecule. For the low-energy vibrational modes, which are mainly dependent on the intermolecular bonding and are studied in this work, the neutron bound cross-section proportionality of $G_i(E)$ is approximately the following:

$$G_i(E) \propto \beta_i g_i(E)$$  \hspace{1cm} (4.3)

where:

$$\beta_i = \sum_j c_j \sigma_j / M_j$$  \hspace{1cm} (4.4)

with $c_j$, $\sigma_j$ and $M_j$ respectively the (mass) concentration, the total neutron bound cross-section and the mass of atom $j$ in the molecule or monomer $i$.

From these equations, the fit of $G(E)/E^2$ for PMMA-D/DBP corresponding to that for PMMA-H/DBP (4.1) is given by the following equation:

$$G_{\text{PMMA-D/DBP}}(E) = a(0.98\rho + 0.02)G_{\text{PMMA-H}}(E) + bG_{\text{DBP}}(E)$$  \hspace{1cm} (4.5)

In this equation the fractions 0.98 and 0.02 accounts for the degree of PMMA deuteration, that is equal to 0.98. The coefficient $\rho$ is equal to $\beta_{\text{PMMA-D}}/\beta_{\text{PMMA-H}}$. Using the total neutron bound cross-sections of the different atoms in PMMA-D and PMMA-H given in [5], it is found $\rho = 0.079$. This small value is due to the very large value of the incoherent cross-section of hydrogen in comparison with the total cross-sections of the other atoms including deuterium. The $G(E)/E^2$ curve given by (4.3) is plotted in Figure 2. As expected, due to the weak value of $\rho$, this calculated $G(E)/E^2$ curve is not very different from the experimental one for pure DBP. One observes in Figure 2, that the experimental $G(E)/E^2$ of PMMA-D/DBP is more intense at low energies than the corresponding one calculated by (4.5). Furthermore it is remarked (Figure 1) that the $G(E)/E^2$ shapes of PMMA-H/DBP and PMMA-D/DBP are similar. The difference between the experimental and calculated $G(E)/E^2$ of PMMA-D/DBP is explained by the motion of the DBP plasticizer dragged
along by the low-energy vibrations of PMMA-D and reciprocally. This difference is so large that it is impossible to explain it by an underestimation of the PMMA-D VDOS in that of PMMA-D/DBP.

B. Discussion

The first interesting result is the good fit of PMMA-H/DBP $G(E)/E^2$ obtained by the addition of the PMMA-H and DBP VDOS ([1.1]). It means that the neutron boson peak is not enhanced by the plasticization: the low-energy VDOS of the plasticized sample is equal to the sum of the component ones. As noted in the previous subsection, the low-energy VDOS depends on the intermolecular bonding. In consequence, if the VDOS of the plasticized PMMA is given by the sum of those of PMMA and DBP, one deduces that the bonding, on the one hand, between PMMA macromolecules, and on the other hand, between DBP molecules, is not significantly changed by plasticization. As the low-energy modes observed in the boson peak are extended on nanometric distances, such unchanged intermolecular bonding is possible if, at the nanoscale, there is separation of both components. This interpretation confirms the observation by SAXS of a correlation peak at $1.5 \text{ nm}^{-1}$ [1]. The distribution of DBP in PMMA is quasiperiodic.

The non-enhancement of the neutron boson peak or of the low-energy VDOS, means that observed enhancement of the Raman boson peak by plasticization is due to the amplification of the vibration modulated polarisability. This is explained by the increase of the spatially fluctuating static polarisability due to the heterogeneous distribution of the plasticizer in PMMA and the nanodomain vibrations, which have a strong amplitude at the interface between PMMA and DBP phases. This explanation is consistent with the interpretation of the boson peak due to an inhomogeneous cohesion of the glassy network [2,3].

The second interesting result is the excess of the experimental $G(E)/E^2$ of PMMA-D/DBP at low-energies in comparison with $G(E)/E^2$ calculated by using the total neutron bound cross-sections of atoms in PMMA-D. Because the VDOS of the plasticized PMMA is
given by the sum of the components, as shown above, one deduces, while the total VDOS is conserved, there is a redistribution of the low-energy VDOS among the PMMA and DBP components in the plasticized glassy polymer. As noted above the vibrations of one component drag along the motion of the other. This VDOS redistribution is more effective for the vibrational modes on the low-energy side of the boson peak (Figure 2). The reciprocal partition of vibrational amplitude of both components will be more effective for the vibrations which have a strong amplitude at the interface between PMMA and DBP phases. Again this explanation is in agreement with the model, in which the modes on the low-energy side of the boson peak correspond to the fundamental modes of the nanodomains.

V. CONCLUSION

The total low-energy vibrational density of states of PMMA plasticized by DBP is well fitted by the sum of the component ones. It means that the plasticization does not change significantly the PMMA and DBP intermolecular bonding. However, both components do not vibrate independently: vibrations of PMMA, appearing in the low-energy side of the boson peak, were observed in the inelastic neutron scattering of DBP. This behavior means that the neutron boson peak is not enhanced by plasticization. Therefore, the enhancement by plasticization of the boson peak observed by Raman scattering comes from the increase of the electric polarizability modulated by low-energy vibrations, and not from the increase of the vibrational density of states. These results are in agreement with an inhomogeneous distribution of the plasticizer at the nanoscale, as it was observed by small angle X-ray scattering, and, on the other hand, with an inhomogeneous intermolecular bonding in polymeric glasses.
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FIGURES

FIG. 1. Vibrational density of states divided the square of energy, $G(E)/E^2$, deduced from the inelastic neutron scattering at 30 K. PMMA: empty circles; PMMA-H/DBP: empty squares; PMMA-D/DBP: full squares; DBP: full circles The normalization is obtained by an arbitrary equalization of $G(E)/E^2$ at 4 meV.

FIG. 2. Comparison of the measured vibrational density of states with the calculated ones. Density of states of plasticized hydrogenated (empty squares) and deuterated (full squares) poly(methyl methacrylate) compared with the ones calculated by Equations 4.1 (full line) and 4.3 (dashed line) respectively.