Investigation of Relaxation Processes in Nanocomposites by Transient Grating Experiments

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Keywords: polymeric nanocomposite, inorganic nanotube, time-resolved optical spectroscopy.

Abstract. We report a comparative study on the photo-elastic and photo-thermal features of two nanocomposites based on MoS_2 nanotubes dispersed into two different polyurea elastomeric matrices, which have different crosslinking properties. The time-resolved laser spectroscopic investigation on these nanocomposites by transient grating (TG) experiments has been performed. The relaxation kinetics on a very wide time scale has been measured from nanosecond to hundred of microseconds. The TG data on both pure polymers shows fast acoustic oscillations and a slow thermal decay. No structural relaxation is appearing in the experimental time window. Surprisingly, the presence of nanotubes in both the polymeric matrixes induces intermediate dynamics clearly detected by the TG signal. The features of this unexpected dynamic features recall the structural relaxation typical of glass-formers but its origin is still unclear.

Introduction

From several years nanocomposite materials are a very important topic in material science [1]. In particular polymeric nanocomposites are becoming the most important materials due to their interesting properties, e.g. electrical, optical, magnetic and structural properties. The new properties arise from the nanofiller nature, the polymer properties, the interface by which these two components interact as well as from the microstructures produced while fabricating and processing these nanocomposites [2]. The interaction phenomena taking place at the surfaces between the nanoparticles and the polymer chains are surely a fundamental issue in order to define, and possibly tailor, the new material characteristics. Despite its importance, the surface phenomena taking place in polymeric nanocomposites remains an open question that requires suitable experimental investigations [3] and theoretical/simulation studies [4].

In a previous paper [5], we measured the relaxation kinetics on two polymeric nanocomposites by laser time-resolved experiments. The investigated nanocomposites were made by dispersing inorganic nanotubes (MoS_2) or inorganic nanowires ($Mo_6S_2I_8$) into a polyurea elastomeric matrix. The transient grating (TG) experiment enabled to measure the elastic and thermal dynamics in a large time window, from nanosecond to milliseconds, giving a complete view of the different relaxation phenomena present in these nanocomposites, showing unexpected dynamic features appeared in the TG results.

In the present paper, we extend and compare the previous studies with TG data on a different nanocomposite made by mixing the same inorganic nanotubes (MoS_2) with a new polyurea elastomer. The presence of the unexpected dynamic feature is confirmed by this experimental investigation and it is enhanced by the new polymeric matrix.
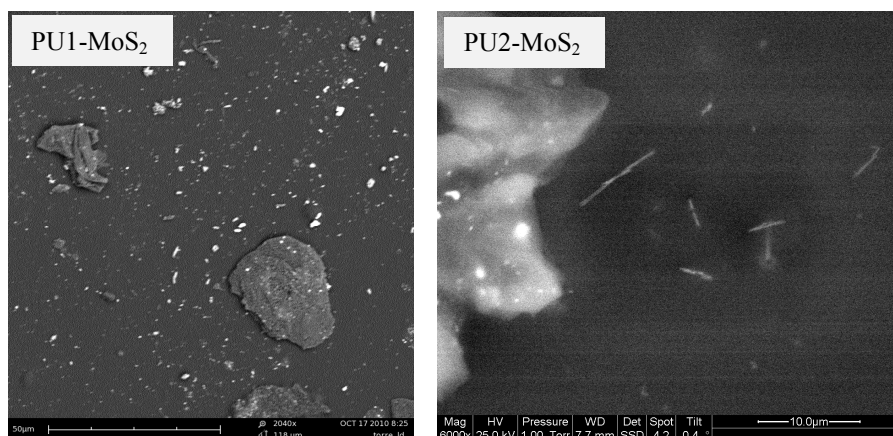

Figure 1. Scanning electron microscopy images of the a nanocomposite samples. The PU1 (on left side) and PU2 (on right side) polyurea MoS_2 nanocomposites. These images clearly show a non uniform dispersion of the nanotubes, forming aggregates characterized by different structures and sizes.

Sample Preparation

We investigated two different polyurea elastomers, with or without dispersion of MoS_2 nanotubes [6]. The first polyurea elastomer (PU1) is obtained from the crosslinking of the primary diamino-terminated poly(propylene oxide) Jeffamine D-2000 (Hunstman) and a trifunctionalized crosslinker Basonat HI-100 (BASF) as described in literature [7]. The second elastomer (PU2) is obtained by crosslinking the secondary diamino-terminated poly(propylene oxide) Jeffamine SD-2001 (Huntsman) with the same triisocyanate crosslinker.

