

Green synthesis of Reduced Graphene Oxide (RGNO) / Polyvinylchloride (PVC) composites and their structural characterization

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Abstract. Graphene and graphene derivatives are widely used as fillers for polymer composite materials. The Reduced Graphene Oxide (RGNO) is usually considered as one kind of chemically derived graphene, just like Graphene Oxide (GO). However, very dangerous chemicals are used for synthesis of RGNO. Specially, hydrazine hydrate used to form RGNO is highly toxic and unstable. In this paper, a green strategy was reported for the synthesis of RGNO. To this aim, firstly GO was prepared from natural graphite by Hummers method and then obtained GO was reduced by vitamin C. Structural characterization results revealed that GO was successfully reduced to RGNO. RGNO filled polyvinylchloride (PVC) composites were prepared by colloidal blending method. The structural changes were observed in RGNO/PVC composites as a function of RGNO loading and confirmed by FTIR, XRD and SEM analyses. These analyses indicated that RGNO layers were fully exfoliated and well-dispersed in the PVC matrix.

Introduction

Graphene has recently attracted attention as inexpensive filler in composite materials that can be used in a wide range of potential applications due to its excellent structural, mechanical, thermal, and electrical properties [1, 2]. The most common method for producing graphene is chemical reduction of graphene oxide (GO) [3]. However, negative aspect of the reduction process is the high toxic nature of the reducing agents (hydrazine hydrate, di-methylhydrazine, hydroquinone, sodium borohydride, metal hydrides) [4]. These agents are harmful to both humans and the environment [5]. Specially, hydrazine hydrate is the widely used as reduction agent but it is highly toxic and dangerously unstable [6]. Therefore, it is very important to find harmless and efficient reducing agents to reduce GO [7]. Recently, nontoxic or natural products such as non-aromatic amino acids [3], leaf extracts of natural products [4], ethylene glycol [6], sodium carbonate [8], ascorbic acid [9], sugar [10], green tea [11] etc. that offer environmentally friendly approaches to reduce GO have been developed [12]. PVC is a common thermoplastic as a host polymer matrix for preparing polymeric composite materials because of its low cost and excellent chemical stability and biocompatibility [13, 14]. But PVC has disadvantageous properties such as poor processability, thermal stability and weatherability [15]. Recently, the improvement in thermal, electrical and mechanical properties of PVC matrix with graphene derivatives has been reported in many literatures [15 - 21]. However, there are no published data concerning the effect of the different amounts of RGNO that prepared with Vitamin C on the properties of RGNO/PVC composites. In the present study, we prepared RGNO filled PVC composites by a solution

blending method and we are reporting a simple method of preparation of RGNO using Vitamin C. The effect of RGNO on structural properties has been investigated. This research opens a new route to fabricate composites with green synthesis of filler which can be a promising material for many applications.

Material and Method

Graphite powder (GF), concentrated sulfuric acid (98 % - H₂SO₄), potassium permanganate (KMnO₄), hydrogen peroxide (30 % - H₂O₂) solution, hydrochloric acid (HCl) and Vitamin C (L(+) - Ascorbic Acid) were of reagent grade and purchased from Merck. All the reagents were used without further purification. All solutions were prepared using deionized (DI) water. GO was prepared from natural graphite (45µm nominal particle size) by the Hummers method [22]. Graphite (1 g) was mixed with 69 mL of concentrated H₂SO₄ and the mixture was stirred in an ice bath for around 30 min. After homogeneous dispersion of the GF in the solution, KMnO₄ (8 g) was added slowly to the solution in an ice bath and the reaction mixture was stirred for 15 min. under a reaction temperature of 20°C. Then the ice bath was removed and the mixture was stirred at 35°C overnight to form thickened paste. Afterward 70 mL of de-ionized water was added slowly into the reaction solutions to avoid the reaction temperature rising to a limit of 98 °C. After 2 hours of vigorous stirring, 12 mL of 30 % H₂O₂ was added and the color turned golden yellow immediately. Finally, the mixture was then filtered and washed several times with 3 % HCl and DI water until pH 7 and dried at 65°C for 12 hours to obtain GO powder.

