Graphene Aerogel for the Removal of Bad Smells from Recycling of Post-Consumer Polymers

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Graphene aerogel was fabricated by a facile chemical reduction of a graphene oxide dispersion. The chemical reduction of graphene oxide was confirmed by different techniques. The resulting graphene aerogel showed large specific surface area (163 m^2 g^{-1}), high absorption capacity to incorporate odour and superior absorption recyclability. When graphene aerogel was added to the melting waste plastics, all the GC peaks of classified VOCs were reduced in intensity: of about 85% alcohols and carboxyl acids compounds; of more than 70 % aldehydes, ketones, esters and ethers; and in a lower content (62 % and 68 %, respectively) aliphatic and aromatic compounds, i.e. they were absorbed by GA. Thus, it displays promising application prospects in the field of organic volatile compounds treatment techniques, while allowing the adsorption and removal of molecules responsible for bad smells.

1. Introduction

Recycled polymers are generally characterized by qualitative levels that strongly depend on the degree of purity of the recovered polymer, through the separation technologies used in the collection and recycling of post-consumer materials. Furthermore, the properties of thermoplastic polymeric materials are negatively influenced by the degradation phenomena which inevitably take place during the transformation processes. However, it is known from the literature that it is possible to improve the quality of the recycled material through appropriate physical rehabilitation operations by mixing with other organic or inorganic materials. This approach is totally compatible with the mechanical recycling operations, the set of selection and transformation processes that involve exclusively thermal and mechanical operations by means of extrusion and melt granulation processes. Today, this type of recycling is the most efficient in terms of costs and environmental impact compared to other types of recycling (chemical and energy recovery). On the other hand, the growing use of recycled polymers determines an urgent need for plastics odour controls. Odour in recycled comes from many sources, including odours from the polymer, odours from degradation products of polymer additives, and odour specific to where the recycled polymer had been used, such as in milk cartons or oil containers. An obvious problem is that consumers don't like unpleasant odours in products they buy. In addition, recyclers often want to reduce odour to improve the operators' environment during compounding and pelletizing of recycled resins, or in downstream processing such as bottle production or filling. The plastics industry currently uses various methods and additive technologies to solve the odour problem. In some applications, pleasant fragrances such as citrus or vanilla are added to mask odour. Some additives, including microporous materials, like activated carbon and aluminasilicates, adsorb or trap odour compounds and organic volatile compounds (VOCs). The use of neutralizing additives, that bond with the odour compound to reduce their volatility, is an alternative solution to stripping agents which remove volatiles by degassing in the extruder.

Here we propose the use of a graphene aerogel, obtained by freeze drying of reduced graphene oxide, as and innovative adsorbent to incorporate during extrusion in recycled polymer and obtain odour control. The additive results also able to give substantial improvements in mechanical, thermal, optical and barrier properties (Zare and Garmabi, 2012). These are able to increase the inter-phase surface of the matrix-reinforcement system modifying drastically the rheological behaviour of the melted material, also increasing its

melt strength (Garofalo et al., 2009) and leading to improved overall performance. Our results showed that our approach is an innovative alternative to the traditional VOCs treatment techniques, while allowing the adsorption and conversion/removal of molecules responsible for bad smells.

2. Experimental Section

2.1 Materials

Graphite powder (synthetic, 99.9 %, Sigma Aldrich), sulfuric acid (H_2SO_4, 95-97%, Sigma Aldrich), potassium permanganate ($KMnO_4$, ≥99%, Sigma Aldrich), hydrogen peroxide (H_2O_2, 30%, Sigma Aldrich), L-Phenylalanine (Fluka, Ultra ≥ 99%) were used as received.

2.2 Preparation of graphene oxide

The graphene oxide (GO) was prepared from pristine graphite through a modified Hummers' method and subsequent sonication as previously reported (Casa et al., 2016; Sarno et al., 2017; Casa et al., 2018).