These two elastomers are characterized by having different hydrogen bonds in the polymeric network and this turns into different elastic features. In elastomer based on primary amine chemistry, the resulting motives after reacting with isocyanates is a urea group, which might interact with an other urea motif in a bi-dentate way. Bulky secondary amines end up into substituted urea motives with only one hydrogen to be able to interact with other urea groups (mono-dentate) or even with no interaction at all. Thus, the mechanical properties of the polymer networks from PU1 are improved with respect to those coming from PU2.

The inclusion of nanotubes into PU1 and PU2 polymer matrices was made by adding the nanoparticles to the crosslinker solution, and using this solution to crosslink another solution containing the swollen diamino-terminated polymer chains. In both samples, the concentration of nanoparticles was less than 1 wt-%. In Fig. 1, the scanning electron microscopy images of the polyurea elastomeric nanocomposites containing MoS_2 nanotubes are shown.

Experimental

In a heterodyne-detected transient-grating (HD-TG) experiment [5,8-11], two infrared laser pulses, typically obtained dividing a single pulsed laser beam, interfere within the sample producing an impulsive spatially periodic variation of the material optical properties. The spatial modulation is characterized by a wave vector which is given by the difference of the two pump wave vectors. The relaxation toward equilibrium of the induced modulation is probed by measuring the Bragg scattered intensity of a second continuous wave laser beam. A sketch of the experimental set-up and details on the laser systems can be found in ref. 5 and ref. 10, respectively.

Results and Discussion

We performed four HD-TG measurements on pure polyurea elastomeric samples (PU1 and PU2), and on samples containing nanotubes (PU1-MoS$_2$ and PU2-MoS$_2$). The temperature and wave vector have been fixed to T = 293 K and q = 0.63 μm^{-1}, for all measurements. Fig. 2 shows the HD-TG signal measured on the pure PU1 system (top), and on the corresponding nanocomposite sample PU1-MoS$_2$ (bottom). The HD-TG data measured on the pure elastomer PU2, and the corresponding nanocomposite PU2-MoS$_2$ are represented in Fig. 3. There is a clear similarity between the HD-TG data measured in both pure systems (PU1 and PU2) and the corresponding nanocomposite (PU1-MoS$_2$ and PU2-MoS$_2$).

A simple inspection of the data from the pure elastomeric systems (Fig. 2 top and 3 top) show a first damped oscillating contribution followed by a slower monotonic decay. The former corresponds to a damped acoustic wave, whereas the slower relaxation dynamics is the thermal diffusion process [8,9]. These results are in perfect agreement with the typical HD-TG results in polymeric samples [11]. Differently, the results from the nanocomposites (Fig. 2 bottom and 3 bottom) show a new feature corresponding to an intermediate rise of the measured signal intensity. These results prove that this phenomenon is strongly correlated with the composite. The fast oscillating and slow relaxing contributions (corresponding to the acoustic wave propagation and thermal diffusion, respectively) show some weak variations, either by changing the polymeric matrix or by introducing the nanotubes.
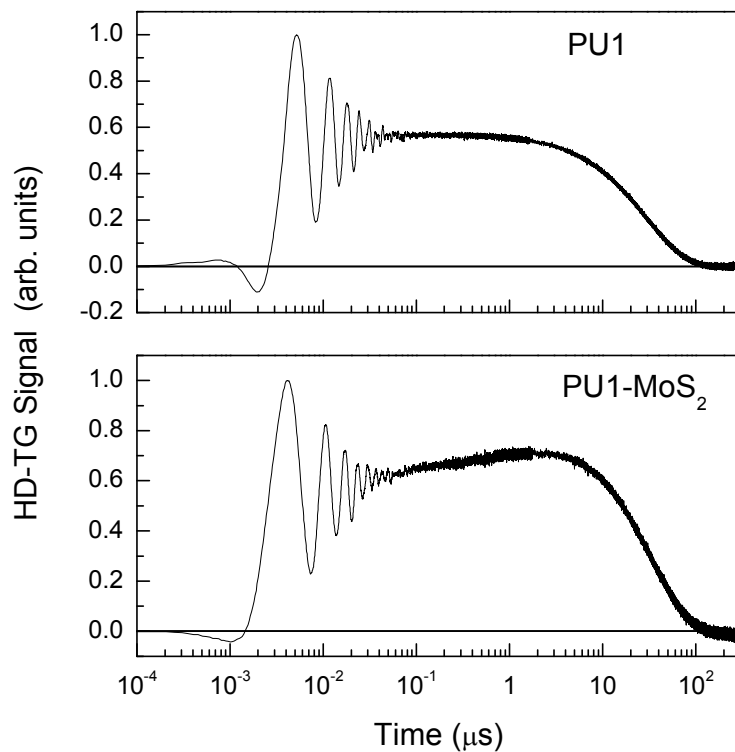

Figure 2. HD-TG signals from the pure elastomer PU1 (top) and the corresponding nanocomposite PU1-MoS$_2$ (bottom). The measurements were performed at room temperature (T = 293 K) and with a wave vector q = 0.63 μm^{-1}.