To prepare RGNO, 0.5 g of GO was dispersed in 100 mL of DI water. pH of the GO suspension was adjusted to ~10 by using ammonia solution. Then 0.75 g of Vitamin C was added to the mixture and heated at 95°C for 12 hours. After that the mixture was filtered and the RGNO was obtained as a black powder. This powder was washed with DI water several times.

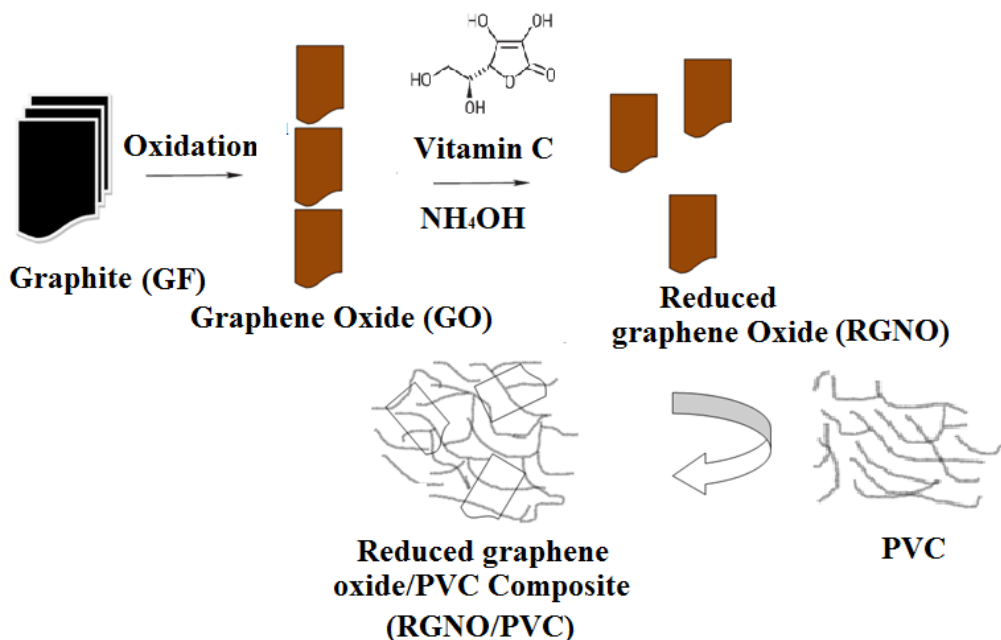


Fig. 1. Synthesis process of RGNO/PVC composites.

RGNO/PVC composites were prepared by a colloidal blending method. PVC (1 g) was first dissolved in Tetrahydrofuran (THF) at 70 °C and was cooled to room temperature. RGNO powder was separately dispersed in THF at 25°C. The two solutions were stirred for 2 hours at 60°C. The

resulting homogeneous dispersion was poured into glass petri dish and kept in an oven at 60 °C for slow evaporation of the solvent to get RGNO/PVC composite. The synthesis process of RGNO/PVC composites is illustrated in Fig. 1. The RGNO content in the RGNO/PVC composite was varied from 0.1 – 1 wt. % (Table 1).

Table 1. Ratios and codes of RGNO in the composites.

Samples	RGNO Content (wt. %)
0.1-RGNO/PVC	0.1
0.3-RGNO/PVC	0.3
0.5-RGNO/PVC	0.5
1-RGNO/PVC	1

Structural analyses of the RGNO powders and composites were carried out by FTIR spectra (Spectrum 100, Perkin Elmer) in the range of 4000–400 cm^{-1} and X-Ray Diffraction (XRD, PAN analytical, Empyrean) in the range of 5 – 40°. The surface morphology was examined by a Scanning Electron Microscopy (SEM, Supra 40VP, Zeiss). EDS analyses were performed on the same instrument.

Results and Discussion

FTIR spectra for GO, RGNO, neat PVC and RGNO/PVC composites were presented in Fig. 2. Fig. 2 showed the stretching of hydroxyl group at 3214 cm^{-1} , the C=O carbonyl stretching at 1720 cm^{-1} , and the C–O epoxide group stretching at 1160 and 1040 cm^{-1} [6, 8]. These results suggested that the GO sample was oxidized and presented mainly oxygen-containing functional groups. After the reduction reaction, no obvious peak could be observed, which means that successful reduction of GO into RGNO [11].

