

Facile synthesis of 2D carbon structures as a filler for polymer composites

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The method of self-propagating high-temperature synthesis has been employed to prepare 2D graphene structures (SHS-graphSHS procedure for carbonizing cyclic organic structures is a simple accessible method for making 2D graphene structures in practically needed amounts. The material obtained is designated as SHS-graphene. The study on starch carbonization product by combined complementary methods has shown the structure of SHS-graphene particles is similar to 2–3-layered graphene particles. The addition of graphene to NBR matrix results in the significant (to twice) enhancement of strength and thermal characteristics of composition material obtained, as compared to unfilled rubber. A set of complementary methods (scanning electron microscopy, Raman microscopy, X-ray diffraction analysis) evidenced 2–3-layer graphene structure of the substance obtained. SHS-graphene has been utilized to modify NBR and thereby markedly strengthen the polymer matrix.

Keywords: graphene, nitrile-butadiene rubber, self-propagating high-temperature synthesis.

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1. Introduction

Graphene (Gr) has emerged as a subject of enormous scientific interest due to its exceptional electron transport, mechanical properties, and high surface area. When incorporated appropriately, these atomically thin carbon sheets can significantly improve physical properties of host polymers at extremely small loadings. In the past, several synthetic approaches for graphene monolayers have been reported, including epitaxial growth on single-crystal SiC, direct growth on single-crystal metal film or polycrystalline film through chemical vapor deposition, and chemical reduction of exfoliated graphene oxide layers. Two obstacles prevent of Gr application in real industry of polymer composites: poor efficiency of modern methods of their preparing and, accordingly, their high price.

The present paper was aimed at the development of a single-step highly effective procedure for obtaining 2D carbon structures of reasonable cost and, therefore, useful in real polymeric material science.

The selection of initial organic as a base for synthesizing 2D structures was based on the fact that the said structures were polymers of hexatomic carbon cycles – hexagons. Thus, natural candidates for the initial substance were polysaccharides and starch in particular. The latter is a branched high-molecular plant polysaccharide of amylose and amilopectine [1]. Starch monomer unit is six-carbon sugar (hexose) – glucose. Currently, starch is widely being carbonized to make porous carbon sorbents which are turbostrat structure where, unlike graphite, alternate ordered and disordered regions of carbon rings – hexagons [2]. It could be consistently supposed that starch carbonization at temperatures much higher than those of pyrolysis (~800 °C) and with much faster carbonization rate would avoid hexagon turbostrat assembly, i.e., obtain 2D graphene structures.

The so-named process of hard-flame combustion, i.e. self-propagating high-temperature synthesis (SHS) is known to be characterized by extreme values of both rate and reaction temperature [3]. As compared to pyrolysis and hydrothermal carbonization, SHS processes are advantageous by the simple implementation method, high rate of the synthesis, no need in continuous power feed from external power sources, synthesis in any atmosphere or vacuum and no principal scale limits [4, 5].

2. Experimental

Synthetic procedure. Starch/oxidizer mix in a 1:1 stoichiometric ratio was charged to glass reactor purged with dry argon for 5 min. To start the SHS process, the reactor was lowered into Wood alloy pre-heated up to 200 °C. Start/end of intensive gas evolution in the trap with water evidenced the reaction start/end. The product obtained – carbonized starch (SC) – was a black powder. The yield of final product was approximately 40 %.

Composition material polymer–SC. Low-molecular nitrile-butadiene rubber (NBR) with chlorine-containing end groups was used. SC was gradually added with stirring to pre-heated NBR. The composition thus obtained was ultrasonicated for 1 h, then vulcanized and subjected to testing.

Raman spectroscopy. Spectrometer InVia (Renishaw, GB).

Electron microscopy. Electron micrographs of powders were taken by Raster electron microscopy Supra55VP (Carl Zeiss, Zeiss AG).

X-ray diffractometry. Pictures were taken by diffractometer Shimadzu XRD 7000, within the angle range $2\theta = (10 - 100)^\circ$, pitch 0.02 degree, point exposure 1 s.

3. Results and discussion

Electron micrographs of SC powder see in Fig. 1(a,b). As can be concluded from the data in Fig. 1, SC particles are bulk-plane scales.

