

Transient Grating Experiments on Inorganic–elastomer Nanocomposites

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Received: 15 June 2011 / Accepted: 18 July 2011 / Published: 31 October 2011

Abstract: We studied the photo-elastic and photo-thermal response of two new nanocomposites based on a polyurea elastomer mixed with inorganic nanotubes (MoS_2) or nanowires ($\text{Mo}_6\text{S}_2\text{I}_8$). The investigation has been performed using time-resolved laser spectroscopy, transient grating technique (TG), based on short laser pulses. This spectroscopic tool enables the measurement of the thermo-elastic response of the nanocomposites covering a very large time window, from nanoseconds to milliseconds, revealing the different dynamic phenomena present in these materials. On the fast timescale (from 1 to 100 ns) the TG signal shows the propagation of a high frequency acoustic wave enabling the measure of its sound velocity and damping time. In the slow time window (from 5 to 100 μs) the TG signal presents a slow decay due to the thermal diffusion process. As expected, these features are common for both pure polymeric and nanocomposite samples. Surprisingly, the presence of nanotubes or nanowires in the polymeric matrix produces on the intermediate time scale a new dynamic phenomenon in the experimental data, whose origin is not clear. *Copyright © 2011 IFSA.*

Keywords: Inorganic nanotubes, Polymer nanocomposites, Photo-thermal and photo-elastic phenomena, Time-resolved laser spectroscopy, Elastomer, Polyurea.

1. Introduction

The assembly and characterization of composite materials made by mixing nanoparticles with polymers is becoming an important topic in material science. Typically, these materials present interesting improvements of several structural characteristics [1, 2], that arise both from the nanofiller nature and the polymer properties, as well as from the microstructures produced while fabricating and processing these nanocomposites. The intrinsic properties of nanotubes and nanowires locate these nanoparticles between the more promising polymer fillers for nanocomposites [3].

Recently the production of new type of inorganic nanotubes and nanowires been has reported [4]. These are molybdenum halide or chalcogenide cluster polymers presenting unique properties that set them apart from the other numerous kinds of nanoparticles. These inorganic nanoparticles can be synthesized in a large variety of forms (e.g. multiwalled nanotubes and nanowires, ropes, ribbons, or thin microtubes) and this richness in form promises a large spread of the structural features with potential applications going beyond those of carbon nanotubes. In particular, these different structures make inorganic nanotubes particularly attractive for reinforcement in composite materials.

The production and characterization of nanocomposite based on inorganic nanowires is still at the very beginning and here we report some preliminary studies of the photo-elastic and photo-thermal features of new nanocomposites, based on inorganic nanotubes MoS_2 [5] and nanowires $\text{Mo}_6\text{S}_2\text{I}_8$ [6] used as fillers into a polyurea polymer matrix [7]. The experimental techniques used for such investigations are the transient grating spectroscopy, and time-resolved non-linear spectroscopy based on ultrafast laser pulses [8-9].

2. Experimental

2.1. Samples Preparation

We investigated three samples: the first was made of pure polyurea elastomer (PU) [7], the second one was made of PU with MoS_2 (PU- MoS_2) nanotubes [5], the third one was PU with $\text{Mo}_6\text{S}_2\text{I}_8$ (PU- $\text{Mo}_6\text{S}_2\text{I}_8$) nanowires [6].

For the synthesis of the three samples, two solutions in acetone were prepared as described in literature [7]: one containing the diamino-terminated polymer, and the other the trifunctionalized crosslinker with or without nanoparticles. In order to obtain a final solid content of 15% w/v, 3.85 g of Jeffamine D-2000 (Hunstman) was dissolved in 11.1 mL of acetone, and 0.65 g of Basonat HI-100 (BASF) was dissolved in 14.5 mL of acetone. In the case of samples containing nanoparticles, the Basonat HI-100 was dissolved in an ultrasonicated acetone dispersion of the corresponding nanoparticles to be incorporated. The two solutions were mixed and gently stirred for 5 min, and the final solution was cast onto the glass surface of a Petri dish. One day after the samples were cast, the obtained film was allowed to dry in the atmosphere and peeled from the surface. Samples were cut from their corresponding free-standing films ($14.6 \times 5.0 \times 0.75 \text{ mm}^3$). The final concentration of nanoparticles was less than 1 wt-%.