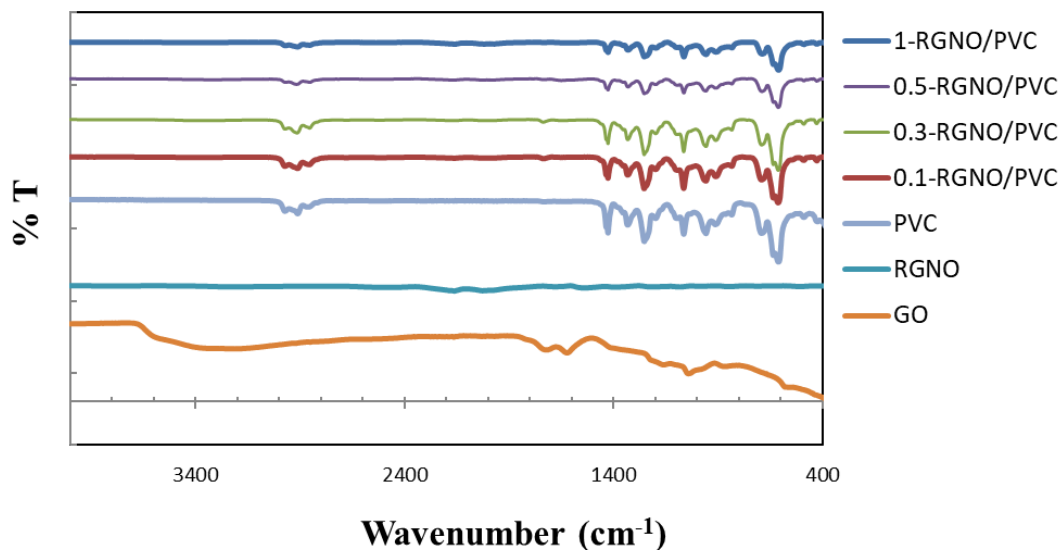


Fig. 2. FTIR spectra of GO, RGNO and RGNO/PVC composites.

Characteristic peaks of carbon-oxygen functional groups of RGNO were just very weak. For neat PVC and the RGNO/PVC composites, the characteristic C–H in phase and out of phase stretching vibrations bands can be observed at 2911 cm^{-1} and 2859 cm^{-1} , respectively. The peaks at $1426, 1252, 956, 834, 611\text{ cm}^{-1}$ in the FTIR spectra of neat PVC and RGNO/PVC composites were attributed to the CH_2 deformation, CH-rocking, trans CH wagging, C-Cl stretching and cis CH wagging vibration, respectively [18, 23]. As seen from Fig. 2, FTIR spectra of RGNO/PVC composites showed a decrease in the intensities of the peaks with increase of RGNO loading content. This result indicated that RGNO prevented intermolecular vibrations with increase of RGNO loading content.

Fig. 3 showed XRD patterns of the GF and prepared GO and RGNO powders whereas Table 2 showed 2θ values and d-spacing data of the same materials.

Table 2. 2θ values and d spacing data obtained from XRD results.

Samples	$2\theta^\circ$	d (nm)
GF	26,4	0,337
GO	9,95	0,888

The crystalline GF had a strong characteristic peak at $2\theta=26.4^\circ$. The corresponding interlayer distance was observed to be 0.337 nm. Fig. 3 exhibited a sharp peak at 9.95° corresponding to the (002) plane of GO and inter planner spacing of 0.888 nm, which confirms the successful preparation of GO from graphite powder by the modified Hummers method [6]. The increase in the interlayer distance from 0.337 nm to 0.888 nm was due to oxygen-containing functional groups intercalated within the layered structure (Table 1) [24]. For RGNO in Fig. 3, the diffraction peak at 9.95° has disappeared, indicating the complete reduction of GO to RGNO by Vitamin C and a broad peak appears at 24.04° . This indicated that the GO is completely exfoliated to a single layer of graphene [25, 26]. The XRD patterns of all RGNO/PVC composites were shown in Fig. 4 and no peak was seen for any of the RGNO-containing composites. XRD analysis result demonstrated that the amorphous structure of the PVC was maintained.