2.3 Preparation of graphene aerogels

The graphene aerogel was prepared by in situ chemical reduction-induced assembly using L-phenylalanine as a reducing agent.
Briefly, 5 mL GO water dispersion with a concentration of 4 mg/mL was obtained at the maximum power for ultrasonication (Hielscher UP 400S), then 100 mg L-phenylalanine was dissolved in 5 mL deionized water on heating to form a homogeneous solution. Successively, GO dispersion and L-phenylalanine solution were mixed in a glass vial. After sonicating the mixed solution for 10 min, the vial was sealed and immersed in a bath oil at 95°C for 48 h. The black reduced graphene oxide hydrogel was produced and then washed with deionized water to remove the residual soluble impurities. Finally, the wet hydrogel was freeze-dried under vacuum for two days to achieve the graphene aerogel (GA).

2.4 Plastic samples

Waste plastic pellets from containers and packaging facility (municipal solid waste-Campania Italy) were used. The collected plastic wastes were washed and shredded. The waste plastic pellets consisted mainly of low density polyethylene (LDPE), polypropylene (PP), and polystyrene (PS).

2.5 Adsorption experiments

All adsorption studies were done in a tubular furnace equipped with a temperature controller and heated at the controlled temperature in air flow. In particular, an experimental apparatus scheme was shown in Figure 1. Plastic pellets or pellets and GA were placed in a tubular furnace and melted at 200 °C in air with a flow rate of 150 mL/min. The outline was branched into 2 different lines, and an ATD tube (adsorbent) connected on one of them. VOCs contained in the out gas were collected via the tube pumped at 100 mL/min for 10 min. Prior to sampling, two minutes preheating was conducted. ATD tubes from PerkinElmer were used.
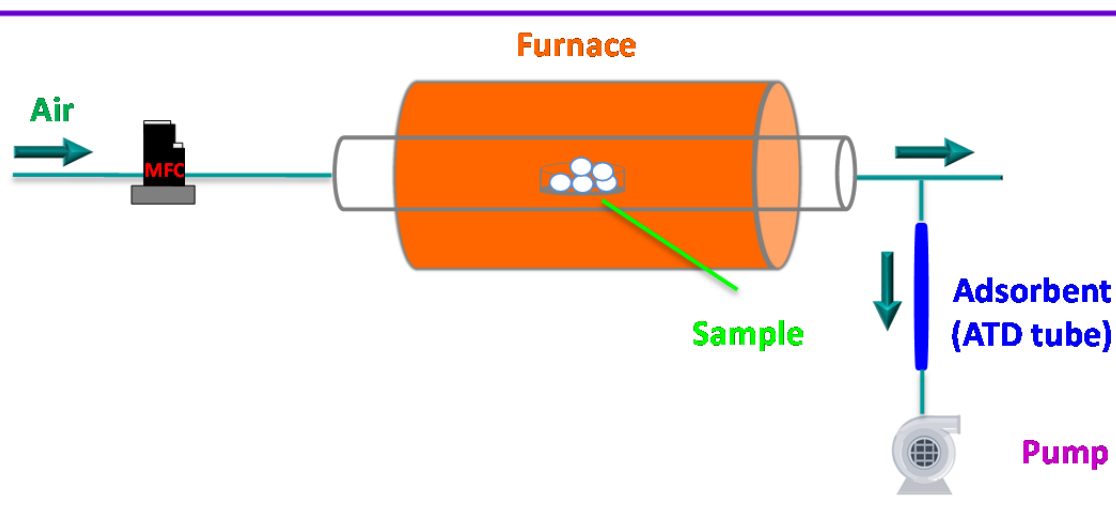

Figure 1: Experimental apparatus

The VOCs collected by the ATD adsorbents were desorbed by a thermal desorption system and analysed by gas chromatography-mass spectrometry (GC-MS). The desorption conditions were set as follows: 200 °C for 40 min. GC/MS conditions: column HP-1 MSC 60 m * 250 μm * 1 μm; carrier He 1.2 mL/min; column temperature 40 °C to 280 °C.