In Fig. 1, the optical and scanning electron microscopy images of the two nanocomposite samples are shown. Both the images clearly show nanotubes/wires aggregates in various dimensions. In the PU- MoS_2 sample, the length scale of aggregation seems limited to few micrometers, whereas in the PU- $\text{Mo}_6\text{S}_2\text{I}_8$ sample the aggregation can extent to several tenth of micrometers. Nevertheless both the samples present a non uniform dispersion of the nanotubes and nanowires, which are far from being well dispersed.

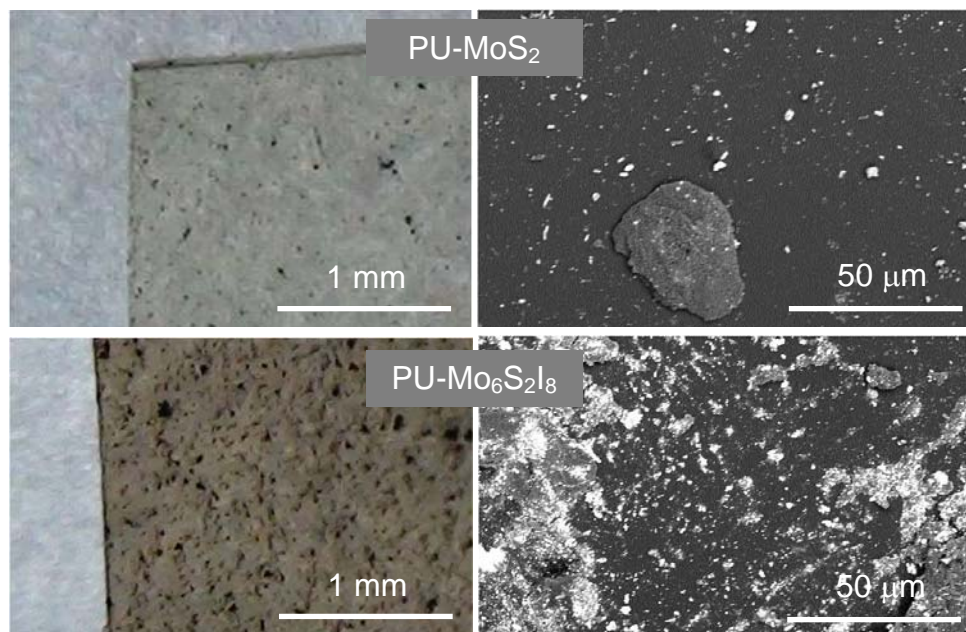


Fig. 1. Optical (on left side) and scanning electron microscopy (on right side) images of the nanocomposite samples. These images clearly show a non uniform dispersion of the nanotubes and wires, forming large aggregates.

2.2. Experimental Method

In a heterodyne-detected transient-grating (HD-TG) experiment [8-10], two infrared laser pulses, E_{ex} , typically obtained dividing a single pulsed laser beam; interfere within the sample producing an impulsive spatially periodic variation of the matter optical properties (Fig. 2). The spatial modulation is characterized by a wave vector q which is given by the difference of the two pump wave vectors. Its modulus is $q = 4\pi \sin\theta / \lambda$, where λ and θ are the wavelength and the incidence angle of the exciting pumps, respectively. The relaxation toward equilibrium of the induced modulation can be probed by measuring the Bragg scattered intensity of a second continuous wave laser beam, E_{pr} . In order to perform a heterodyne-detection, the signal field E_s is beaten with a reference beam, not reported in Fig. 2, and measured by a fast photodiode detector. The time evolution of the diffracted signal supplies information about the dynamic of the relaxing TG and, consequently, of the dynamical properties of the studied sample. A detailed description of the experimental set-up, laser system and detection techniques can be found in literature [10, 11].