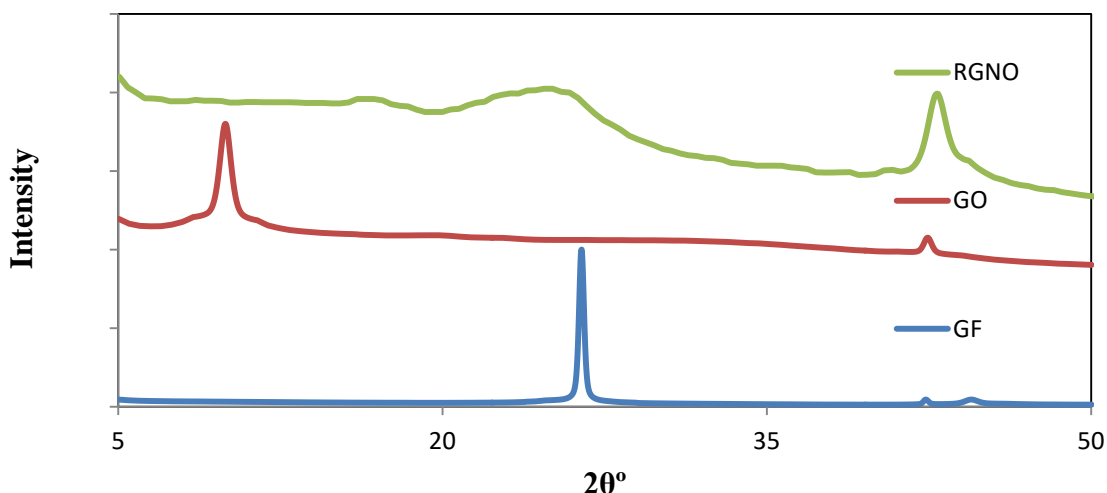


Fig. 3. X-ray diffraction patterns of GF, GO and RGNO powders.

Fig. 5 presented the micrographs of GO and RGNO powders. It could be seen clearly from the SEM image of Fig. 5 a that the morphology of GO appeared as a randomly aggregated [27, 28]. As shown in Fig. 5b, the SEM image of the RGNO showed that wrinkle-like structure due to the rapid removal of oxygen containing functional groups in GO (hydroxyl, carbonyl and epoxy groups) [25]. According to EDS results of the GO and RGNO, oxygen content decreased from 46.78 atom % to 24.03 atom % (Table 3) which indicated successful reduction of GO.

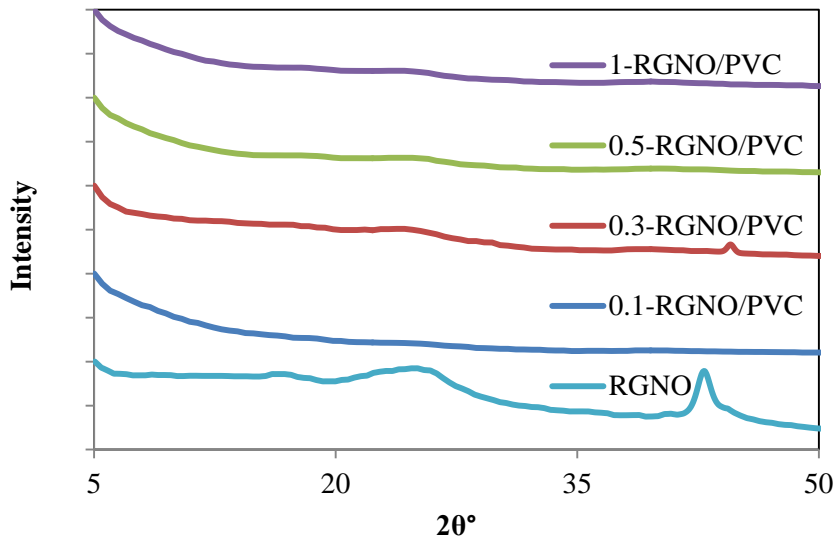


Fig. 4. X-ray diffraction patterns of RGNO and RGNO/PVC composites.

