

GRAPHITE NANOPATELETS CHEMICAL CROSS-LINKING BY ELEMENTAL SULPHUR

G. Carotenuto^{1*}, V. Romeo¹, L. Nicolais²

¹*Institute of Composite and Biomedical Materials, CNR. P.le Tecchio, 80 – 80125 Naples, Italy.*

²*Department of Materials and Production Engineering, University of Naples Federico II, P.le Tecchio 80 – 80125 Naples, Italy.*

*giancaro@unina.it

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Abstract

The reaction of graphite nanoplatelets (GNPs) with elemental sulphur provides a mechanically stable spongy material characterized by good electrical conductivity and high surface development; such unique property combination makes these novel nanostructured materials very useful for applications in different technological fields. The carbon-sulphur reaction can be accurately investigated by thermal analysis (DSC and TGA) and energy-dispersive X-ray spectroscopy (EDS) combined to scanning electron microscopy (SEM). The thermal treatment required for the formation of electrically conductive mono-sulphur connections among the GNP unities has been investigated.

1 Introduction

Graphene, a single layer of carbon atoms arranged in a hexagonal network, is a 2D-nanostructure with outstanding physical properties [1]. The successful isolation of graphene has had great interest for experimental investigations and has opened the way to a wide range of novel technological applications [1]. Recent studies have been directed toward using graphite nanoplatelets (GNPs) and graphene as a substrate to support nanostructures (e.g., quantum-dots, metal catalysts, magnetic nanoparticles, etc.), because of their high surface area, chemical stability, mechanical strength and flexibility [2-4].

Sp₂-carbon nanoforms (e.g., fullerenes, CNTs, graphite nano-platelets, and graphene) can be chemically cross-linked and polymerized by reaction with elemental sulphur. The resulting synthetic solid-phases can be considered as a sort of three-dimensional co-polymers of sulphur and these structurally complex carbon-based monomers. This carbon-sulphur chemical reaction may result of a certain importance in the preparation of novel bulky nanostructured materials [5]. For example, a high spongy graphite based material (graphite aerogels) can be prepared by drying concentrated graphite nano-platelet (GNP) colloids, achieved by exfoliation of expanded graphite in non-polar liquids with ultrasounds [6]. This novel material is quite fragile and a mechanical stabilization treatment is required for its exploitation in technological applications. The carbon-sulphur chemical reaction can be advantageously used for the mechanical stabilization of the very fragile spongy graphite material. The introduction of sulphur in this spongy graphite structure is quite simple since the sulphur molecules (S₈) are soluble into non-polar organic media (hydrocarbons, etc.) and it can be dissolved in the GNPs colloid before the drying process. Then, the dry GNPs-based

material is heated at ca. 180°C to allow the sulphur molecules to open, producing sulphur bi-radicals ($\cdot S_8\cdot$) which bridge the graphene layers of close nano-platelets [7]. In particular, the ring of sulphur molecule (S_8) breaks at a temperature of ca. 169°C, producing linear sulphur bi-radical fragments and such endo-thermal process is named as λ -transition [8]. The permanence of the system at temperatures above the λ -transition allows the poly-sulphur molecular chains ($C-(S)_n-C$) to break successively and the generated sulphur radicals to react again with the edges of graphene sheets up to achieve a high density of mono-sulphur chemical cross-links ($C-S-C$) between them. The mono-sulphur bridges allow electron delocalization among the graphene sheets and therefore they represent a sort of electrical connections in the material. When the spongy graphite is devoted to technological applications in the electrical/electronic field (e.g. supercapacitor electrodes, battery cathodes, electrodes for electrolytic cells, etc.) [9], the presence of mono-sulphur bridges among the GNP unities is a very convenient characteristic. In addition, the material stiffness is related to the length of sulphur bridges, and monosulphur connections lead to a much more rigid and tough material.

