CHARACTERIZATION OF MWNT/TPU SYSTEMS USING LARGE AMPLITUDE OSCILLATION

C. A. Gracia-Fernández[a*],

[a]TA Instruments (Waters Cromatografía) Parque científico de Madrid, Campus de Cantoblanco. C/Faraday, 7. 28049 Madrid.
[*]cgracia@tainstruments.com

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Abstract
In the recent years, the interest of dispersed nanotubes in polymeric materials has grown exponentially. There are several methods to characterize this dispersions looking at the percolation concentration, the "goodness" of the dispersion and the interphase between the matrix and the nanotubes, using among other techniques, rheology and conductivity measurements. Commonly, the oscillatory rheology measurements are performed within the linear viscolelastic range, which is achieved by operating at small amplitude oscillation shear. Nevertheless, these measurements do not show the complete picture of the dispersion structure.

In this work, we propose the use the medium amplitude oscillation shear (MAOS) and the large amplitude oscillation shear (LAOS) to characterize the dispersion/structure of a Polystyrene (PS) matrix filled with multiwalled nanotubes (MWCNT).

The Ewoldt framework mathematical approach is used to analyze the non-linear stress response. That approach allows obtaining physically sounded magnitudes from the experimental data presented in this work. These magnitudes allow for a better understanding of the effects of the filler content.

1. Introduction

Nowadays, the intense development of new nanocomposites, consisting of a polymer matrix and an inorganic phase, originated an important increase of the number of studies focused on the characterization of the organic-inorganic interphases. Those studies are justified from the perspective that a proper characterization of the interphase produced in a nanocomposite is crucial to understand the properties and behavior of the final material. Despite the utility of those studies, identification, characterization and subsequent relationship with the final properties of the material presented varied difficulties depending on each specific case. Particularly, most of the results are not applicable outside of the linear viscoelastic region. That is the reason why a large amplitude oscillation shear (LAOS) experimental setup is used in the present work to identify and characterize the organic-inorganic interphases of multiwalled nanotube (MWNT)-Polyestirene nanocomposites.

The degree of interaction between the filler and the matrix and thus the composite properties has been related to the interphase. In fact, synergistic effects were found in the form of a further increase in wear resistance, stiffness, fracture toughness and tensile and impact strengths when using filler composed of nano and microparticles [1-3]. As defined by

Drzal et al. [4], and Schadler [5], the interfacial region is the region beginning at the point in the fiber at which the properties differ from those of the bulk filler and ending at the point in the matrix at which the properties become equal to those of the bulk matrix. The thickness of the interphase is usually in the range between 2 and 50 nm [5] and has a very significant effect on the properties of the nanocomposite. In short, the change of the nanocomposite properties with the addition of nanofiller informs about the existence of an organic-inorganic interphase. The direction and magnitude of that change is an additional information to better characterize the interphase. This paper shows the benefits of applying LAOS to the interphase characterization. The addition of MWCNT to a PS matrix can produce improvements in all the thermophysical properties [6-9].

A good dispersion of the filler agglomerates promotes an increase of the organic-inorganic interfacial surface and, thus, is necessary for obtaining improvements in the mentioned properties. The aim of this work is to provide a new insight into identification of the interfacial regions, whose relaxation times are different from those of the matrix, by rheology and, to a greater extent, by LAOS.

The theoretical background used in this work was extensively explained by other authors [10]. In the present work we will only focus in the physical meaning of the parameters obtained in that framework.
Here we define the strain-stiffening ratio, S, as

$$S = G'_L - G'_M / G'_L \tag{1}$$

where G'_M is the minimum-strain modulus and G'_L is the large-strain modulus. Accordingly, S = 0 for a linear elastic response, S > 0 indicates intra-cycle strain-stiffening, and S < 0 corresponds to intra-cycle strain-softening.

Similarly, the shear-thickening ratio, T, can be defined as

$$T = \eta'_L - \eta'_M / \eta'_L \tag{2}$$

where η'_M is defined as Minimum-Rate Dynamic Viscosity and η'_L is the Large-Rate Dynamic Viscosity. T = 0 indicates a single harmonic linear viscous response, T > 0 represents intra-cycle shear-thickening, and T < 0 intra-cycle shear-thinning.

In our opinion, the behavior of a given material at large strains and large deformations separately contents an important amount of information that can be used to better understand the underlying physics.

2. Results and Discussion
The rheological experiments were performed with a TA Instruments RPA *elite* (TA Instruments), strain control, separated motor transducer instrument. The TRIOS software has the capability of the LAOS analysis both in the McKinley and the Wilhelm approach. Two kinds of experiments where performed at 160º C and at 0.1 Hz

Small amplitude oscillation shear (SAOS) frequency sweeps with strains within the linear viscoelastic range, and SAOS, medium amplitude oscillation shear (MAOS) and LAOS strain sweeps at 1 Hz. For the case of PS–MWCNT nanocomposites, the matrix is a thermoplastic amorphous PS. MWCNT consisting of multiple rolled layers (concentric tubes) of graphite

were provided by Helix, *Texas, US*. Purity is about 95% as determined by chromatography, their length is in the range from 0.5 to 40 μm and the specific surface area is in the range from 40 to 300 m2·g–1. The MWCNTs concentrations were 0, 2, 3, 4, 5 %.

