

Control of structure-property relationships in polymer/graphene oxide nanocomposite films

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Introduction. Ever since the discovery of graphene in 2004, there has been a strong interest to develop polymer/graphene oxide (GO) nanocomposites for various applications including catalysis, sensing, energy storage, water filtration and bioengineering.¹ Despite considerable research in the field of polymer/GO nanocomposites, there is a persistent interest in developing approaches to regulate and control the arrangement of GO sheets within the polymer matrix to achieve desirable physicochemical, mechanical and electrical properties.² However, the problem of restacking of the GO sheets within the nanocomposite matrix remains a significant challenge.

Aims. To fabricate polymer/GO nanocomposites with the ability to undergo film formation under ambient conditions with concomitantly control of the distribution/self-assembly of GO sheets within the film matrix to regulate electrical conductivity.

Methods. The polymer/GO nanocomposites were fabricated using miniemulsion polymerization and physical mixing methods. Poly(styrene-*stat*-*n*-butyl acrylate) was synthesised either using miniemulsion polymerization employing GO as a surfactant or as soap-free emulsion polymerization followed by mixing with aqueous GO dispersion. The polymer particles have the innate ability to undergo film formation under ambient conditions. The nanocomposite films were fabricated by dropcasting and thermally reduced to introduce electrical conductivity. The electrical conductivity was measured using the 4-point probe method while the distribution of the GO sheets within the matrix was characterised using TEM analysis.

Results. The physical mixing method resulted in most uniform films followed by blend physical mixing and miniemulsion methods. The electrical conductivity assessment of the films revealed significantly higher conductivity in films fabricated by the physical mixing method (9×10^{-4} S/m) compared to the miniemulsion approach (3.4×10^2 S/m). Cross-sectional TEM analysis demonstrated more even, homogenous distribution of randomly interconnected GO sheets within the film fabricated using the miniemulsion method compared to thicker, quite well-defined linear domains in the films made from the physical mixing method.

Discussion. In physical mixing, the GO sheets self-assemble in linear domains as the polymer particles undergo coalescence during the film formation process and facilitate undeterred movement of electrons. In miniemulsion, the presence of GO sheets at the polymer particle interface direct the distribution of GO sheets as the polymer particles start to coalesce, thus resulting in randomly distributed shorter networks of GO sheets with restricted and slow movement of electrons. Furthermore, the lower electrical conductivity and distribution of GO within films fabricated from miniemulsion polymerization may be partially attributed to *in situ* polymer grafting onto GO sheets.³

Conclusion. In summary, simple variation of the synthetic strategy can be used to precisely control the surface and bulk structure of the GO sheets, which has a profound impact on the electrical properties of the resulting nanocomposite films. It will be demonstrated that simply achieving homogenous distribution of GO within the polymer matrix does not always lead to higher conductivity against the widely accepted notion.

References

1. B. Sreenivasulu, B. Ramji and M. Nagaral, *Materials Today: Proceedings*, 2018, **5**, 2419-2428.
2. Y. Fadil, V. Agarwal, F. Jasinski, S. C. Thickett, H. Minami and P. B. Zetterlund, *Nanoscale*, 2019, **11**, 6566-6570.
3. Y. Cai, Y. Fadil, F. Jasinski, S. C. Thickett, V. Agarwal and P. B. Zetterlund, *Carbon*, 2019, **149**, 445-451.