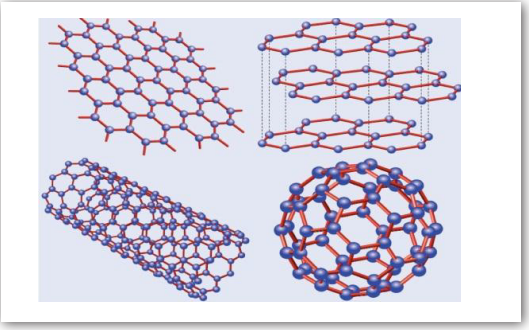
Applications of thermal analysis techniques to Graphene and Graphene based materials

GENERAL INTRODUCTION

Graphene is a two dimensional material consisting of a single layer of carbon atoms arranged in a honeycomb or chicken wire structure. It is the thinnest material known and yet is also one of the strongest. It conducts electricity as efficiently as copper and outperforms all other materials as a conductor of heat. Graphene is almost completely transparent, yet so dense that even the smallest atom helium cannot pass through it.



The outstanding properties of graphene make it attractive for applications in flexible electronics.
Graphene is one of the strongest and stiffest known materials and is also very light weight. These properties mean that graphene can be mixed with plastics such as epoxy to make composites which have good specific physical properties Graphene is the ideal electrode material. There is huge effort in developing batteries, fuel cells, photovoltaic cells and supercapacitors based on graphene.
All these new developments require a good knowledge of the physical and chemical properties of graphene and the corresponding composites. As in many other new fields, thermal analysis offers a large range of methods to fulfil the experimental needs.
Some examples are given to illustrate the works that are done with Setaram thermoanalyzers.

1- Characterization of Polyvinylbutyral/Graphene composite (THEMYS ONE TGA)

INTRODUCTION

Dispersion of graphene nanosheets in polymer hosts are challenges in the development of highperformance graphene-based nanocomposites to develop high thermal and mechanical properties.

EXPERIMENT

THEMYS ONE TGA is used to investigate the enhancement of the thermal properties of a composite based on polyvinyl butyral (PVB) loaded with different concentrations of graphene (from 0.1 to 0.6%).

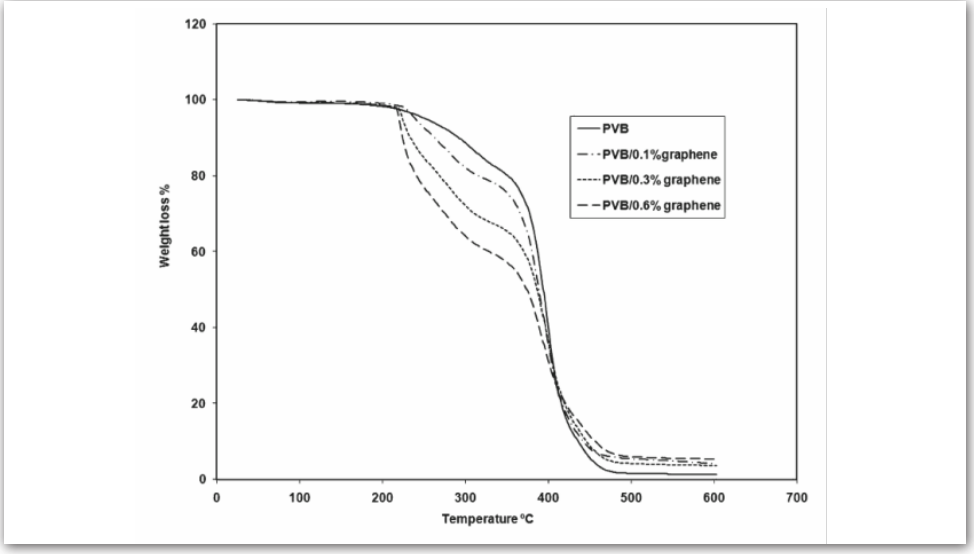


Figure 1: TGA curves of PVB and PVB/ graphene nanocomposites

RESULTS AND CONCLUSION

The TG curve of the PVB alone (Figure 1) shows two main mass losses corresponding to the liberation of OH groups under the form of water, followed by the degradation of especially the butyral group.
As soon as a certain small amount of graphene is added to the PVB, the onset temperature of butyral degradation is shifted to higher temperature and in the same time the mass loss corresponding to this step is decreased.
As the graphene sheets prevent the emission of thermally degradated gaseous molecules, the thermal stability of the composite containing grapheme is enhanced compared to the pure PVB.

