A DIFFERENT VIEW ON THE β-RELAXATION OF A POLYMER GLASS: A NEUTRON SPIN-ECHO STUDY

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ABSTRACT

Biodegradable polymers (e.g. poly(lactic acid), PLA) are of great importance to modern science and technology of polymer-based materials. They find extensive use in medicine, agriculture, and in the production of throw-away wrappings and goods. However, in some cases their usage is limited due to some of their specific properties. For example, the rapid physical ageing of PLA considerably limits its applications, as it results in a brittle material. The ageing phenomenon of the PLA was intensively studied by macroscopic measurements, but the results are sometimes in contradiction with the expectations and raise several questions.

In many glass-forming materials, such as amorphous and semicrystalline polymers, there is clear evidence of the presence of relaxation processes below the glass transition (α-relaxation) temperature. These are generally referred to as β, γ, etc. transitions, in the order of decreasing temperature. However, the molecular origin of these relaxations is still a matter of controversy. Most literature sources agree in that glass transition is associated with the coordinated motion of a high number of atoms in the polymer backbone, i.e. that of polymer segments. Secondary relaxations, on the other hand, are most likely related to the motion of smaller numbers of atoms, i.e. that of repeating units or substituent groups. However, these kind of non-equilibrium processes are very difficult to study experimentally, especially on the nanometric lengthscale, and the interpretation of the results of indirect measurements is often ambiguous. The clarification of what is really happening during the physical ageing of PLA can be answered only if direct measurements can follow the incurring changes by following the molecular level dynamics *in-situ*. The available techniques, which have the sufficient time and space resolutions to perform these kinds of studies are limited. Neutron spin-echo (NSE) is one of the very few tools, which beside these can also provide information about the wave vector dependence of the dynamical processes. In our presentation we will show the first results of a detailed NSE study, which as of our knowledge has been performed for the first time deep in the glassy state of a polymer glass. Poly(lactic acid) was found to exhibit a β-relaxation attributed to local motions in the backbone, the temperature of which greatly depends on isomer ratio and crystallinity, and a γ-relaxation attributed to the motion of methyl side groups. In various polymeric materials these transitions have been correlated with several physical and mechanical characteristics with considerable practical importance, e.g. impact strength and gas permeability.

Acknowledgement: The authors gratefully acknowledge the Institut Laue-Langevin, Grenoble, for access to the IN11 instrument.