In a typical experiment, to characterize the species of volatile compounds emitted from waste plastics in air atmosphere, about 0.2 g of heterogeneous waste plastic pellets were tested. To test the efficiency of GA, 0.02 g were added to the waste plastic pellets. For both experiments, with plastic pellets and plastic pellets/GA, triplicate tests were performed.

2.6 Characterization

Raman spectra were obtained at room temperature with a micro-Raman spectrometer Renishaw inVia with a 514 nm excitation wavelength (laser power 30 mW) in the range 100-3000 cm^{-1}. XRD measurements were performed with a Bruker D8 X-ray diffractometer using CuKα radiation. TEM images were acquired using a FEI Tecnai electron microscope, operating at 200 kV with a LaB$_6$ filament as the source of electrons, equipped with an energy dispersive X-ray spectroscopy (EDX) probe. The specimens for TEM analysis were prepared by suspending GO in water, homogenizing the suspension, and allowing a drop of this suspension to evaporate on an amorphous carbon-coated Cu grid. N$_2$ adsorption−desorption isotherms at 77 K, on powder samples previously outgassed in He flow at 523 K for 4 h, were obtained with a Thermoquest Sorptomatic 1900.

3. Results and discussion

3.1 Graphene aerogel characterization

TEM image of produced GO is shown in Figure 2a. Thin layers with sizes in the range of half to tens of square microns were observed. GO exhibits a rough surface showing wrinkles (Chai et al., 2014; Yu et al., 2014). A photograph of the obtained graphene aerogel (GA) is shown in Figure 2b.
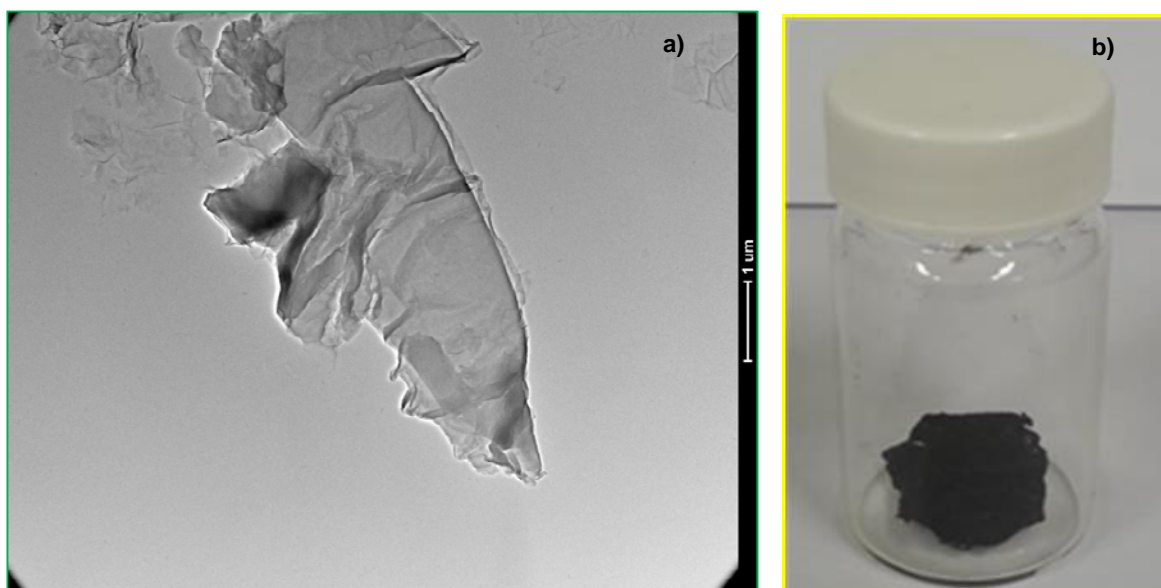

Figure 2: TEM image of GO (a); Photograph of the obtained graphene aerogel (b)

Raman spectroscopy was used to characterize the structural changes before and after the reduction of GO. The Raman spectra of GO (a) and GA (b) are exhibited in Figure 3a. The D and G bands of GO were located at 1348 and 1590 cm^{-1}, while those of GA were situated at 1345 and 1601 cm^{-1}, respectively. Compared to the G band of GO that of GA was shifted by 11 cm^{-1} from 1601 to 1590 cm^{-1}, indicating that GO had been reduced efficiently by L-phenylalanine (Glover et al., 2011; Sarno et al., 2013; Sarno et al., 2014).