2 Experimental

2.1 Material preparation

Expandable graphite flakes (Asbury-USA) has undergone a thermal shock at 750°C for 3 minutes in a muffle furnace to obtain the expanded graphite (worm-like graphite). As received elemental sulphur (Sigma-Aldrich, 99.9%) was dissolved in octane (Carlo Erba, purum), and the expanded graphite filaments were added step-by-step to this sulphur solution, during an ultrasounds processing of the liquid system, made by a horn sonicator (Bandelin Sonoplus, Mod. UW2200, 20KHz, 200W) at room temperature. After application of ultrasounds the expanded graphite filaments were completely converted to GNPs. The final product was a sort of paste which was dried in air at room temperature for producing a high porous graphite/sulphur mixture, successively annealed in oven at 300°C.

2.2 Characterization methods

Dynamic calorimetric tests were carried out by a differential scanning calorimeter (DSC-Q2920, TA-Instruments). Measurements were performed under fluxing nitrogen at a rate of 10°C/min ranging from 20°C to 300°C. Thermogravimetric analysis was carried out by using a thermobalance (TGA-Q5000, TA-Instruments). In particular, the samples were heated from 30°C to 800°C at a rate of 10°C/min in fluxing air.

3 Results and discussion

The GNP-sulphur chemical interaction can be accurately studied by differential scanning calorimetry (DSC). Elemental sulphur crystallizes from solution in the β -form, however such solid phase is not thermodynamically stable under standard conditions for temperature and pressure (25°C and 1atm pressure) and therefore it spontaneously transforms in α -sulphur after an aging period of a few days (the $\alpha \leftrightarrow \beta$ equilibrium is at 95.4°C and therefore above room temperature) [10]. As visible in the DSC thermogram shown in Figure 1a, the β -sulphur contained in this GNP/sulphur mixture melts at a temperature of 115.21°C. The cyclic sulphur molecules are stable in the liquid phase up to a temperature of 169°C; the S_8 rings are cleaved at this temperature, thus producing bi-radical molecules that in presence of carbon-carbon double bonds ($C=C$) react with formation of the more stable C-S bonds. Cooling down the system to room temperature both the exothermic λ -transition peak and the crystallization peak of non-reacted sulphur molecules are visible (a significant undercooling characterizes the liquid-solid transition of sulphur). However, the permanence of the carbon-sulphur reactive

system at a temperature above the λ -transition allows the full amount of sulphur contained in the system to react with carbon, with a consequent disappearance of the sulphur melting peak (crystallization peak) in the DSC heating run (see the DSC run in Figure 1b). However, a low-intensity endo-thermal λ -transition signal is visible in the DSC thermogram because short sulphur chains ($\cdots S-S-S-S \cdots$) are still present at GNP crystal edges. However, the permanence of this reactive system at temperatures higher than the λ -transition point allows further breaking of the S-S bonds with formation of shorter sulphur chains among the graphene sheets. When most of these sulphur chains are converted to mono-sulphur bridges the λ -transition almost completely disappears in the DSC-thermogram. The kinetic of S-S bonds conversion to C-S bonds can be established by evaluating the area below the λ -transition peak after different thermal annealing periods, and comparing it with the starting ΔH_0 value obtained from the first DSC run (see Figure 2).

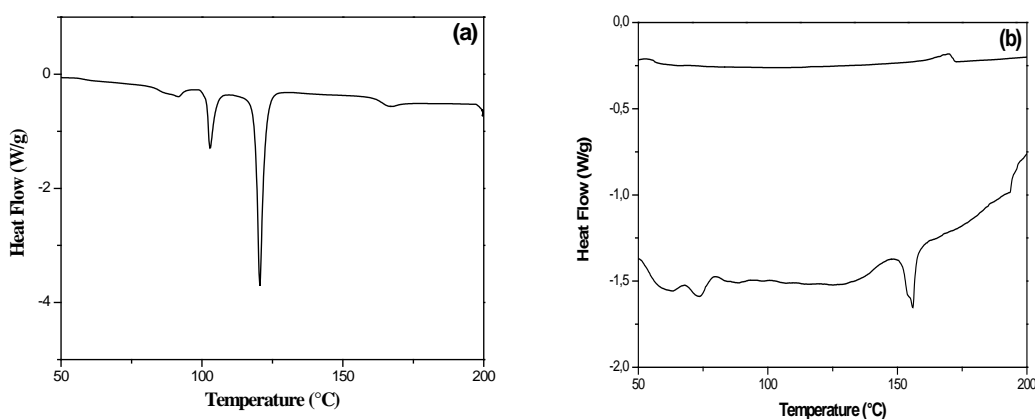


Figure 1. DSC-thermograms of the GNP/S system: a) first heating run; b) cooling and second heating run.