Adapted from Mortaza Hajian and al., J Polym Res (2012) 19, 9966

2- Characterization of PMMA/Graphene nanocomposites (THEMYS TGA)

INTRODUCTION

Poly(methyl methacrylate) (PMMA) is a nonconductive polymer, but inexpensive and available in large quantity. In order to enlarge the application range of PMMA with a higher thermal stability, improved mechanical properties, graphene, under the form of Reduced Graphene Oxide (RGO) is added to prepare a PMMA composite.

EXPERIMENT

On Figure 2, are seen the mass loss curves obtained with the THEMYS TGA on pure PMMA and different composites containing RGO from 0.1% to 2%.

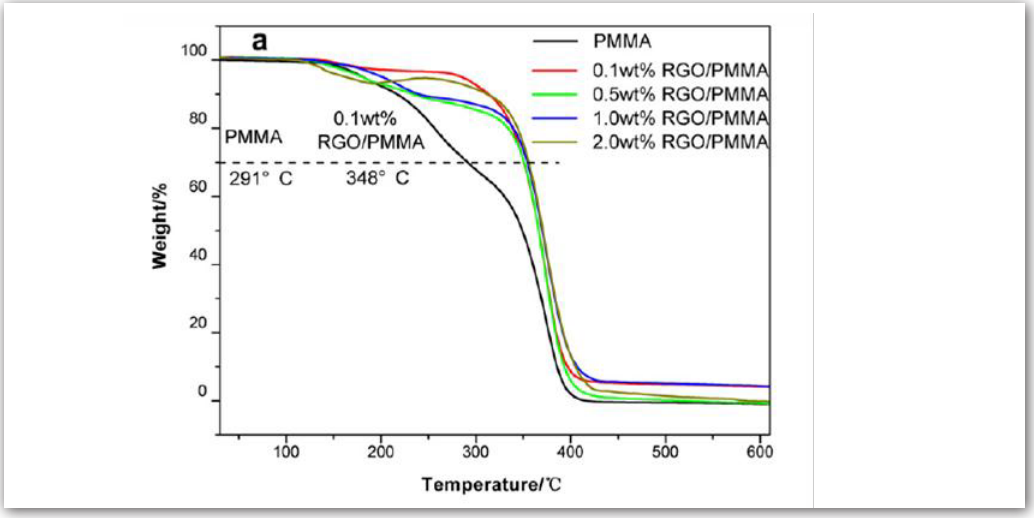


Figure 2: TGA curves of PMMA and PMMA/ Reduced Graphene Oxide nanocomposites

RESULTS AND CONCLUSION

The addition of RGO improves in a large scale the thermal stability of PMMA. For example, for a given mass loss of 30%, the temperature of degradation of PMMA is shifted from 291°C up to 348°C when only 0.1% of RGO is used for the composite. It is seen that an increase amount of RGO has not a significant effect on the thermal sability.

Adapted from Xiaopeng Zeng and al., European Polymer Journal 48 (2012) 1674–1682

3 - Characterization of PMMA / Graphene nanocomposites (THEMYS TMA)

EXPERIMENT

For the investigation of the mechanical properties, the THEMYS TMA has to be used with a preload of 20 g applied on a probe with a diameter of 1 mm. The test is run at 2°C/min.

