Stability of graphene dispersions

- Study of polymer-assisted exfoliation -

Introduction

Two-dimensional graphene is of great interest in various fields: composites, barrier coatings, solar cells, transistors, biomedical applications. This material of nanometric thickness offers remarkable mechanical properties but its mass production at a reasonable cost remains a challenge. Mechanical or chemical exfoliation of graphite may be a promising solution.
This intercalation process, resulting in the complete separation of the material's layers, suffers however from several drawbacks, such as reaggregation of graphite platelets or migration of surfactant molecules, which could be a source of reduced material properties. This paper describes how Turbiscan® technology can be used to study the stability of graphene platelets dispersions (GPD) to detect nascent evolutions and select best suited polymer to stabilize the dispersion.

KEY BENEFITS

- FAST
- NO DILUTION
- SENSITIVE

Reference

Y. Kim et al. «A Study on amphiphilic fluorinated block copolymer in graphite exfoliation using supercritical CO2 for stable graphene dispersion » *J of Colloid and Interface Science 510* (2018): 162-171

Reminder on the technique

Turbiscan® technology, based on Static Multiple Light Scattering, consists on sending a light source (880nm) on a sample and acquiring backscattered (BS) and transmitted (T) signal all over the sample height. By repeating this measurement over time at adapted frequency, the instrument enables to monitor physical stability.
The signal is directly linked to the particle concentration (φ) and size (d) according to the Mie theory knowing refractive index of continuous (n_f) and dispersed phase (n_p):

$$\boldsymbol{BS} = \boldsymbol{f}(\varphi, \boldsymbol{d}, \boldsymbol{n_p}, \boldsymbol{n_f})$$

Method

The dispersions were prepared with an amphiphilic fluorinated block copolymer PTFEMA-*b*-PVP in supercritical CO_2 at different concentrations and molecular weights. The affinity between the polymer and the platelets contributes to keeping the dispersion stable (the platelets remain in independent state).

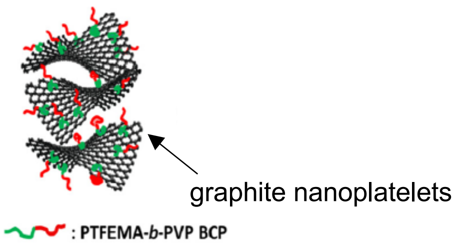

Figure 1: Exfoliation of graphite nanoplatelets with PTFEMA in supercrititcal CO_2

In this note, six dispersions at 1.6% concentration of graphite were prepared in methanol.

Sample name	Description
GD	Graphite Nanoplatelets Dispersion
GT	GD $SCCO_2$-treated without the block copolymer
G5L	GD $SCCO_2$-treated with 5% of the block copolymer at low molecular weight (L)
G10L	GD $SCCO_2$-treated with 10% of the L block copolymer
G5H	GD $SCCO_2$-treated with 5% of the block copolymer at high molecular weight (H)
G10H	GD $SCCO_2$-treated with 10% of the H block copolymer

Table 1: Sample description and composition details

Samples were analyzed at 30°C using Turbiscan®.

Results

Stability TSI and dispersibility

To measure the efficiency of exfoliation process of graphite and thus the ability of the polymer to prevent the reaggregation of graphene sheets, the global stability of the sample was evaluated. The Turbiscan Stability Index (TSI) was automatically computed to quantify the evolution of the dispersion state. This parameter sums all the variations detected in the sample (sedimentation, clarification, size variation,...) and express it in a single value. *At given ageing time, the higher the TSI, the more significant destabilization has occurred.*

Figure 2a shows the evolution of the TSI for all the 6 samples. Figure 2b gives a closer look for the samples exfoliated with polymer.

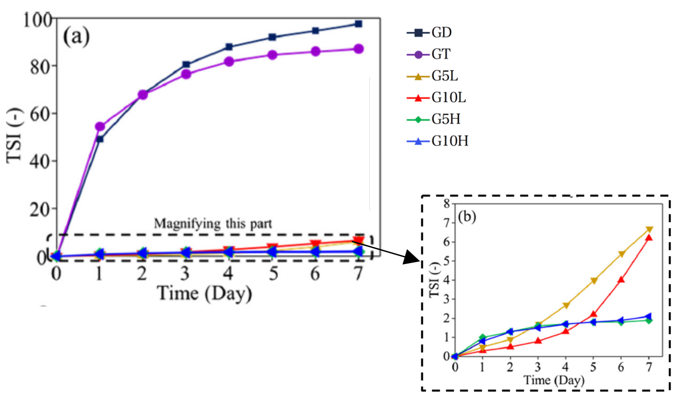

Figure 2: TSI for graphite platelets dispersion (GD) and samples treated with polymer of different molecular weights and concentrations

Compared to samples containing polymer, in the first hours, the **GD** and **GT** present a significant increase of TSI values (Fig. 2a). This indicates that the treatment with block copolymer tends to stabilize the dispersions, in particular; with samples treated using long polymer chains - **G5H**, **G10H** – as the TSI value reaches a plateau (TSI =2) after only 3 days (Fig. 2b). After 3 days **GT** presents a smaller value to **GD** indicating that SCCO2 treatment alone also stabilizes the dispersion of graphite platelets.

Prediction of long term behaviour

The analysis of raw transmission signal measured for diluted samples of graphene dispersion without treatment (**GD**), treated with high molecular weight polymer (**G1H**) or with low molecular weight (**G1L**) provides additional information the early dispersion changes.

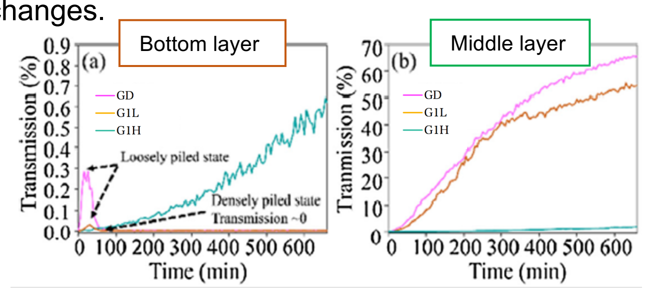

Figure3: Transmission signal at the bottom and middle of the vial containing the GP sample

In the bottom layer of **GD** and **G1L** higher transmission level is observed during the first 100 minutes of analysis. This can be related to the increase of platelets size - platelets aggregate all over the height of the sample.

As the aggregates settle and the concentration in the bottom layer increases, a dense sediment is forming. This phase absorbs the light causing the disappearance of the transmission, hence the existence of the peak (Fig. 3 (a)) at the bottom of the sample. This behavior is not observed in sample **G1H** which is stable versus time.

The presence of the early peak in transmission level at the bottom of the sample could be a sign of destabilization that will occur. In only one hour, Turbiscan allows to predict the long-term behavior and rank sample stability.

CONCLUSION

Turbiscan® offers a quick and easy method to evaluate the efficiency of polymer-assisted exfoliation. This method is of a great interest for industrial mass production of graphene as it requires no dilution. The technology not only gives quantitative information on the global stability of prepared dispersion but also can be used to detect, at an early stage, a behavior representative of destabilization occurring hours later. It could thus be used in research for prescreening of polymeric dispersants to rapidly determine the most suitable graphene stabilizer.