The transient variation of the matter optical characteristics (i.e. transient grating) can be induced by different excitation channels [8-14]. The excitation electromagnetic field might or might not be in resonance with some matter states. The contribution to the signal due to the non-resonant interaction phenomena (e.g. the electrostriction processes) are less important than the resonant process, even if their contribution are not always negligible [12]. Typically the TG signal is dominated by the optical modifications induced by resonant field-matter interactions that can be either with electronic states or with nuclear rotational/vibrational states. The resonant photo-excitation induces a periodic modulation of the population states (i.e. population grating), that relax into temperature/density gratings in a time scale defined by the state life times. So the definition of the TG response function is quite complicated and needs to be examined carefully for each sample [9, 12-14].

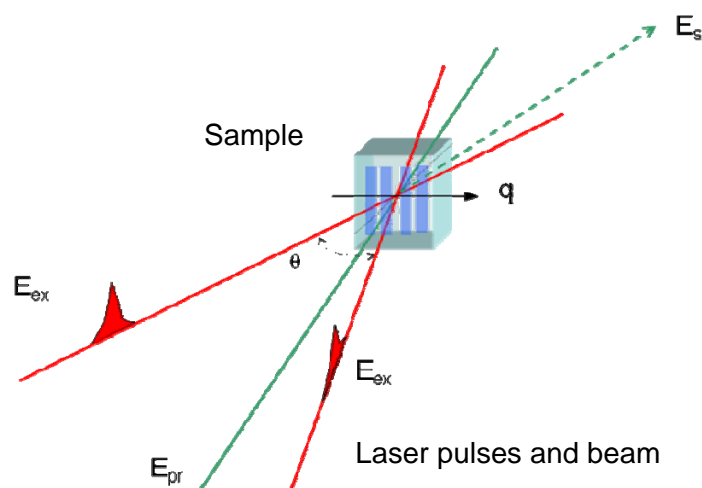


Fig. 2. Sketch of the optical set-up used in a TG experiment: E_{ex} are the excitation laser pulses ($\lambda = 1064$ nm, $\tau = 25$ ps), E_{pr} is the probing continuous wave ($\lambda = 532$ nm), and E_s is the diffracted beam.

The HD-TG experiments have been largely utilized to investigate the dynamics of molecular liquids. Typically, these optically transparent homogenous media present a weak absorption of the pump infrared radiation due to the resonance with some vibrational states. The induced vibrational population quickly thermalizes by fast non-radiative channels and builds up a temperature grating. This produces a pressure grating that launches two counter-propagating acoustic waves whose superposition makes a standing acoustic wave. Besides the acoustic waves, the laser excitation generates density grating supported by the temperature grating via thermal expansion, which relaxes on a slower time-scale by thermal diffusion. In molecular liquids these photo-elastic and photo-thermal processes can be described by relatively simple models based on hydrodynamic equations. Using these models the TG response can be calculated [9, 12-14].

In heterogeneous matter, the TG signal shows atypical contributions and the definition of response function become more complex because comprehensive thermal-elastic models must be used to describe the material response [10, 15, 16].

2.3. HD-TG Experiments

We performed three HD-TG measurements on samples made of pure polyurea elastomer (PU) and PU mixed with nanotubes (PU-MoS₂) or nanowires (PU-Mo₆S₂I₈). The temperature and wave vector has been fixed to $T = 293$ K and $q = 0.63 \mu\text{m}^{-1}$, for all the measurements. The top panel of Fig. 3 shows the HD-TG signal measured in PU sample. A simple inspection of the data shows 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. These results are in perfect agreement with the typical HD-TG results in polymeric samples [11]. In the middle and bottom panels in Fig. 3, the HD-TG data measured in both nanocomposite samples are shown.