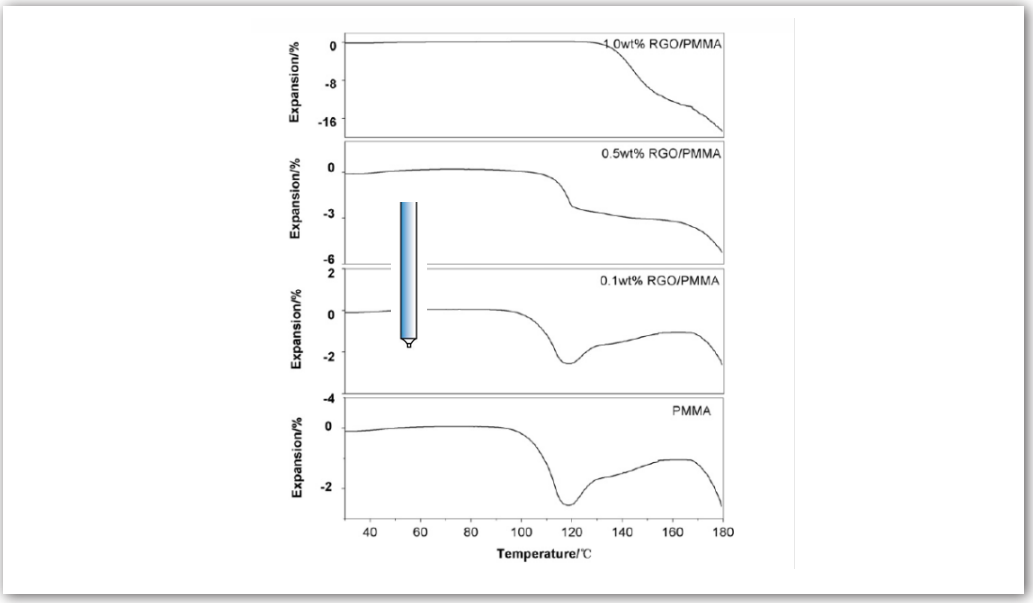


Figure 3: TMA expansion curves of PMMA and PMMA/ Reduced Graphene Oxide nanocomposites

RESULTS AND CONCLUSION

The TMA curve of pure PMMA (Figure 3) shows the characteristic length change variation due to the glass transition (Tg) at 98°C, followed by a second length decrease at 162°C due to the softening of the polymeric material.
When adding 0.1% RGO, the change in Tg is not significant but as soon as more RGO is added, the shift in temperature is increased. With 1% RGO, the increment in Tg is equal to 37°C and corresponds to a large improvement of the mechanical properties of the composite.
The combined use of the thermogravimetric and the thermomechanical techniques give an efficient information on the evolution of the thermal and mechanical properties of PMMA/Graphene nanocompoites with an indication on the amount of grapheme to be added for the enhancement of the corresponding properties.

Adapted from Xiaopeng Zeng and al., European Polymer Journal 48 (2012) 1674–1682

4 - Characterization of sulphur-graphene composites (THEMYS TGA)

INTRODUCTION

In recent years, graphene, has attracted appreciable attention for use as an energy storage material due to its specific properties (especially electrical conductivity). As a consequence, graphene can be used as a carbon matrix to improve conductivity of electrode materials for lithium-ion batteries. As an example, graphene nanosheets are investigated as a carbon matrix to improve the performances of sulphur cathodes for rechargeable lithium batteries.

EXPERIMENT

The THEMYS TGA is used to investigate and compare the pure materials and the corresponding composite. The thermogravimetric test is run under air in order to quantify the amount of graphene in the synthetized composite (Figure 4).

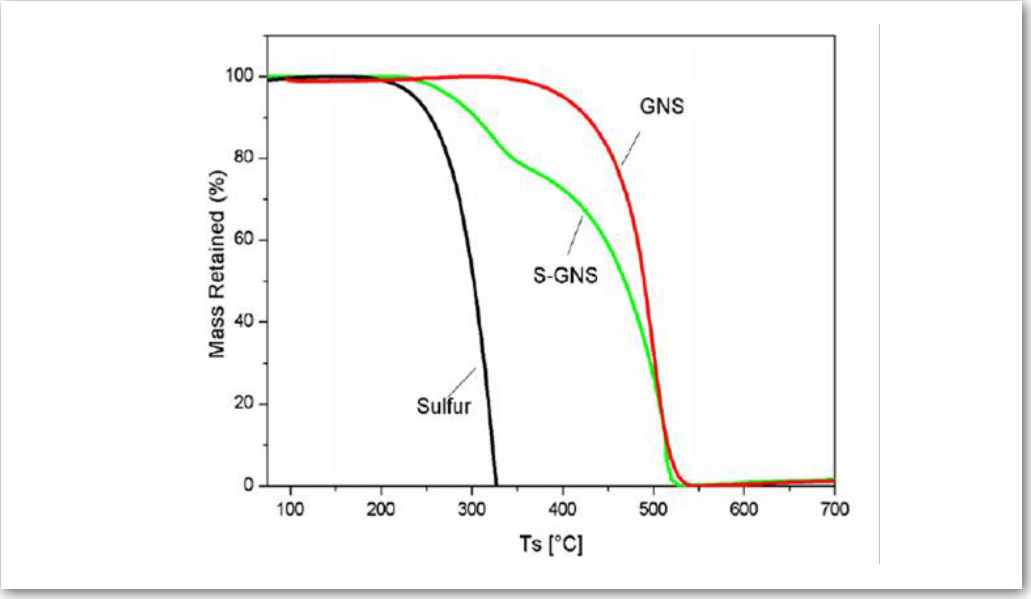


Figure 4: TGA curves of sulphur (S), pure graphene nanosheet (GNS) and S-GNS compositenanocomposites