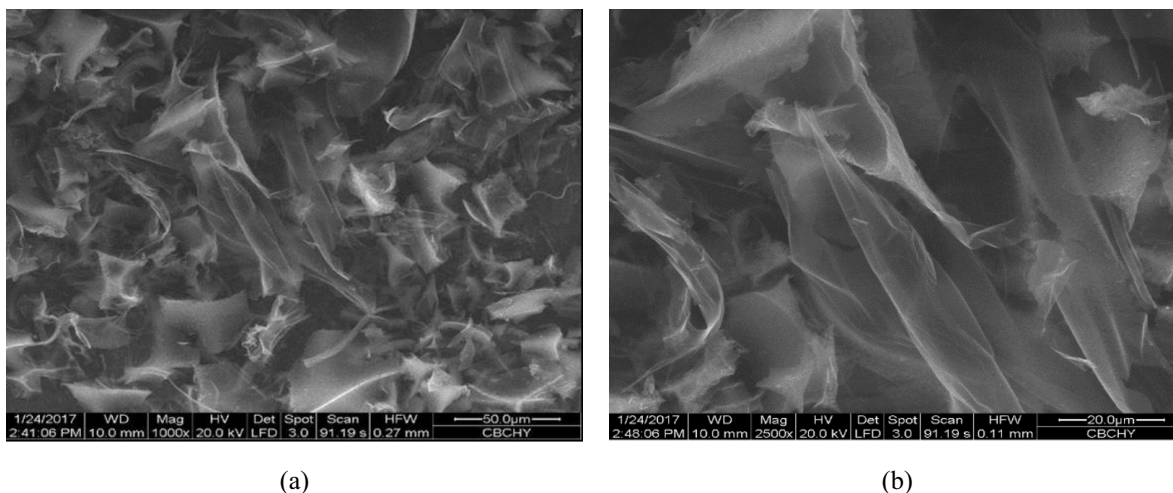


FIG. 1. Electron micrograph of SC powder: a) Mag=1000×; b) Mag=2500×

It should be noted that particles with SC-like geometry are typical for graphene particles [6].

To clarify the nature of the particles obtained, we used the method of X-ray diffractometry (Fig. 2). As can be seen from the data in Fig. 2, the structure of SC particles is radiomorphic and hence, graphite particles do not form in the carbonization by the method used.

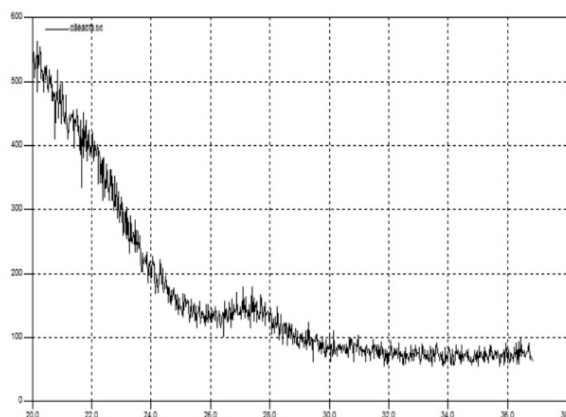


FIG. 2. X-ray diffractometry of SC powder

It is believed that the most reliable information about the architecture of carbon structures can be obtained from Raman spectroscopy data [7]. The corresponding data obtained for SC have been presented in Fig. 3. The general view of the curve by both the shape and peak maxima of respective bands (G peak – $1500\text{--}1630\text{ cm}^{-1}$; D peak – 1355 cm^{-1}), correspond to 2D-graphene structures. Indirect conclusions about the number of graphene layers in the SC powders made can be drawn from the comparison of the view of so called 2D band (2700 cm^{-1}) with the reported data (presented in the in cut of Fig. 3). Comparing this data, we can assume without significant error that the mean value of graphene layers in our experiments is 2–3.

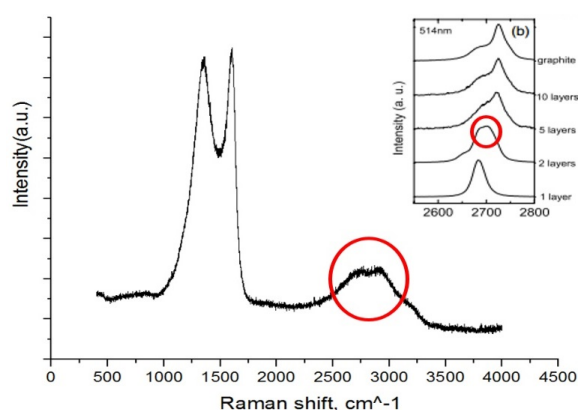


FIG. 3. Raman spectrum of carbonized starch powder

In general, SHS process is a redox chain reaction running under specific conditions. As classified, our version of SHS process falls under “solid–gas” systems, where polysaccharide (starch) is employed as reducing agent and gaseous products of ammonium nitrate thermal decomposition are oxidizers.

It should be emphasized that the proposed method for preparing 2D graphene structures principally differs from methods currently in use. Namely, it is based not on the exfoliation of ready graphene, but on complex processes of degradation/self-assembly of cyclic organics. In this regard, it is advisable to designate 2D carbon structures obtained as SHS-graphene.