Both these data show a new feature corresponding to an intermediate rise of the measured signal intensity. Moreover the fast oscillating and slow relaxing contribution are still present and apparently a little bit affected by the presence of the nanoparticles. These intermediate dynamics are quite common in the HD-TG signal of homogenous matter as supercooled liquids and glass-formers are [9, 12, 17]. This phenomenon is due to the structural relaxation of the samples. The intermediate rise is also present in the HD-TG data of water filled nanoporous materials [10], but in this heterogeneous media is due to the water flow processes inside the nanopores. The nature of this intermediate dynamics in

these nanocomposite materials cannot be immediately explained using one of the available TG response models and it requires further investigations and understandings.

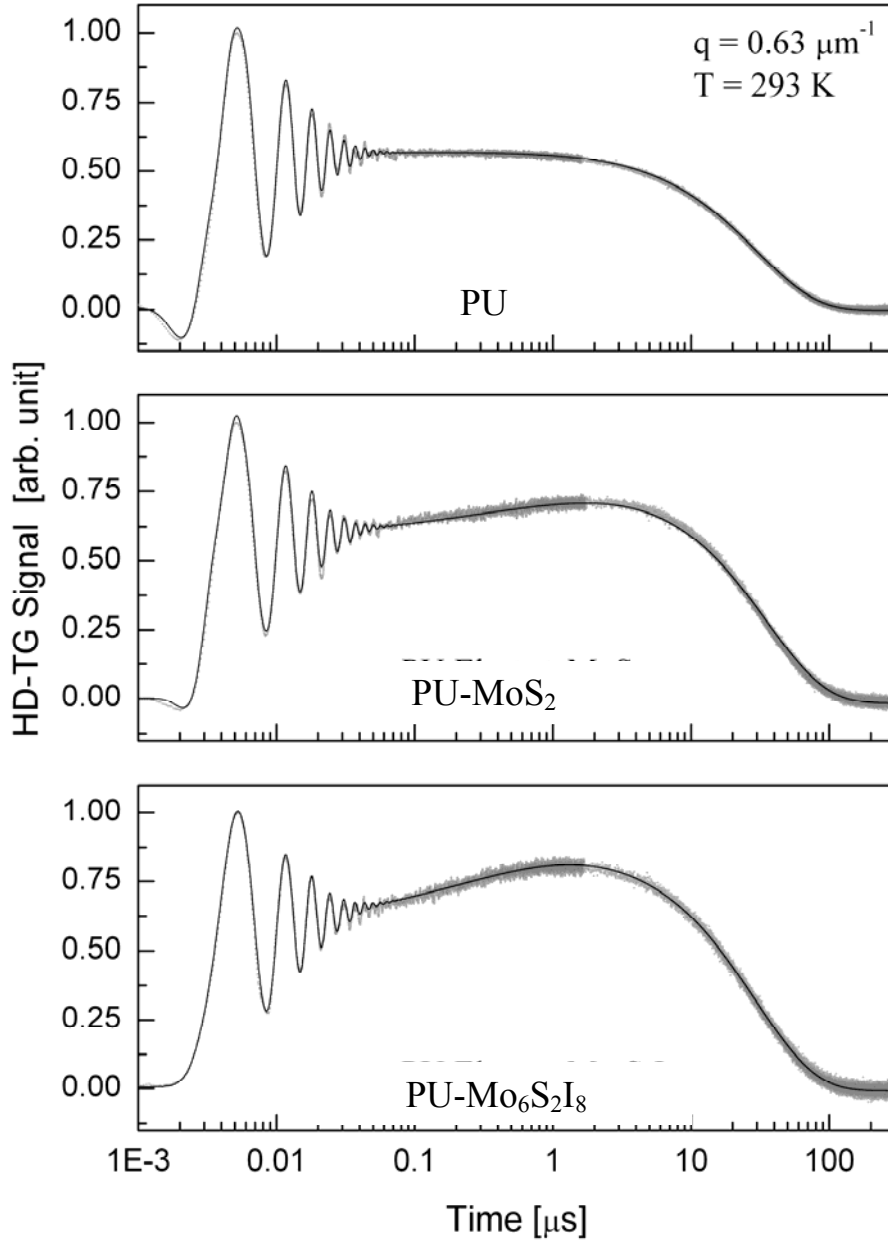


Fig. 3. TG signal from pure elastomer (PU), and containing nanotubes (PU-MoS₂) or nanowires (PU-Mo₆S₂I₈). The measurements were performed at room temperature ($T = 293$ K), and at identical wave vector ($q = 0.63 \mu\text{m}^{-1}$). The grey points are the experimental data and the black lines correspond to the best fit results according to Equation 1.