This intermediate dynamics are quite common in the HD-TG signal of homogenous matter as supercooled liquids and glass-formers [8,9]. In these materials, this behavior is due to the presence of structural relaxation processes. Also in water filled nanoporous materials, an intermediate rising signal has been revealed in the HD-TG data and it has been addressed to the water flow processes inside the nanopores [10].

In nanocomposite materials, the nature of this intermediate dynamics is quite unexpected and cannot be immediately explained using the available TG response models [12]. We can only speculate about its origin. In the nanocomposite samples the signal contribution from the intermediate dynamics is characterized by similar time scales but different intensities: it is clearly stronger in the PU2-MoS$_2$ sample. The most plausible explanation is that this dynamics is coming from the interfacial polymer in contact or in the close vicinity of the nanotube surfaces. In fact the interaction of the polymer with a surface of the nanoparticles can modify its glass transition temperature (T_g) either lowering or raising it respect to the bulk T_g. In our case, the presence of nanotubes could lower the T_g of the poly(propylen oxide) chains close to the nanoparticle surfaces. Thus, the structural relaxation time would be reduced and becoming visible in the investigated TG time window. Moreover, the weaker hydrogen bonding physical network present in the PU2 polymer would allow a more effective modification of T_g induced by the interaction with the dispersed nanotubes, producing a stronger contribution in the TG signal.
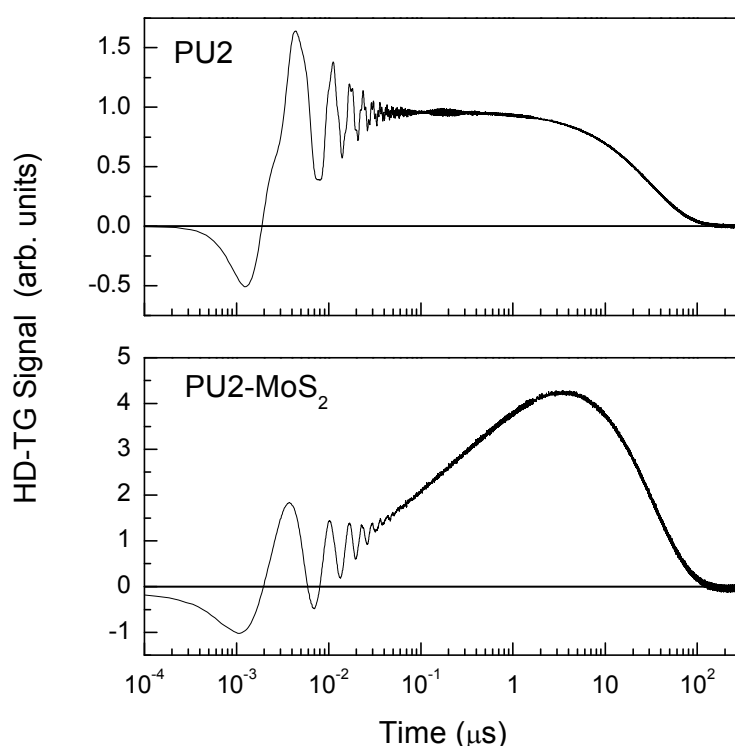

Figure 3. HD-TG signals from the pure elastomer PU2 (top) and the corresponding nanocomposite PU2-MoS$_2$ (bottom). The measurements were performed at room temperature ($T = 293$ K) and with a wave vector $q = 0.63$ μm^{-1}.

Conclusions

We are reporting here a comparative experimental investigation of the elastic, structural and thermal properties of two nanocomposites obtained by dispersing inorganic nanoparticles (MoS$_2$ nanotubes) in two different polyurea elastomeric matrices. The investigation has been performed using a time-resolved spectroscopic technique. The experiment clearly reveals the presence of a surprising intermediate dynamic process induced by the presence of inorganic nanoparticles into the polyurea matrix. A comparison of the data from the sample with or without nanotubes suggests that the source of this signal contribution could arise from the polymer chains close to the nanotube surfaces. If this is the case, the measured intermediate dynamics would show a softening process of the polymeric matrix induced by the nanoparticle surfaces. Other samples and measurements are required in order to get further understanding of the measured phenomena.

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