In particular, the following equation has been used for evaluating the conversion degree:

$$\alpha = 1 - \Delta H / \Delta H_0 \quad (1)$$

The amount of sulphur chemically reacted with GNPs with formation of covalent bridges among the GNPs can be accurately estimated by thermogravimetric analysis (TGA). Elemental sulphur boils at 444.6°C, however its evaporation takes place at much lower temperatures (starting from ca. 200°C). According to the TGA shown in Figure 3, the free sulphur molecules result completely lost by evaporation at a temperature of 200°C, and the residual sulphur in the TGA-thermogram is the sulphur covalently bonded to carbon. Tests performed both in fluxing air and nitrogen provided a sulphur content of 26-29% by weight.

t_a (min)	$T_{\alpha \leftrightarrow \beta}$ (°C)	$\Delta H_{(\alpha \leftrightarrow \beta)}$ (J/g)	T_β (°C)	ΔH_β (J/g)	T_λ (°C)	ΔH_λ (J/g)
30	91.3	1.08	116.3	12.5	164.5	0.47
60	85.5	0.30	116.3	10.6	165.4	0.30
120	0	0	116.1	8.47	165.1	0.15
180	0	0	115.6	5.83	0	0

Table 1. Thermodynamic properties of the GNP/S system obtained by DSC after different thermal annealing treatments at 300°C.

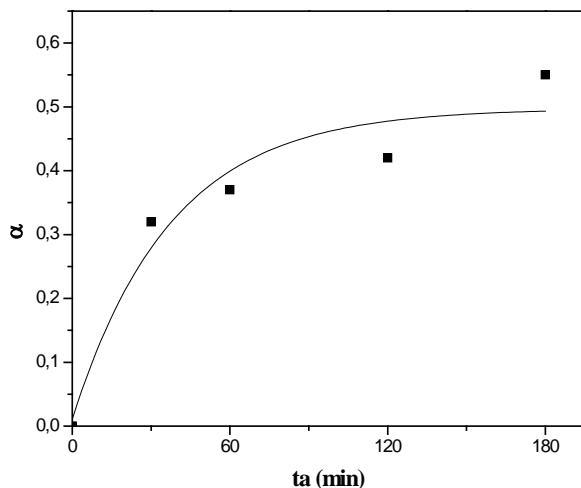


Figure 2. The sulphur reacted fraction as a function of time for annealing temperature of 300°C.

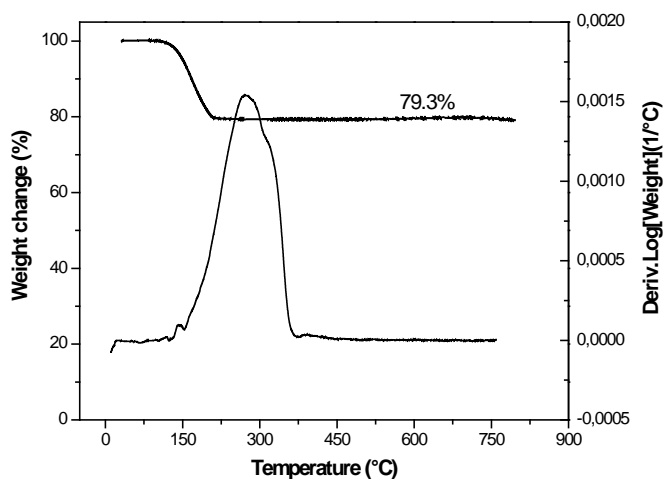


Figure 3. TGA-thermogram of a GNP/S system.