One of the ways to present the data is using what it is called "Lissajous-Bowditch" Figure. In this representation we show the stress versus the strain. At 1300 % in the LAOS regimen all the curves show a non linear behavior. This nonlinear profile is more evident at 0 % of concentration.
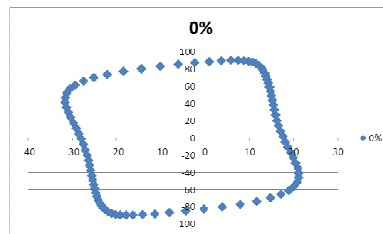
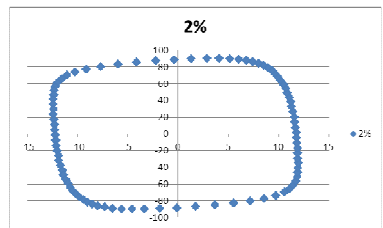**Figure 1.** Stress versus Strain of 0 % concentration.

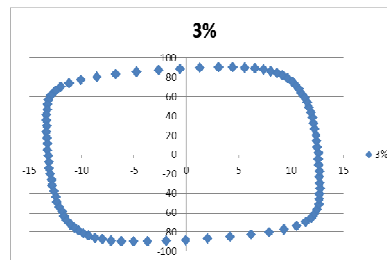**Figure 2.** Stress versus Strain of 2 % concentration.

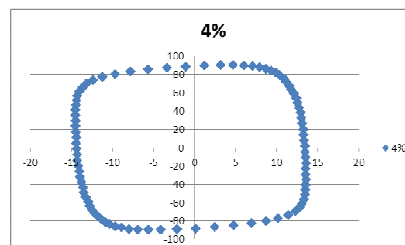**Figure 3.** Stress versus Strain of 3 % concentration.
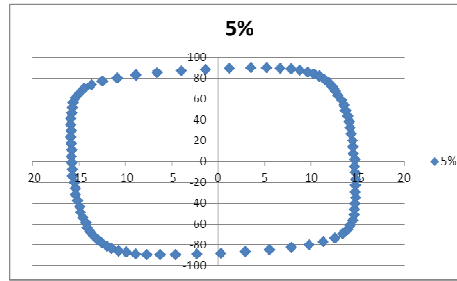
Figure 4. Stress versus Strain of 4 % concentration.

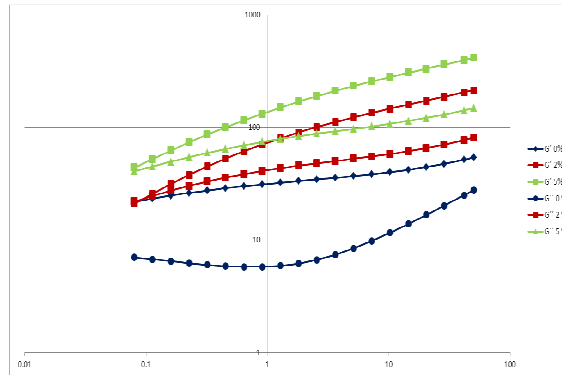**Figure 5.** Stress versus Strain of 5 % concentration.

Figure 6. G´ and G´´ versus frequency (0 %, 3% and 5 % concentration)

We have shown in Figure 6 only 0 %, 2 % and 5 % of concentration for visual purposes. The behavior of the viscoelastic magnitudes is completely different from the 0 % to the other samples. The 0 % concentration shows the typical behavior of an amorphous polymer in the rubbery region. At 160º C, the experimental freq range is far away from the freq cross over. The presence of the CNTs changes completely the freq sweep profile. The freq crossover value increases and the trend remind more to the terminal region. The presence of the CNTs acts like a plasticizer decreasing the relaxation time of the material.
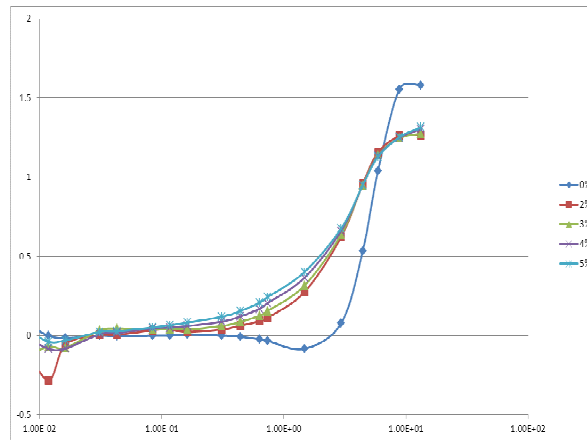

Figure 7. S versus strain. 0%, 2%, 3%, 4%, 5% concentration.