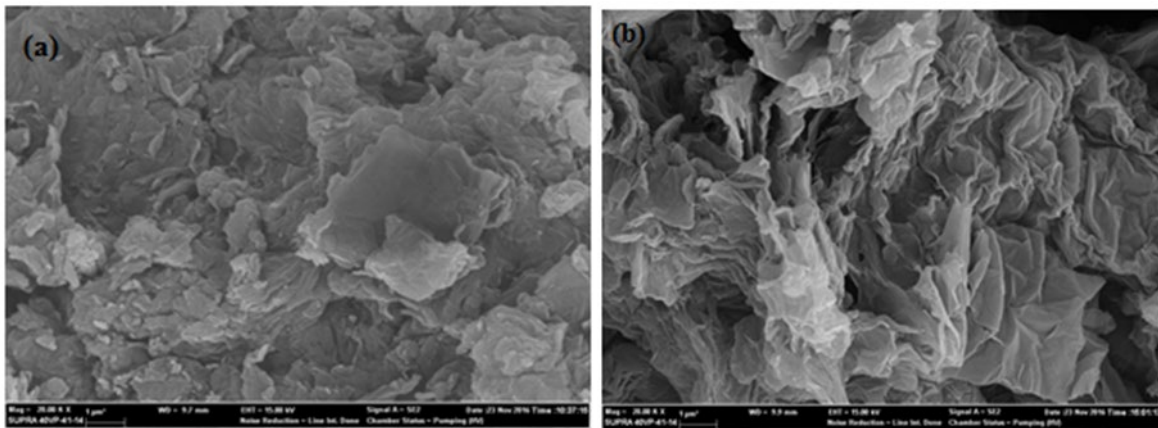


Fig. 5. SEM images of (a) GO, (b) RGNO (magnification 20.000 KX).

Table 3. EDS results of GO and RGNO

Samples	Oxygen Content (atom %)
GO	46.78
RGNO	24.03

Fig. 6 showed the surface morphologies of the neat PVC and RGNO/ PVC composites. When compared to the straight surface of neat PVC shown in Fig. 6a, the PVC composite with 0.1 wt. % RGNO showed irregular and bumpy with a rough surface (Fig. 6b). The SEM image of the PVC composite with 0.3 wt. % RGNO showed that compact and highly porous (Fig. 6c). The PVC composite with 0.5 wt. % RGNO exhibited slightly lower porosity (Fig. 6d) owing to polymer growing in the pores and galleries of RGNO [17]. From the SEM image of the PVC composite with 1 wt. % RGNO (Fig. 6e), it could be seen that the porosity increased as the large-grained. It is evident that the RGNO led to porosity in the PVC matrix. The same structure was also observed previously study [29].

