Experimental report

16/09/2024

Proposal: **9-12-723**

Council: 4/2024

Title: Dynamical characterization of carbonaceous fillers in UV curable conductive composites

Research area: Materials

This proposal is a new proposal

Main proposer: **Cristian MENDES**

Experimental team: Maksym GOLUB
Joerg PIEPER
Timur TROPIN
Cristian MENDES

Local contacts: Mohamed ZBIRI

Samples: SPOT-E resin
MWCNT
rGO
ANYCUBIC resin

Instrument	Requested days	Allocated days	From	To
IN5	2	2	01/07/2024	03/07/2024

Abstract:

Nowadays, smart materials capable to respond to external stimulus are highly requested. Thus polymer-based composites giving rise to a variety of multifunctional responses. Behaviour and interactions of polymer and fillers during the various processing stages allows to enhance physico-chemical properties of composites. They are generally obtained from solvent-based processes, which can induce non-desirable environmental issues. Thus, UV-curable materials, that capable of suffering a process of rapid conversion from liquid solventless compositions to solid films upon UV-visible light irradiation, represent an interesting alternative. It was observed that structure and macroscopic properties of UV-curried nanocomposites depends on type/concentration of fillers and type of the matrix. The current proposal is directed towards exploring the dynamics of UV-curable polymer composite with carbonaceous fillers (conductive composites), a pivotal aspect that significantly influences the material's ultimate properties. It's crucial to delineate the relationship between the dynamics of the composite and their performance in electrical conductivity and its improvement for further application.

Experiment number: 9-12-723
Dynamical characterization of carbonaceous fillers in UV curable conductive composites

Scientific Background: Nowadays, research and technological developments are increasingly focusing on smart and multifunctional materials, i.e., materials capable to respond to external stimulus. A particular type of these materials is based on polymer composites, which take advantage of the synergistic combination of their inorganic and organic constituents, giving rise to a variety of multifunctional responses. In these composites, the behaviour and interactions of polymer, filler, and other additives during the various processing stages allows to enhance one or more physico-chemical properties. Most of those materials are obtained from solvent-based processes, but the use of solvents usually induces non-desirable environmental issues and waste generation. Thus, UV-curable materials, which are those materials capable of suffering a process of rapid conversion from liquid solventless compositions to solid films upon UV-visible light irradiation, processed at room temperature, without solvent emissions and with high energy efficiency, represent an interesting alternative to overcome these issues.

In particular, electrically conductive polymer-based composites have gained special attention due to many benefits in comparison to traditional conductive materials for applications such as electronic packaging, capacitors, thermistors or piezoelectric functions. Among the most used composites, the ones based on carbonaceous fillers stand out, including multiwalled carbon nanotubes (MWCNT) or reduced graphene oxide (rGO). The different shape/structure of these carbonaceous particles causes that the electrical conductivity of each composite increases in a very different way. Therefore, the electrical percolation threshold (the critical concentration where the composite turns abruptly from insulator to conductor) change drastically from one filler type to another. This percolation threshold can be dramatically affected by the polymer chain density, which is directly related to the rigidity of the material. Further, the inability to incorporate higher amounts of carbonaceous fillers to UV-curable polymers is ascribed to the fact that those fillers absorb UV light and competes with the photoinitiator.

In this context, enormous efforts are being put in the development of UV curable conductive polymer composites in order to face critical troubles to enhance their performance; i.e. the limitation of filler amount or a bad ageing of their mechanical properties. Furthermore, the impossibility to cure the material up to the same extent due to the presence of different carbonaceous fillers, can influence the dynamics of both the fillers and the polymer chains on the final material. This could be translated in a different conductivity thus influenced by the degree of curing of the material and at the same time affected by the type and content of the carbonaceous filler. In order to tackle these problems, a deep-learning of the dynamics of the composites in liquid state and after the curing process in solid samples is of crucial importance. Further, this knowledge will critically impact the preparation methods of the composites.

For all this, the proposal was directed towards exploring the dynamics of UV-curable polymer composite with fillers, a pivotal aspect that significantly influences the material's ultimate properties. It's crucial to delineate the relationship between the dynamics of the composite and their performance in electrical conductivity.

Preliminary Work: In our previous work different macroscopic characterization techniques were employed for MWCNT/PUA composites including DSC, thermogravimetric analysis or mechanical stress-strain tests, among others. It was observed that, due to the impossibility of photocrosslinking a completely entire film with higher filler contents, a maximum filler concentration of 0.6wt.% was incorporated in our composites. The microstructure characterization and filler dispersion were studied by SEM analysis, showing an apparently good filler dispersion. High electrical conductivities are achieved with MWCNT amounts lower than 0.5 wt.%. Similarly, rGO was dispersed in a vegetable oil-based acrylate polymer matrix and SEM results again indicated a good filler dispersion. The thermal, mechanical and dynamo-mechanical analysis indicated the potentiality of these material for smart sensing applications. However, in this case, a total amount of 5 wt.% of filler was needed to achieve a proper increase in electrical conductivity. This difference in electrical conductivity is probably ascribed to the different filler shape and possible aggregation compared with MWCNT, but also, the type of polymer matrix (vegetable oil-based acrylate polymer matrix is more rigid than PUA matrix) can play an important role. In these studies, a lack of knowledge on the nanoscale structure of the composites was preventing us from establishing a clear relation between the properties of the composites and their structure. Particularly, electrical conductivity and mechanical properties are macroscopic properties directly related to the filler type, content and dispersion, in which studying the filler aggregation is crucial to optimize the response. Thus, preliminary SANS data were collected for both MWCNT/PUA and rGO/PUA composites with 0.6 and 5 wt.%, respectively. These results evidenced us that SANS signal depends on the filler used, which could be ascribed to different nanostructural organization of polymer films. In fact, according to the test SANS measurements, we anticipate that the complementary SANS experiments (recently accepted proposal for SANS2D instrument at ISIS, UK) with different polymer matrices and various concentrations of carbonaceous fillers will provide unique structural insight into the materials proposed here.