One of indirect proof for the correlation of SHS-graphene and 2D carbon structures made through graphite exfoliation, can be significant strengthening attained by graphene adding to host polymer [8]. Nitrile-butadiene rubber with chlorine-containing end groups have been chosen as a base polymer.

Below are tabulated data on strength properties for initial and SHS-filled polymers (Table 1).

TABLE 1. SHS-graphene influence on nanocomposite strength characteristics

Indices	SHS-graphene content, % mass					
	0	1	2	4	6	6 ¹
Tensile strength at 20 °C, MPa	1.62	1.81	2.10	2.70	2.92	3.19
Elongation at break at 20 °C, %	182	173	163	176	124	134
Tensile strength at 125 °C, MPa	0.86	0.89	1.45	1.43	1.70	1.72
Elongation at break at 125 °C, %	59	50	41	54	47	36
Tear strength, kgf/cm	7.4	7.6	11.0	11.7	11.9	11.0

¹composition material was thermo-treated at 200 °C for 15 min.

As it is shown in Table 1, strength values of composition material increase (almost twice) with increasing SHS-graphene content. The increase in tensile strength at higher temperature (also twice as well) should be emphasized. The latter ensures a satisfactory stability of service properties.

Interesting results have been obtained after thermal treatment of filled polymer followed by the curing. Short-term heating of composition material over degradation temperature of initial NBR was found not to reduce, but improves strength characteristics of finished articles to some extent. One more characteristic of interest from practical viewpoint is tear strength (crack resistance) – it grows by 50 %. Tear strength characterizes the contribution of local tension centers in the bulk of polymer matrix to strength properties of composites. The higher the value, the lesser are defects in composite structure and, hence the longer service life of the finished product under, e.g. enhanced vibration. The growth of the value can be related to the fact that graphene particles fill in the elements of polymer void volume and thereby decrease the number of local tension centers and, respectively, lower the possible propagation of the main crack in the bulk of composition material. The said assumption is corroborated by polymer matrix T_g independence of graphene content (Table 2).

TABLE 2. Glass-transition temperature of NBR-based composition materials with SHS-graphene loading

Indices	Graphene content, % mass					
	0	1	2	4	6	6 ¹
T_g , °C	-59.3	-60.0	-59.9	-59.3	59.7	-

¹composition material was thermo-treated at 200 °C for 15 min.

Thus, the development of composite materials using graphene is a real prospect. It is easily introduced and distributed throughout the volume of the nitrile-butadiene polymer. Also graphene significantly improves the strength and thermal characteristics of the polymer matrix.

4. Conclusion

SHS procedure for carbonizing cyclic organic structures is a simple accessible method for making 2D graphene structures in practically needed amounts. The material obtained is designated as SHS-graphene.

The study on starch carbonization product by combined complementary methods has shown the structure of SHS-graphene particles is similar to 2–3-layered graphene particles.

The addition of graphene to NBR matrix results in the significant (to twice) enhancement of strength and thermal characteristics of composition material obtained, as compared to unfilled rubber.

References

- [1] *Starch in food: structure, function and applications*, ed. by Ann-Charlotte Eliasson. CRC Press, Cambridge: Woodhead Pub., 2004, 605 p.
- [2] Jin Dingfeng, Yang Xiao, Zhang Ming, Hong Bo, Jin Hongxiao, Peng Xiaoling, Li Jing, Ge Hongliang, Wang Xinqing, Wang Zhengbao, Lou Hui. A novel high surface area spherical carbon from cassava starch. *Mater. Lett.*, 2015, **139**, P. 262–264.
- [3] Sytshev A.E., Merzhanov A.G. Self-propagating high-temperature synthesis of nanomaterials. *Rus. Chem. Rev.*, 2004, **73**, P. 147–159.
- [4] Shuck C.E., Manukyan K.V., Rouvimov S., Rogachev A.S., Mukasyan A.S. Solid-flame: Experimental validation. *Combust. Flame*, 2016, **163**, P. 487–493.
- [5] Merzhanov A.G. History and Recent Developments in SHS. *Ceramics International*, 1995, **21**, P. 371–379.
- [6] Stankovich S., Dikin D.A., Piner R.D., Kohlhaas K.A., Kleinhammes A., Jia Y., Ruoff R.S. Synthesis of graphene-based nanosheets via chemical reduction of exfoliated graphite oxide. *Carbon*, 2007, **45**(7), P. 1558–1565.
- [7] Ferrari A.C., Basko D.M. Raman spectroscopy as a versatile tool for studying the properties of graphene. *Nat. Nanotechnol.*, 2013, **8**(4), P. 235–246.
- [8] Kim H., Abdala A.A., Macosko C.W. Graphene/Polymer Nanocomposites. *Macromolecules*, 2010, **43**(16), P. 6515–6530.