Experimental Report

Proposal: **6-05-917** **Council:** 10/2012

Title: Neutron Spin-Echo study of the structural relaxation in poly(lactic-acid) polymer glass

This proposal is a new proposal

Researh Area: Physics

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Experimental Team: IMRE Balazs
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Local Contact: CZAKKEL Orsolya

Samples: poly(lactic-acid)
Poly(methylmethacrylate) (C5H8O2)n
calcium sulphate CaSO4

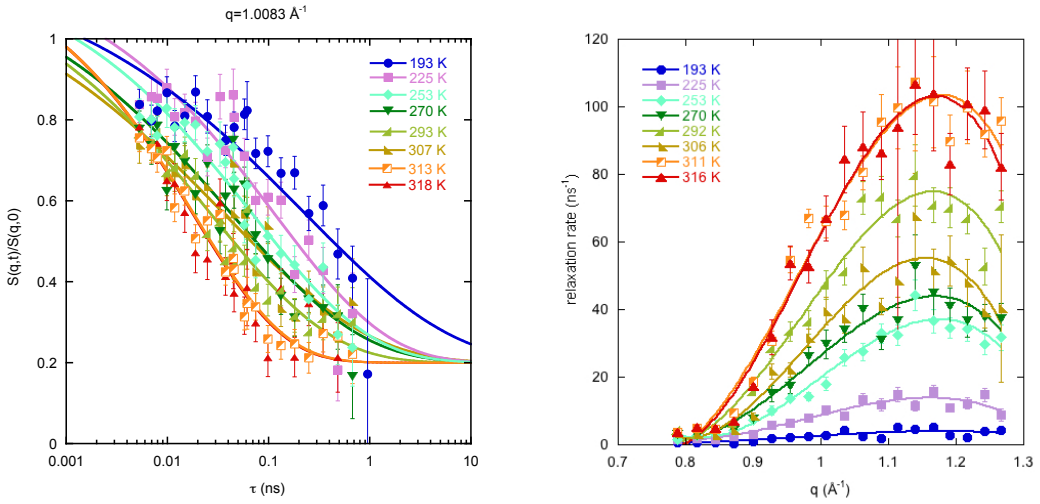
Instrument	Req. Days	All. Days	From	To
IN11	10	6	27/03/2013	02/04/2013

Abstract:

Poly(lactic-acid) (PLA) as a biodegradable polymer has high potential in a wide range of applications. Owing to the relatively small difference between the glass transition temperature (55-60°C) and the temperature of usage (ambient conditions) the occurring physical ageing has significant impact on the macroscopical properties of the material. Several studies have been made, by using macroscopic measurements, to find out the mechanism of ageing in PLA, but the results are often ambiguous, and there are still several open questions. To answer these, direct measurements are needed, which are able to follow in-situ the changes in the system in the nanometric lengthscale. To answer these we propose a Neutron Spin-Echo study which allows to follow the changes in the dynamics of the system in the atomic lengthscale.

The aim of the experiment was to check the feasibility of measuring dynamical processes deep in the glassy state of a polymeric glass, namely poly(lactic-acid), PLA. The neutron spin-echo (NSE) measurements were performed on the IN11C spectrometer with an incident neutron wavelength of 5.5 Å. The instrument setup was tuned to a q range of 0.7885 - 1.292 Å^{-1} in order to cover the first peak q_0 at ~1.1 Å^{-1} in the static structure factor of PLA and observe directly the molecular level motions with a Fourier time range of 0.08 - to 0.6 ns. The measured temperature range was 193 - 318 K, and was controlled by the standard ILL Orange cryofurnace.

Despite the short experiment time, the test was successful. Correlation functions have been measured in the full q and temperature window of the experiment. A set of characteristic curves is presented on Figure 1a.



(a) (b)

Figure 1. (a) Dynamic structure factors of PLA from neutron spin-echo experiment measured below the glass transition temperature of the amorphous poly(lactic-acid) at q=1.0083 Å^{-1} **(b)** q vector and temperature dependence of the relaxation rate, Γ (=1/τ).

The dynamical structure factors could be fitted by the Kohlrausch-Williams-Watts formula,

$$\frac{S(q,t)}{S(q,0)} = A \cdot e^{\left[\left(\frac{t}{\tau}\right)^{\beta}\right]} + b \qquad (1)$$

where A is the amplitude, τ is the characteristic decay time, β is the shape parameter and b is the baseline. Interesting behaviour of the relaxation rate has been observed.

As it is shown in Figure 1b, Γ shows a strong wave vector and temperature dependence. The *q*-vector dependence follows the structure factor peak of the PLA (not shown here, measured separately with wide-angle X-Ray scattering measurements), while the temperature dependence of the relaxation time, τ (τ=1/Γ) obeys the Arrhenius low (Figure 2). We attribute this observed local motion to the beta-relaxation of the glass. However, further measurements are necessary to confirm our findings and fully understand the observed dynamical process.

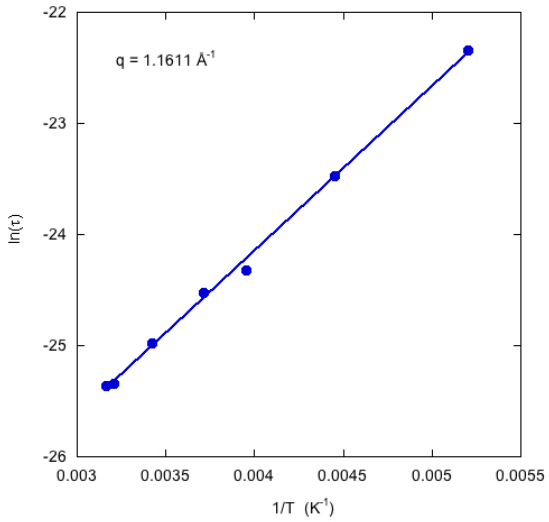


Figure 2. Arrhenius plot of the relaxation time, τ obtained at the maximum of the structure factor peak q=1.16 Å^{-1}.