Polymeric Scaffolds reinforced with Graphene-Based Nanomaterials obtained by SLA: Preliminary study of the effect of nanofillers on curing and printability

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INTRODUCTION

Despite the inherent capacity of the bone to regenerate and repair itself, when an irregular or a large defect appears, external solutions must be applied. Traditionally, autografts have been the gold standard; however, due to their drawbacks, like donor-site morbidity [1,2], alternative solutions have been explored. In this context, porous scaffolds hold great promise for bone tissue regeneration [3]. They act as extracellular matrix that supports cell growth, promoting cell adhesion and proliferation. For an adequate performance, they must meet some requirements: e.g. biocompatibility, interconnected porosity, mechanical properties and biodegradability. Conventionally, different methods have been used for their manufacturing (e.g. electrospinning [4,5] and freeze-drying [6,7]). However, these methods do not allow an adequate control of geometry and porosity of the scaffolds.

The development of additive manufacturing techniques offers a promising solution since it allows the complete customisation and control of scaffolds geometry and porosity. To allow cells to adhere and proliferate on its surface, the material used to manufacture the scaffold must have a proper wettability. In general, polymers show a hydrophobic behaviour, which hinders cell adhesion. It has been proved that the incorporation of graphene (G)-based nanomaterials, like graphene oxide (GO) [8], improves hydrophilicity of different polymers. Furthermore, G-based nanomaterials present osteoconductivity and antimicrobial effect [9,10], besides, they reinforce the matrix from a mechanical point of view. It makes them suitable for being used as nanofillers to improve the properties of scaffolds.

Amongst the different additive manufacturing technologies, stereolithography (SLA) shows many advantages: high accuracy, anisotropy, and liquid raw material, which favours the addition of nanofillers. However, when nanofillers are added to the resin, there is a competition in terms of light absorption between the photoinitiator and the nanofiller.

Nanofillers may influence the UV curing process due to modifications in optical properties, which results in changes in absorbance or transmittance of the resin [11,12]. They also can act as points for light scattering and shielding [13]. Besides, polymerisation may be influenced by nanofillers if they act as chain transfer agent, inhibiting the growth of polymer chain [14], or as free radical scavengers, cutting off the polymerisation process [15,16].

Therefore, the aim of this work is to study the effect of G-based nanofillers on the curing of an acrylic photocurable polymer.

EXPERIMENTAL

As matrix, a commercial photocurable acrylic resin was used (Clear Resin Formlabs, USA). The matrix was reinforced with different G-based nanomaterials: G, GO and graphite nanoplatelets (GOxNP). Nanocomposites were prepared by ultrasonication with a load of 0.1 wt.% and viscosity was measured. Differential Scanning Calorimetry (DSC), Fourier-Transformed Infrared Spectroscopy (FTIR), hardness measurements and the extent of curing degree at different ultraviolet exposure times were conducted. Finally, the printability using a SLA printer (Form 2, Formlabs) and dimensional stability of the different nanocomposites were examined.

RESULTS

An increase in the viscosity of nanocomposites was recorded for all nanocomposites investigated with the exception of G. The latter showed a reduction in the viscosity. This decrease in viscosity could be related with a poor dispersion of G within the resin [17].

The results demonstrated that nanofillers affects the curing of the matrix (R) to a different degree depending on the nanofiller type (Figure 1). Specifically, GO did not significantly affect the degree of curing, whilst GOxNP influence curing at low exposure times and G for all UV exposure times studied, which hampered the UV-curing of the resin. FTIR analysis and hardness test corroborated this trend, with a notable retardation in the UV-curing of the resin with the presence of G.