The combined SEM/EDS analysis of GNP/S system thermally annealed at 300°C shows the presence of residual sulphur everywhere over the sample surface (see Figure 4). However, the intensity of the sulphur signal is not uniformly distributed over the sample surface and the overlap of the EDS element mapping with the corresponding SEM-micrograph shows as the sulphur phase is preferentially located at the edges of the GNPs. Such higher sulphur concentration at the edges of the GNPs can be easily explained on the basis of an easier chemical interaction of sulphur radicals with carbon atoms located in these crystal regions.

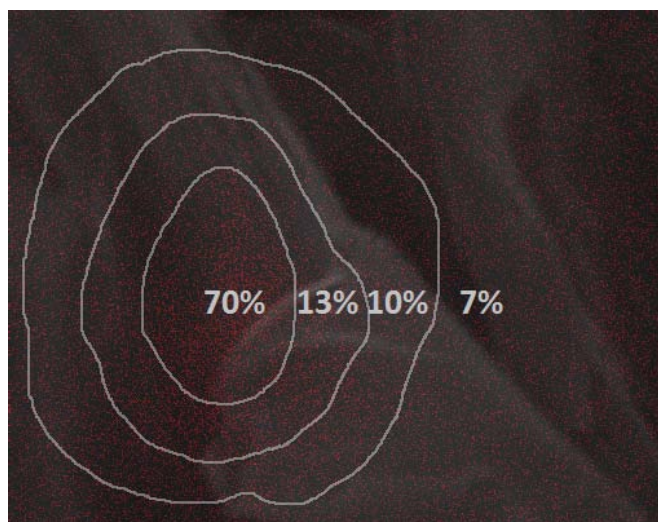


Figure 4. Percentage of sulphur on the aerogel surface evaluated by EDS.

The mechanical properties of the obtained spongy graphite result significantly modified after this vulcanization treatment with pure sulphur. In fact, before chemical cross-linking with sulphur the spongy graphite sample resulted very fragile and it was easily broken by introduction of a nail in its structure (see Figure 5). After the thermal vulcanization treatment, the graphitic material showed a much higher toughness and it resisted to the nail introduction (i.e., the material did not fracture and did not produce debris). After the thermal treatment the obtained material resulted handable and such important characteristic allows to exploit these graphite-based aerogels for technological applications in different industrial fields (e.g., supercapacitor electrodes, cathodes of batteries, support for noble-metal catalysts, etc.).

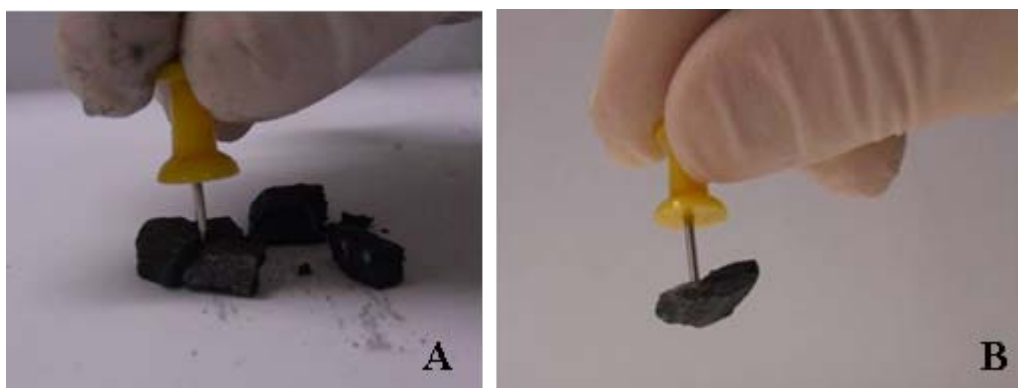


Figure 5. Graphene aerogel sample before (A) and after (B) the vulcanization treatment.

4 Conclusions

In conclusion, the treatment of GNPs with sulphur at a temperature of 300°C allows to obtain a mechanically stable graphite-based nanostructured material, useful for different technological applications. This treatment gives an uniformly cross-linked material and the carbon-sulphur reaction mainly involves the GNPs edges. If the thermal annealing treatment has been long enough, mostly mono-sulphur bridges are present in the material. The presence of a high quantity of mono-sulphur bridges is important especially for electronic applications since C-S-C bonds represent a sort of electrical connections between the GNPs unities.

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