The XRD profiles of GO (blue line) and GA (magenta line) are presented in Figure 3b. GO showed a diffraction peak at 10.5°, giving an interlayer spacing (d-spacing) of 0.84 nm. This interlayer space was much higher than that (0.34 nm) of pristine graphite (Cravotto and Cintas, 2010). This increased d-spacing is because the oxygen-containing functional groups of the graphene sheets enhanced the distance between the

layers. Nevertheless, GA exhibited no peak at 10.5° in its XRD profile, showing most of the oxygen-containing groups of GO were removed after chemical reduction (Lv et al., 2009; Chen et al., 2010). Instead, GA displayed a broad diffraction peak at 24°, the d-spacing of which was about 0.38 nm. This ordered structure was attributed to the stacking of graphene sheets during the process of chemical reduction of GO. The d-spacing of GA was still larger than that of pristine graphite because of the residual oxygen-containing functional groups. In addition, the diffraction peak of GA was quite broad like the previous reduced graphene oxide, suggesting that the graphene nanosheets of GA were poorly ordered along their stacking direction (Wang et al., 2011).
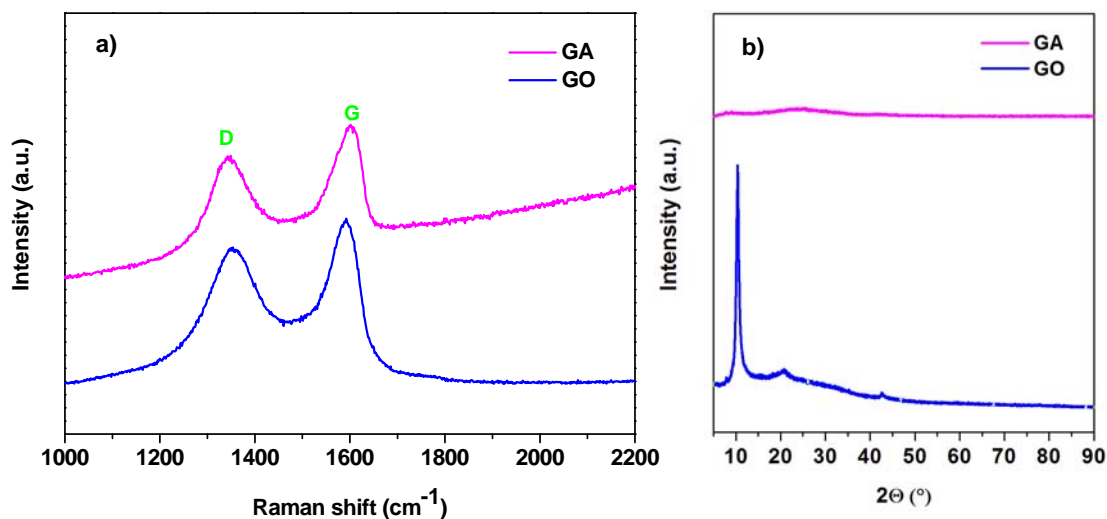