RESULTS AND CONCLUSION

Under air, the sulphur powder is completely burned at 325°C. The oxidation of the pure graphene (GNS) starts around 350°C and graphene is fully burnt at 550°C. For the sulphur-graphene (S-GNS) composite, the burning of sulphur is shifted to a higher temperature and represents aa amount of sulphur of about 22%. Then the remaining amount of graphene is oxidized up to 550°C.

Adapted from Jia-Zhao Wang and al., Journal of Power Sources 196 (2011) 7030–7034

5 -Characterization of SnO_2–graphene–carbon nanotube mixture (THEMYS TGA)

INTRODUCTION

SnO_2 has attracted much attention as an alternative anode material for rechargeable Li ion batteries and Carbon materials have been widely employed to improve the cycleability of SnO_2 (especially to improve the electronic conductivity). Graphene has emerged as an attractive alternative to other carbon materials for applications in energy storage devices. The example is relative to a mixture of SnO_2-graphene-carbon nanotube (SnO_2-G-CNT) for anode material with improved rate capacities.

EXPERIMENT

The THEMYS TGA is used in this application to measure the amount of graphene that is contained in the prepared mixture. For this purpose, different materials are investigated under air in order to burn the graphene fraction.

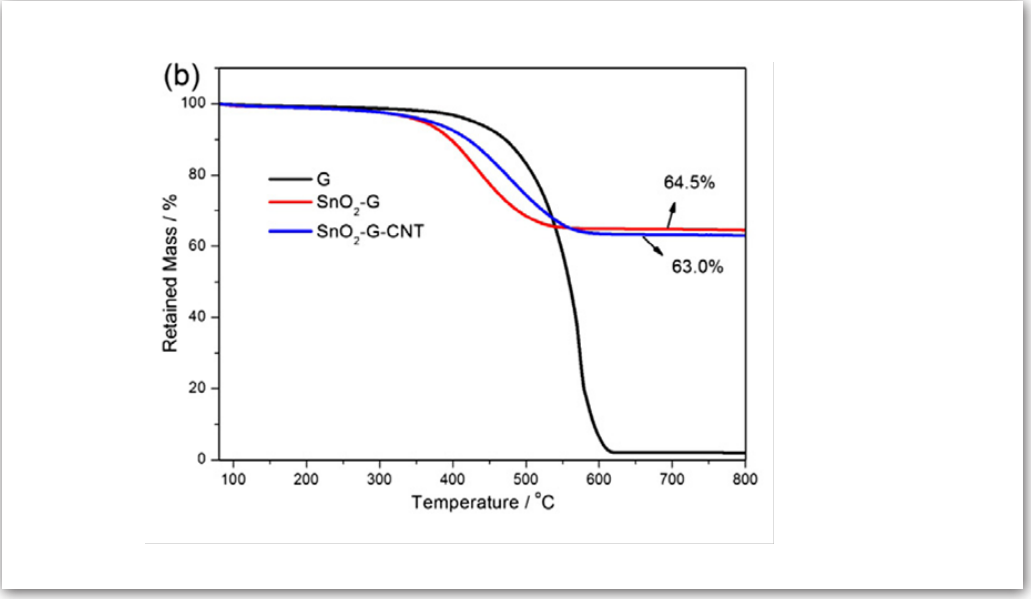


Figure 5: TGA curves of grapheme, SnO_2-graphene and SnO_2-graphene-carbon nanotube under air

RESULTS AND CONCLUSION

The figure 5 shows the different TG curves:
•pure graphene (G): the combustion starts around 300°C and is finished at 600°C
•the SnO_2-G mixture: after burning the graphene, the SnO_2 ratio is 64.5%
•for the SnO_2-G-CNT, the SnO_2 ratio is 63% , meaning that the added CNT amount is small.