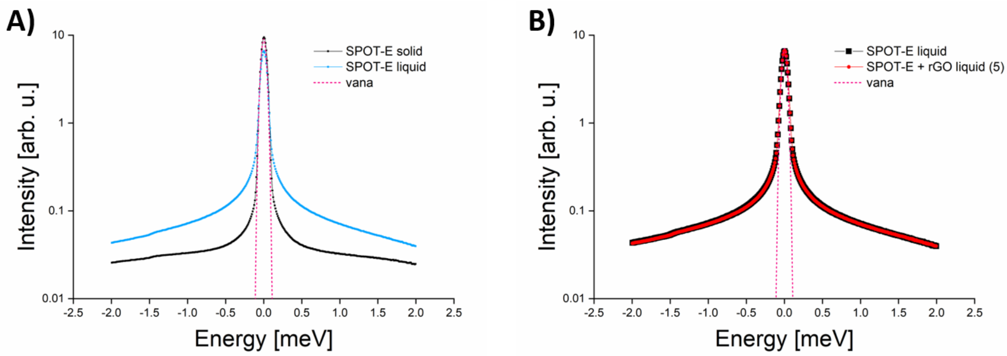

Figure 1: A) The summed QENS intensities over all the Q groups for SPOT-E solid and liquids samples. Intensities are normalized according to their mathematical areas under the peaks. B) The summed QENS intensities of the SPOT-E and SPOT-E + rGO (5) (containing 5 wt.% rGO) liquid samples.

In this sense, the evaluation and the influence of the dynamics of polymer composites during their curing process on the electrical conductivity and mechanical properties will be of great interest. However, the curing process is so fast to perform an *in-situ* QENS study. For this reason, two type of samples were proposed and measured, liquids or uncured materials and solids or cured materials.

Aims: The investigation was delved into how the type of particles, alongside the characteristics of the photocurable polymer, impact the dynamic of UV-curable polymer composites, employing QENS as the investigative tool. Since only polymer has hydrogen atoms, this QENS study was explicitly focused on its dynamic. The findings from the experimentation will be related with final structure of composites and then associated with the materials' macroscopic attributes, such as electrical conductivity. QENS is a potent instrument for spanning dynamics in picosecond to nanosecond time scales, making it exceptionally suitable for delving into the complex dynamics of polymers and polymer composites. Specifically, QENS is adept at examining diffusion processes, which are vital for the rigidity characteristic of polymer matrix. This endeavour aims to garner insights into the dynamics of polymer composite with fillers at picosecond to nanosecond time scales. We will probe composite films comprising MWCNT and rGO, as indicative conductive fillers with two distinct particle shapes, ranging from nanotubes to 2D layers. These carbonaceous fillers will be amalgamated with two commercially accessible UV curable resins, one elastic and one rigid. Consequently, dynamic characterization of diverse nanocomposites will be executed using QENS before and after UV exposure.

Performed Experiments: Two distinct carbonaceous fillers, namely MWCNT and rGO, will be employed, along with two photocurable polymer materials, one rigid and ester-based, the ANYCUBIC resin, and other flexible and polyurethane-based, the SPOT-E resin. For each filler, two loading concentrations will be tested: 0.1 wt.% and 0.6 wt.% for MWCNT and 1 and 6 wt.% for rGO. In sum, the objective is to measure 2 fillers x 2 concentrations x 2 polymers both before and after UV exposure. Moreover, reference measurements for the polymers without fillers before and post-UV exposure are also measured. This aggregates to a total of 20 samples that were tested according to the proposed conditions.

As can be seen in Figure 1, data treatment is initiated and some preliminary results are obtained. From Figure 1A a clear difference can be observed from liquid and solid samples for sample SPOT-E polymer matrix, indicating that the curing process restring the dynamical movements of SPOT-E polymer due to the reticulation process of the material as it was expected. Furthermore, Figure 1B indicates no differences between liquid materials even if the highest filler content was added (5 wt.% of rGO). This elucidates that similar dynamical behaviour is presented for materials independently to the filler type and content. However, the analysis of cured samples and comparison of different filler contents and types is ongoing. Also, data fitting according to some models is carrying out which will provide the dynamic behaviour information of materials obtained, expected to be lest for filler containing samples as filler will restring the movement of polymer chains in the composites. Then, we plan to prepare a manuscript with structure an dynamical characterization of UV curable conductive composites.