Firstly, we can observe in Figure 7 that the S value at low strains are positive but very closed to zero which indicates low intra-cycle strain-stiffening. As soon as the strain reaches

the end of the linear viscoelastic Range and the starting of the MAOS range the S value increases indicating higher intra-cycle strain stiffening. This effect starts at lower strains the higher is the Carbon nanotubes concentration. A possible explanation is the effect of the percolation network built by the CNTs. This network provides strain stiffening that adds to the strain stiffening contribution of the PS matrix. At high strains the S value becomes higher for the 0 % amount of CNTs. This may indicate that the nanoparticles avoid the strain stiffness mechanism of the entanglements of the PS. It is possible to observe that for all the concentrations S reaches a plateau with the same value at a strain of 13 (1300 %). Also the Graphic shows that for the concentration of 0 %, there is a minimum in S prior to the increase. So there is a small strain softening prior to the strain stiffening behaviour. This trend disappears when CNTs are added to the matrix. There could be some reasons for this behaviour but we did not find any good explanation for that up to now.
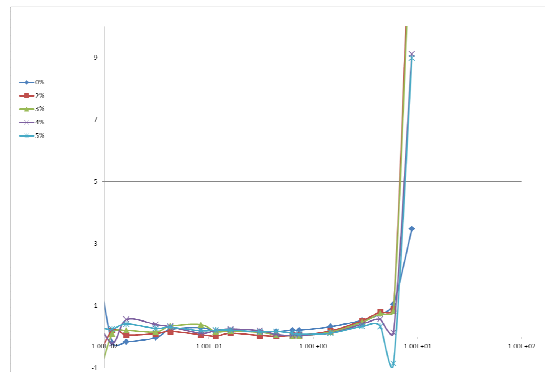

Figure 8. T versus strain. 0%, 2%, 3%, 4%, 5% concentration.

For the T ratio, the values are positive almost in all the samples indicating intra-cycle shear thickening. From the graph, it seems that this behaviour starts at higher strains the higher the concentration but the differences are really small to give a relevant conclusion. This trend is completely different from the TPU+ MWCNTs (same nanofiller) observed by C. Gracia et.al. where the T magnitudes decreased in the LAOS regimen. In this case, they run a thermoplastic over its melting temperature. Here we have an amorphous polymer in the rubbery sate. It is possible to observe also a minimum in the T variable that becomes more important the higher the concentration. We are still working on the interpretation.

Conclusions
LAOS technique gives a deep insight of the effect of the MWCNts in the PS Matrix. From the SAOS measurements, it has being observed that the MWCNTs increase the relaxation time of the Bulk. From the LAOS measurements, it has being observed that both S and T ratios increases with strain indication strain stiffening and shear thickening. And the effect of the MWCNTs concentration has being investigated.

REFERENCES

1. Wetzel B, Haupert F, Zhang MQ. Epoxy nanocomposites with high mechanical and tribological performance. Compos. Sci. Technol. 2003;63:2055–206.
2. Park JH, Jana SC. The relationship between nano-and micro-structures and mechanical properties in PMMA-epoxy-nanoclay composites. Polymer. 2003; 44:2091–2100.
3. Han J., Cho K. Nanoparticle-induced enhancement in fracture toughness of highly loaded epoxy composites over a wide temperature range. J. Mater. Sci. 2006;41: 4239–4245.

4. Drzal LT, Rich MJ, Koenig MF, Lloyd PF. Adhesion of graphite fibers to epoxy matrices: II. Theeffect of fiber finish. J. Adhes. 1983;16:133–152.

5. Schadler LS. Polymer-based and polymer-filled nanocomposites. In 'Nanocomposite Science and Technology' (eds.: Ajayan PM, Schadler LS, Braun PV). Wiley, Weinheim, 77–135 (2003).

6. Xia H, Song M. Preparation and characterization of polyurethane–carbon nanotube composites. Soft Matter. 2005;1:386–394.

7. Xia H, Song M. Preparation and characterisation of polyurethane grafted single-walled carbon nanotubes and derived polyurethane nanocomposites. J. Mater. Chem. 2006;16:1843–1851.

8. Koerner H, Price G, Pearce NA, Alexander M, Vaia RA. Remotely actuated polymer nanocomposites-stress-recovery of carbon-nanotube-filled thermoplastic elastomers. Nat. Mater. 2004;3:115–120.

9. Cho JW, Kim JW, Jung YC, Goo NS. Electroactive shape-memory polyurethane composites incorporating carbon nanotubes. Macromol. Rapid Commun. 2005;26:412–416

10. Ion Fernandez, Anton Santamaría, María Eugenia Muñoz, Pere Castell; European Polymer Journal 43 (2007) 3171–3176