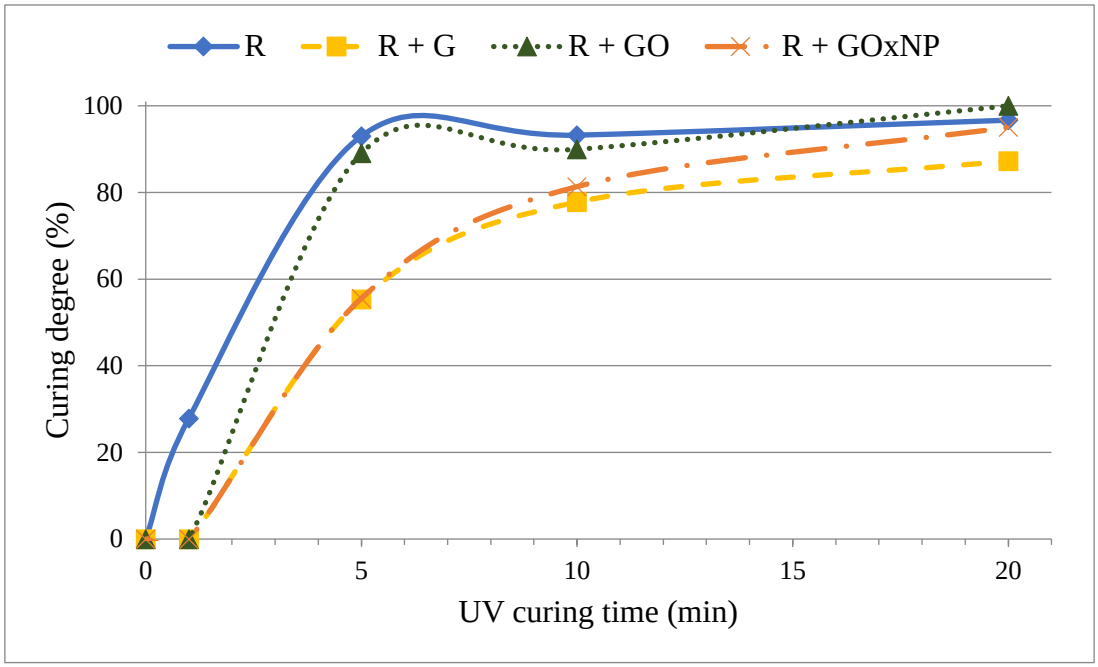

Figure 1. *Curing degree vs UV exposure time of resin and its nanocomposites*

Printability tests were completed in accordance with curing study. G composite did not cure sufficiently to create the part, whilst the other composites did (Figure 2).