Adapted from from Biao Zhang and al., Carbon 49 (2011) 4524-4534)

6 -Formation of Graphene Oxide Nanocomposites from Carbon Dioxide Using Ammonia Borane (MICROCALVET)

INTRODUCTION

CO_2 can be converted to graphene oxide (GO) using ammonia borane (AB) at moderate conditions. The conversion consists of two consecutive steps:
•CO_2 fixation (CO_2 pressure < 3 MPa and temperature < 100 °C)
•graphenization (600–750 °C under 0.1 MPa of N_2).

The first step generates a solid compound that contains methoxy (OCH_3), formate (HCOO) and aliphatic groups while the second graphenization is the pyrolysis of the solid compound to produce graphene oxide-boron oxide nanocomposites. The first step can be investigated using MICROCALVET at high pressure as the second step is devoted to the thermogravimetric technique (THEMYS ONE or THEMYS). In this part, only the first step is described.

EXPERIMENT

8.8 mg of NH_3BH_3 are loaded in the high pressure vessel at room temperature and the vessel is pressurized with CO_2 at a preset value. A first heating is applied at 1°C.k/min up to 65°C, followed by a second heating at a slower scanning rate (0.25°C./min) up to 100°C (Figure 6).

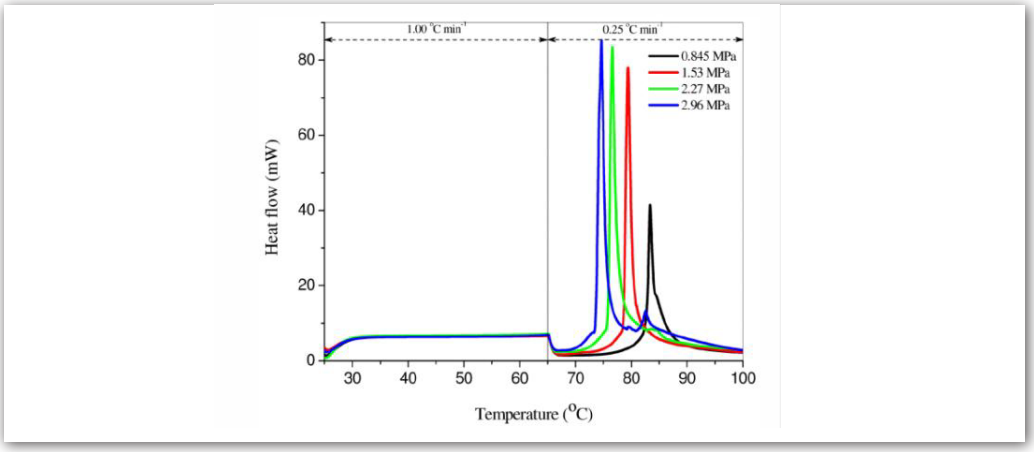


Figure 6: Calorimetric curves of the reaction between CO_2 and NH_3BH_3 at different CO_2 pressures

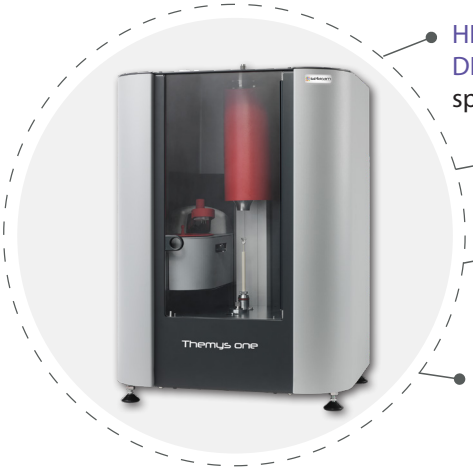
RESULTS AND CONCLUSION

The detected exothermic effect is related to the conversion of CO_2 in a solid compound and the thermal decomposition of NH_3BH_3.It is noticed that the temperature at the maximum of the reaction peak decreases when the CO_2 pressure is increased. With the maximum pressure, the amount of solid material formed during the reaction is twice the initial mass of NH_3BH_3 that is to say 17.2 mg. After cooling, the material is collected and stored in a glass vial for the further pyrolysis investigation.

Adapted from Junshe Zhang and al., J Phys Chem C Nanomater Interfaces. 116(3), (2012) 2639–2644

INSTRUMENTS

THEMYS ONE



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