In order to get the time scales of the dynamical processes measured by the HD-TG experiment, all experimental data were fitted by using a phenomenological equation to describe the response function [9, 12]:

$$S(t) = A e^{-\left(\frac{t}{\tau_a}\right)} \sin(\omega_a t) + B e^{-\left(\frac{t}{\tau_a}\right)} \cos(\omega_a t) - D e^{-\left(\frac{t}{\tau_x}\right)^\beta} + C e^{-\left(\frac{t}{\tau_T}\right)}, \quad (1)$$

where ω_a and τ_a are the sound frequency and damping time, respectively; τ_x is the characteristic time and β is the stretching factor describing the intermediate dynamics; τ_T is the thermal relaxation time. The sound velocity is defined as $V_a = \omega_a / q$, the acoustic damping rate is $\Gamma_a = 1/\tau_a$, and the thermal diffusivity $\chi_T = 1/(q^2 \tau_T)$. The results of the best fit are reported in Table 1.

Table 1. Sound velocity (V_a), damping time (τ_a), characteristic time (τ_x), stretching factor (β), and thermal relaxation time (τ_T) from the fitting curves for the three elastomeric samples.

	V_a (m s ⁻¹)	τ_a (ns)	τ_x (ns)	β	τ_T (μ s)
PU	1544	11.9			29.6
PU-MoS ₂	1523	11.8	799	0.49	35.0
PU-Mo ₆ S ₂ I ₈	1551	13.0	299	0.59	29.7

The acoustic velocities and damping times – at $\omega_a \sim 150$ MHz – are very similar for the PU and both nanocomposite samples. This is in good agreement with the measurement of the real part of the Young's modulus reported by Fuith *et al.* [18], where the elastic differences between PU and the nanocomposites only appear at temperatures much lower than 293 K. Also the thermal diffusion time seems to be almost unaffected by the presence of nanoparticles. Nevertheless, further TG studies of the elastic and thermal properties are required before to get final conclusions. In particular, the temperature dependence of the acoustic and thermal fitting parameters must be investigated, as well as samples characterized by different nanoparticle concentrations. The intermediate rise time shows a clear variation between the two nanocomposites, confirming that the physical phenomenon is not only due to the presence of the nanoparticles, but also its time scale which is dependent on the nanoparticle features. In order to address the nature of this contribution to the TG signal, we are planning to study its temperature and wave-vector dependence.

5. Conclusions

We have presented a preliminary study of the photo-elastic and photo-thermal properties of two nanocomposites base on a polyurea elastomer as matrix, and two kinds of inorganic nanoparticles (nanotubes and nanowires) as fillers. The investigation has been performed using a time-resolved spectroscopic technique, named transient grating. This technique, using a impulsive material excitation obtained by picosecond laser pulses, enables to measure the elastic and thermal response of the studied sample. According to the experimental results, the acoustic wave velocity, damping rate, and the thermalization process appear no appreciably affected by the nanofillers inclusion. Differently, the experiment clearly reveals the presence of a new intermediate dynamic process due to the presence of inorganic nanoparticles into the polyurea matrix.

This preliminary investigation confirms the potentiality of the transient grating experiments for the measurements of dynamics over a very wide time window also in nanocomposite materials. In particular, measurements at various temperatures and wave vectors, in addition to investigations on samples with a larger range of filler concentrations, are required in order to get further understanding.

Acknowledgements

The present work was performed in the frame of the COST Action MP0902 (COINAPO – Composites of Inorganic Nanotubes and Polymers).

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