Figure 3: Raman spectra of GO (blue line) and GA (magenta line) (a); XRD patterns of GO (blue line) and GA (magenta line) (b)
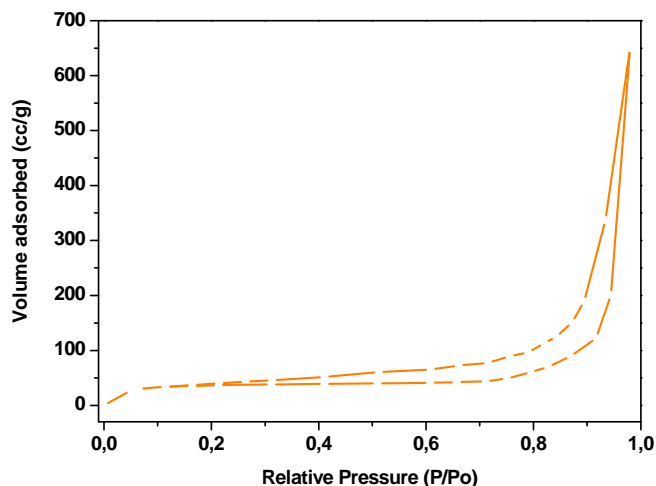

Figure 4: N_2 adsorption–desorption isotherm

The porous property of GA was examined using a N_2 adsorption–desorption test. The adsorption–desorption isotherms of GA, in Figure 4, showed a typical hysteresis loop, indicating that it possessed many mesopores (Huang et al., 2013). The surface area of GA was 163 m^2 g^{-1}, which was obtained by fitting the isotherms with the Brunauer–Emmett–Teller (BET) model. Its surface area was comparable to that of the previous graphene aerogel (Zhao et al., 2012).

3.2 Adsorption tests

To analyzed the species of volatile compounds emitted from waste plastics, GC analysis was carried out. A large amounts of oxygenated organic compounds such as aldehydes, ketones and carboxylic acids were produced (see the as recorded total ion chromatograms of VOCs from melted waste plastics in Figure 5a).
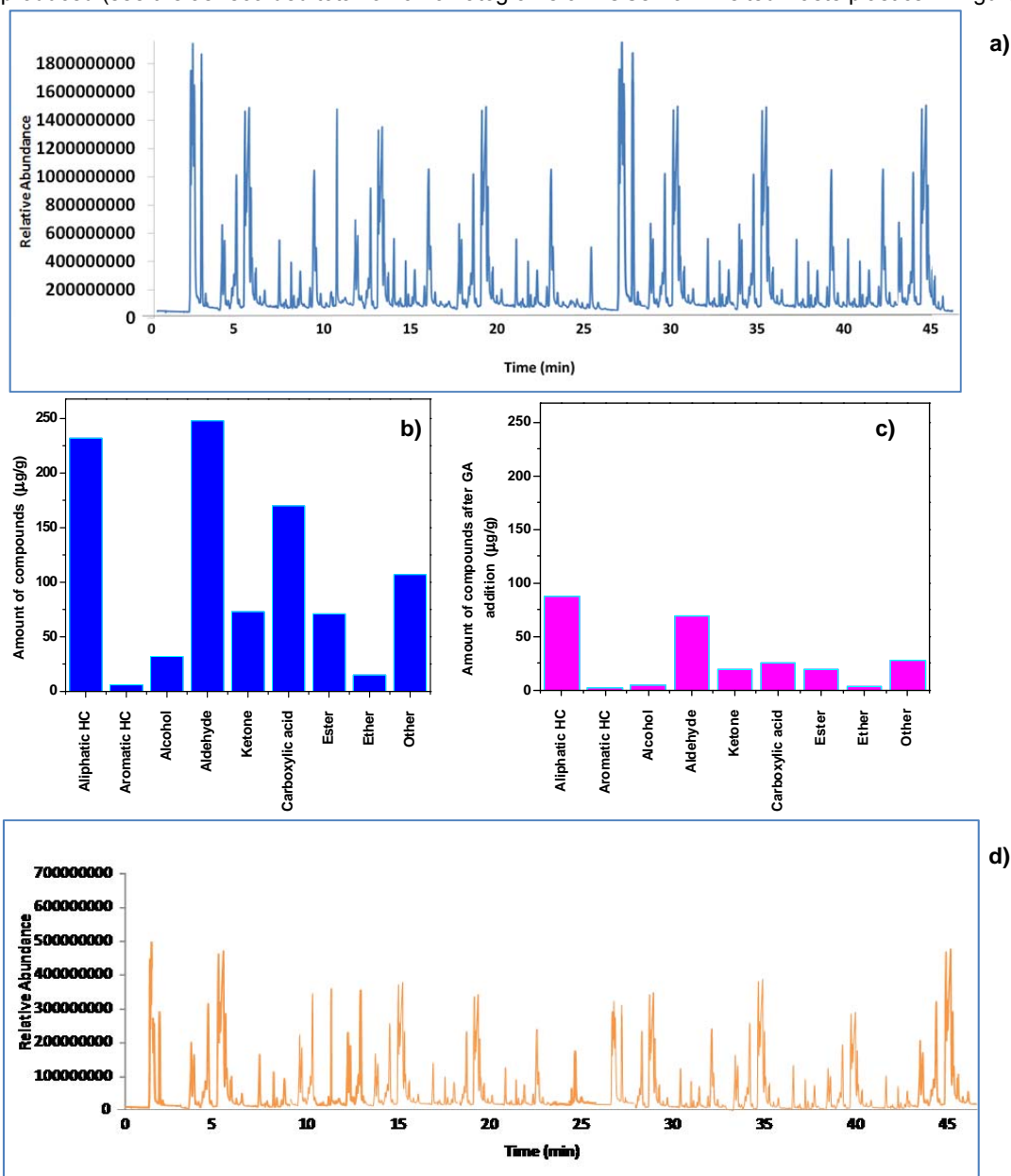