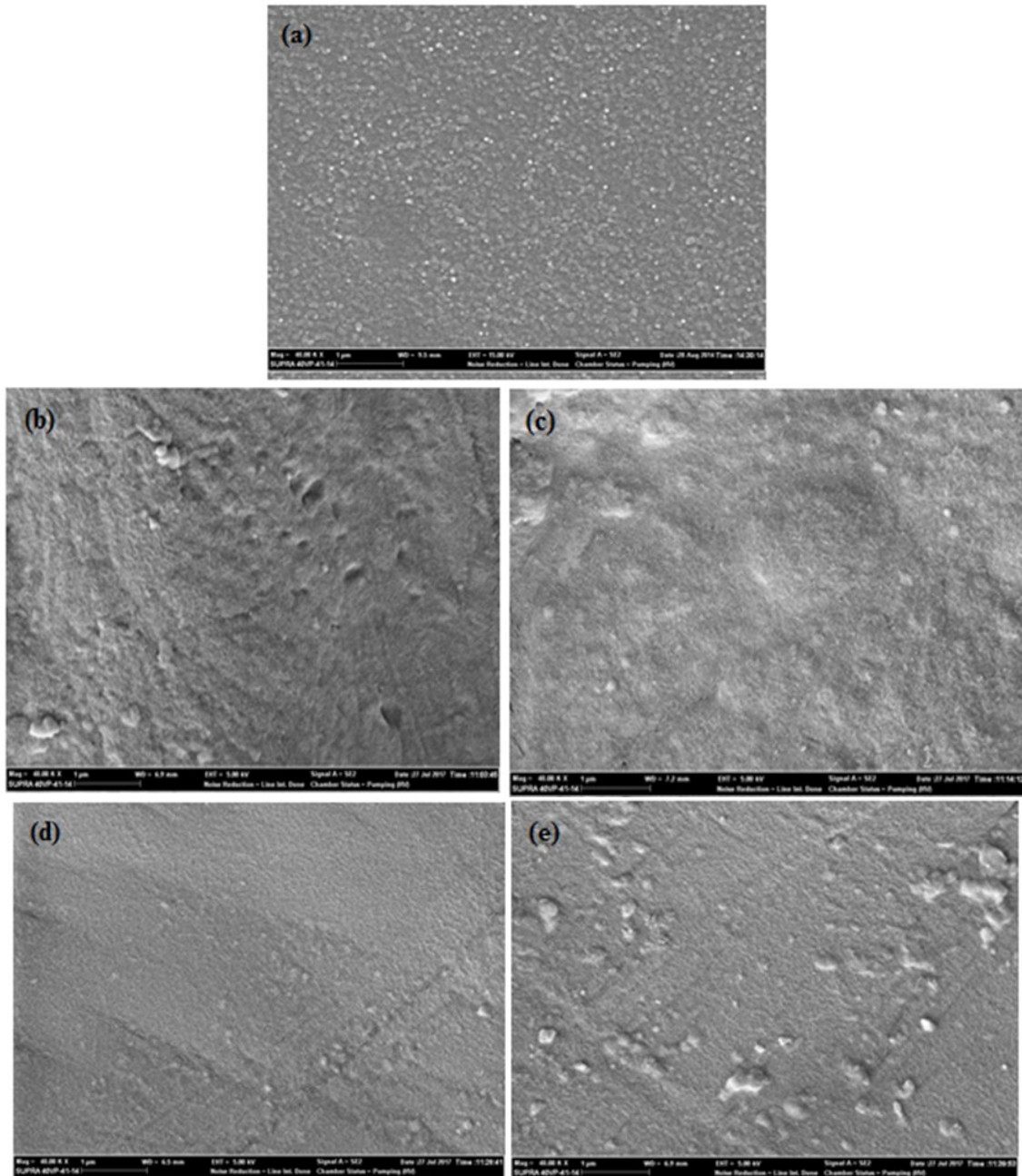


Fig. 6. SEM images of (a) Neat PVC, (b) 0.1-RGNO/PVC, (c) 0.3-RGNO/PVC, (d) 0.5-RGNO/PVC, (e) 1-RGNO/PVC (magnification 40.000 KX)

Conclusion

In this study, the structural changes were observed in PVC composites with 0.1, 0.3, 0.5 and 1 wt. % RGNO. To this aim, firstly, GO was prepared from GF by Hummers method and then obtained GO reduced to RGNO with Vitamin C. FTIR, XRD and EDS results showed that GO and RGNO were successfully synthesized and SEM images proved their characteristic structures. RGNO/PVC composites with dispersion in THF had been synthesized by colloidal blending method. No changes were observed in XRD patterns, but FTIR spectra of RGNO/PVC composites showed a decrease in the intensities of the peaks with an increase of RGNO loading content. XRD and FTIR results of all composites indicated the RGNO layers well-dispersed in the PVC matrix. All composites had a different morphological structure when compared with the neat PVC. The SEM images confirmed the presence of PVC filling the pores and galleries of RGNO in the composites. All results of this study revealed that the structural changes of the RGNO/PVC composites must have influenced their thermal and mechanical properties. Therefore, these properties of these composites will be examined in a future work.

