



Contribution ID: 60

Type: not specified

Polymer dynamics in nanocomposites by NMR relaxometry and dielectric relaxation spectroscopy

Tuesday, July 7, 2015 6:30 PM (1 hour)

Polymer nano-composites represent a class of materials of great interest for many practical applications. In particular, polyvinyl butyral (PVB) is used in automotive and architectural applications for laminated safety glasses thanks to its high binding efficiency, optical clarity, and good adhesion to several different surfaces. Furthermore, its use as a polymer matrix in nanocomposite materials allows interesting properties to be obtained depending on the type of embedded inorganic nanoparticles. For example, the use of Antimony Tin Oxide (ATO) nanoparticles provides the nanocomposite material with the capability of filtering out the near infrared (NIR) waves of sunlight while maintaining transmission in the visible region. This property is becoming of relevance in building and vehicle glass construction as a consequence of the worldwide energy saving and environmental preservation policies.

In this study the effects of loading PVB with ATO nanoparticles on the polymer dynamics were investigated combining high resolution solid state ^{13}C NMR spectroscopy and low resolution ^1H NMR relaxometry. In particular, ^1H longitudinal relaxation times ($T_{1\text{H}}$) were measured in the 0.01 to 35 MHz frequency range by Fast Field Cycling (FFC) NMR relaxometry, whereas ^1H transversal relaxation times ($T_{2\text{H}}$) were determined by Free Induction Decay (FID) analysis at 20 MHz. All experiments were performed on both PVB and PVB-ATO in the temperature range between 30 and 120 °C, the polymer glass transition occurring at about 70 °C. The analyses of the dispersion curves and FIDs showed that loading with ATO nanoparticles results in an increase in polymer mobility.

A comparative study with broadband dielectric relaxation spectroscopy, in a frequency range up to 10 MHz, helped to elucidate peculiar features due to random blocks of polyvinylalcohol and polyvinylbutyral present in the polymer structure. Local dielectric spectroscopy (LDS) experiments were also performed close to the glass transition to highlight changes in the polymer dynamic behavior at the interface with the nano-inclusions.

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Session Classification: Posters