Figure 5. Total ion chromatograms of VOCs from melted waste plastics in air at 200 °C (a); Classified compounds from melting waste plastics in air 200 °C (b); Volatile compounds emitted from waste plastics after GA addition (c); Total ion chromatograms of VOCs from melted waste plastics in air at 200 °C after GA addition (d)

Moreover, many compounds unlikely originated from virgin LDPE, PP or PS were detected. For example, chlorinated hydrocarbons and phthalates were detected which indicates that polyvinyl chloride (PVC) was contained in the waste plastics. Caffeine, nitrogen compounds likely originated from food residues attached to waste plastics, limonene and siloxane were detected. Since these residues may be not only the cause of coloring but also the source of malodor, washing process is very important to overcome these problems.
On the other hand, when GA was added to the melting waste plastics, all the peaks of classified compounds were substantially reduced in intensity: of about 85% alcohols and carboxyl acids compounds; of more than 70

% aldehydes, ketones, esters and ethers; and in a lower content (62 % and 68 %, respectively) aliphatic and aromatics (see Figure 5c and 5d), i.e. they were absorbed by GA. In particular, Figure 5 c showed the volatile compounds emitted from waste plastics when GA was added, which were in the range of 2–88 µg/g.

This is due to the surface chemistry of GA on which hydrophilic functionalities limited the π-π interactions.

In addition, we have also studied the recyclability of our nanomaterials, that is another important property for an ideal absorption material. After 15 absorption–desorption cycles, the absorption capacity of GA was still higher than 60%.

4. Conclusions

In conclusion, we have reported the preparation of graphene aerogels by simple, scalable and cost effective preparation procedure. The resulting graphene aerogel showed large specific surface area, high absorption capacity to incorporate odour during extrusion in recycled polymer and superior absorption recyclability. Due to the surface chemistry of GA, on which hydrophilic functionalities limited the π-π interactions, the adsorption of aromatic and aliphatic compounds results less favoured.

Therefore, this study provides an excellent material for an alternative to the traditional VOCs treatment techniques, while allowing the adsorption and conversion/removal of molecules responsible for bad smells from recycling of post-consumer polymers. An economic evaluation of the idea will be object of study. Indeed, although the nanocarbons have potentially low costs and are present in a low amount, the phases of aerogel preparation must be also taken into account.

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