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References

- [1] S. Stankovich, D. A. Dikin, R. D. Piner, K. A. Kohlhaas, A. Kleinhammes, Y. Jia, Y. Wu, S. T. Nguyen, R. S. Ruoff, Synthesis of graphene-based nanosheets via chemical reduction of exfoliated graphite oxide, *Carbon*. 45 (2007) 1558–1565. <https://doi.org/10.1016/j.carbon.2007.02.034>
- [2] S. Park, J. An, J. R. Potts, A. Velamakanni, S. Murali, R. S. Ruoff, Hydrazine-reduction of graphite- and graphene oxide, *Carbon*. 49 (2011) 3019–3023. <https://doi.org/10.1016/j.carbon.2011.02.071>
- [3] D. N. H. Tran, S. Kabiri, D. Losic, A green approach for the reduction of graphene oxide nanosheets using non-aromatic amino acids, *Carbon*. 76 (2014) 193-202. <https://doi.org/10.1016/j.carbon.2014.04.067>
- [4] S. Thakur, N. Karak, Green reduction of graphene oxide by aqueous phytoextracts, *Carbon*. 50 (2012) 5331-5339. <https://doi.org/10.1016/j.carbon.2012.07.023>
- [5] Y.-K. Kim, M. -H. Kim, D.-H. Min, Biocompatible reduced graphene oxide prepared by using dextran as a multifunctional reducing agent, *Chem. Commun.* 47 (2011) 3195–3197. <https://doi.org/10.1039/c0cc05005a>
- [6] Y. Liu, Y. Zhang, G. Ma, Z. Wang, K. Liu, H. Liu, Ethylene glycol reduced graphene oxide/polypyrrole composite for supercapacitor. *Electrochim. Acta.* 88 (2013) 519-525. <https://doi.org/10.1016/j.electacta.2012.10.082>
- [7] S. Gurunathan, J. W. Han, A. A. Dayem, V. Eppakayala, M.-R. Park, D.-N. Kwon, J.-H. Kim, Antibacterial activity of dithiothreitol reduced graphene oxide, *J. Ind. Eng. Chem.* 19 (2013) 1280–1288. <https://doi.org/10.1016/j.jiec.2012.12.029>
- [8] Y. Jin, S. Huang, M. Zhang, M. Jia, D. Hu, A green and efficient method to produce graphene for electrochemical capacitors from graphene oxide using sodium carbonate as a reducing agent, *Appl. Surf. Sci.* 268 (2013) 541– 546. <https://doi.org/10.1016/j.apsusc.2013.01.004>

- [9] M.J. Fernandez-Merino, L. Guardia, J.I. Paredes, S. Villar-Rodil, P. Solis-Fernandez, A. Martinez-Alonso, J.M.D. Tascon, Vitamin C is an ideal substitute for hydrazine in the reduction of graphene oxide suspensions, *J. Phys. Chem. C.* 114 (2010) 6426–6432. <https://doi.org/10.1021/jp100603h>
- [10] A.I. Kamisan, A.-S. Kamisan, R. Md. Ali, T.I. Tunku Kudin, O.H. Hassan, N. A. Halim, M.Z.A. Yahya, Synthesis of graphene via green reduction of graphene oxide with simple sugars, *Adv. Mat. Res.* 1107 (2015) 542-546.
- [11] Y. Wang, Z. Shi, J. Yin, Facile Synthesis of soluble graphene via a green reduction of graphene oxide in tea solution and its biocomposites, *ACS Appl. Mater. and Interfaces.* 3 (2011) 1127–1133. <https://doi.org/10.1021/am1012613>
- [12] Y. Guo, X. Sun, Y. Liu, W. Wang, H. Qiu, J. Gao, One pot preparation of reduced graphene oxide (RGO) or Au (Ag) nanoparticle-RGO hybrids using chitosan as a reducing and stabilizing agent and their use in methanol electrooxidation, *Carbon.* 50 (2012) 2513-2523. <https://doi.org/10.1016/j.carbon.2012.01.074>
- [13] P. Li, X. Chen, J.-B. Zeng, L. Gan, M. Wang, Enhancement of the interfacial interaction between poly(vinyl chloride) and zinc oxide modified reduced graphene oxide, *RSC Adv.* 6 (2016) 5784–5791. <https://doi.org/10.1039/C5RA20893A>
- [14] X. C. Ge, X. H. Li, Y. Z. Meng, Tensile Properties, Morphology and thermal behavior of PVC composites containing pine flour and bamboo flour, *J. Appl. Polym. Sci.* 93 (2004) 1804–1811. <https://doi.org/10.1002/app.20644>
- [15] J. Hu, X. Jia, C. Li, Z. Ma, G. Zhang, W. Sheng, X. Zhang, Z. Wei, Effect of interfacial interaction between graphene oxide derivatives and poly(vinyl chloride) upon the mechanical properties of their nanocomposites, *J. Mater. Sci.* 49 (2014) 2943-51. <https://doi.org/10.1007/s10853-013-8006-1>
- [16] H. J. Salavagione, G. Martínez, Importance of covalent linkages in the preparation of effective reduced graphene oxide_poly(vinyl chloride) nanocomposites, *Macromolecules.* 44, 2011, 2685–2692. <https://doi.org/10.1021/ma102932c>
- [17] K. Deshmukh, G. M. Joshi, Thermo-mechanical properties of poly(vinyl chloride)/graphene oxide as high performance nanocomposites, *Polym. Test.* 34 (2014) 211–219. <https://doi.org/10.1016/j.polymertesting.2014.01.015>
- [18] K. Deshmukh, S. M. Khatake, G. M. Joshi, Surface properties of graphene oxide reinforced polyvinylchloride nanocomposites, *J. Polym. Res.* 20 (2013) 286. <https://doi.org/10.1007/s10965-013-0286-2>
- [19] M. Hasan, M. Lee, Enhancement of the thermo-mechanical properties and efficacy of mixing technique in the preparation of graphene/PVC nanocomposites compared to carbon nanotubes/PVC, *Prog Nat Sci-Mater Int.* 24 (2014) 579–587. <https://doi.org/10.1016/j.pnsc.2014.10.004>
- [20] S. Vadukumpully, J. Paul, N. Mahanta, S. Valiyaveetil, Flexible conductive graphene/poly(vinyl chloride) composite thin films with high mechanical strength and thermal stability, *Carbon.* 49 (2011) 198-205. <https://doi.org/10.1016/j.carbon.2010.09.004>

- [21] H. Wang, G. Xie, M. Fang, Z. Ying, Y. Tong, Y. Zeng, Electrical and mechanical properties of antistatic PVC films containing multi-layer graphene, *Compos. Part B-Eng.* 79 (2014) 444–450. <https://doi.org/10.1016/j.compositesb.2015.05.011>
- [22] W.S. Hummers, R. E. Offeman, Preparation of graphitic oxide, *J. Am. Chem. Soc.* 80 (1958) 1339. <https://doi.org/10.1021/ja01539a017>
- [23] S. Ramesh, K. H. Leen, K. Kumutha, A.K. Arof, FTIR studies of PVC/PMMA blend based polymer electrolytes, *Spectrochim. Acta A.* 66 (2007) 1237–1242. <https://doi.org/10.1016/j.saa.2006.06.012>
- [24] S. Gurunathan, J. W. Han, E. Kim, D.-N. Kwon, J.-K. Park, J.-H. Kim, Enhanced green fluorescent protein-mediated synthesis of biocompatible graphene, *J. Nanobiotechnol.* (2014) 12:41. <https://doi.org/10.1186/s12951-014-0041-9>
- [25] C. Bora, P. Bharali, S. Baglari, S. K. Dolui, B. K. Konwar, Strong and conductive reduced graphene oxide/polyester resin composite films with improved mechanical strength, thermal stability and its antibacterial activity, *Compos. Sci. Technol.* 87 (2013) 1–7. <https://doi.org/10.1016/j.compscitech.2013.07.025>
- [26] Y. Wu, H. Luo, H. Wang, C. Wang, J. Zhang, Z. Zhang. Adsorption of hexavalent chromium from aqueous solutions by graphene modified with cetyltrimethylammonium bromide, *J. Colloid. Interf. Sci.* 394 (2013) 183–191. <https://doi.org/10.1016/j.jcis.2012.11.049>
- [27] M. Safarpour, A. Khataee, V. Vatanpour, Thin film nanocomposite reverse osmosis membrane modified by reduced graphene oxide/TiO₂ with improved desalination performance, *J. Membrane Sci.* 489 (2015) 43–54. <https://doi.org/10.1016/j.memsci.2015.04.010>
- [28] D. Li, B. Zhang, F. Xuan, The sequestration of Sr(II) and Cs(I) from aqueous solutions by magnetic graphene oxides, *J. Mol. Liq.* 209 (2015) 508–514. <https://doi.org/10.1016/j.molliq.2015.06.022>
- [29] F. Mindivan, The Synthesis, Thermal and structural characterization of Polyvinylchloride/Graphene Oxide (PVC/GO) composites, *Mater. Sci. Non - Equilib. Phase Transform.* 3 (2015) 33-36.