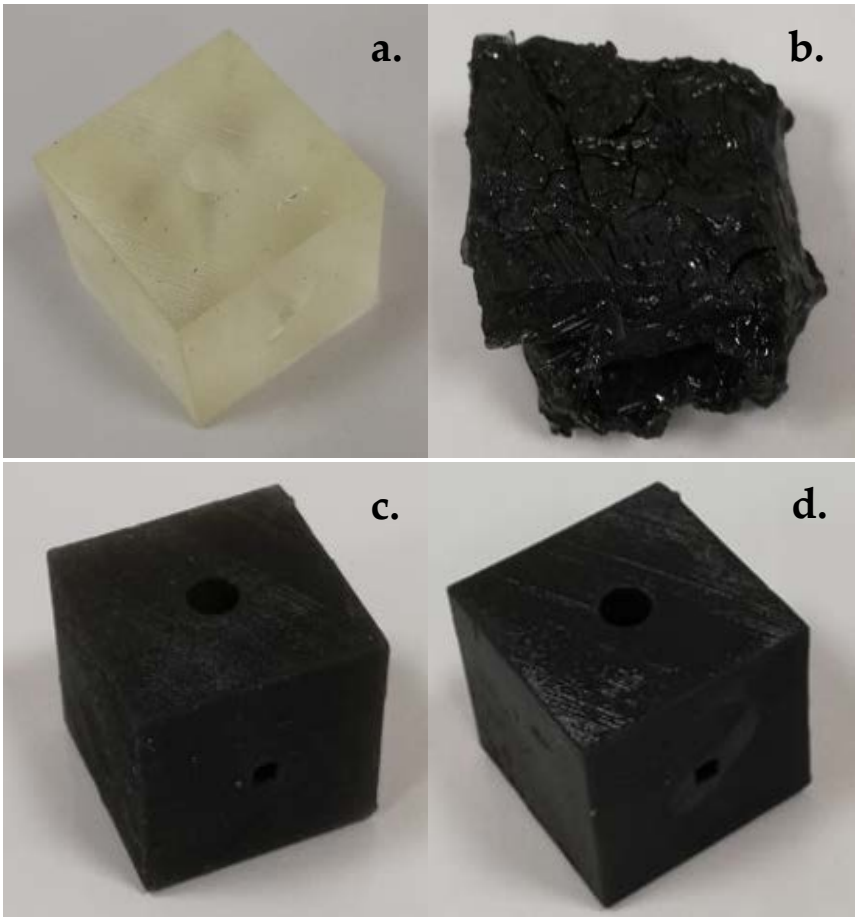

Figure 2. *Printed cubes with R (a), R+G (b), R+GO (c) and R+GOxNP (d).*

In terms of dimensional stability, it was found that the addition of GOxNP provided an improvement. However, the incorporation of GO did not affect dimensional stability.

CONCLUSIONS

It was found that the addition of GO and GOxNP to an acrylic resin do not affect the curing process or printability. Conversely, the incorporation of G affected both, probably due to the darker colour of this nanofillers, which absorbs more light and reduces the performance of the photoinitiator, negatively affecting the printability. Besides, GOxNP improved the dimensional stability of printed parts.

References

1. Dimitriou, R.; Mataliotakis, G.I.; Angoules, A.G.; Kanakaris, N.K.; Giannoudis, P. V. Complications following autologous bone graft harvesting from the iliac crest and using the RIA: A systematic review. *Injury* **2011**, *42*, S3–S15, doi:10.1016/j.injury.2011.06.015.

2. Vail, T.P.; Urbaniak, J.R. Donor-site morbidity with use of vascularized autogenous fibular grafts. *J. Bone Jt. Surg.* **1996**, *78*, 204–211, doi:10.2106/00004623-199602000-00006.

3. Kellomäki, M.; Niiranen, H.; Puumanen, K.; Ashammakhi, N.; Waris, T.; Törmälä, P. Bioabsorbable scaffolds for guided bone regeneration and generation. *Biomaterials* **2000**, *21*, 2495–2505, doi:10.1016/S0142-9612(00)00117-4.

4. Naderi, P.; Zarei, M.; Karbasi, S.; Salehi, H. Evaluation of the effects of keratin on physical, mechanical and biological properties of poly (3-hydroxybutyrate) electrospun scaffold: Potential application in bone tissue engineering. *Eur. Polym. J.* **2020**, *124*, 109502, doi:10.1016/j.eurpolymj.2020.109502.

5. Barati, G.; Rahmani, A.; Nadri, S. In vitro differentiation of conjunctiva mesenchymal stem cells into insulin producing cells on natural and synthetic electrospun scaffolds. *Biologicals* **2019**, *62*, 33–38, doi:10.1016/j.biologicals.2019.10.004.

6. Fereshteh, Z.; Fathi, M.; Bagri, A.; Boccaccini, A.R. Preparation and characterization of aligned porous PCL/zein scaffolds as drug delivery systems via improved unidirectional freeze-drying method. *Mater. Sci. Eng. C* **2016**, *68*, 613–622, doi:10.1016/j.msec.2016.06.009.

7. Ge, Z.; Jin, Z.; Cao, T. Manufacture of degradable polymeric scaffolds for bone regeneration. *Biomed. Mater.* **2008**, *3*, 022001, doi:10.1088/1748-6041/3/2/022001.

8. Lipovka, A.; Rodriguez, R.; Bolbasov, E.; Maryin, P.; Tverdokhlebov, S.; Sheremet, E. Time-stable wetting effect of plasma-treated biodegradable scaffolds functionalized with graphene oxide. *Surf. Coatings Technol.* **2020**, *388*, 125560, doi:10.1016/j.surfcoat.2020.125560.

9. Dong, X.; Duan, X.; Sun, Z.; Zhang, X.; Li, C.; Yang, S.; Ren, B.; Zheng, S.; Dionysiou, D.D. Incorporation of graphene oxide into poly(ε-caprolactone) 3D printed fibrous scaffolds improves their antimicrobial properties. *Mater. Sci. Eng. C* **2019**, *In press*, 110537, doi:10.1016/j.apcatb.2019.118214.

10. Unagolla, J.M.; Jayasuriya, A.C. Enhanced cell functions on graphene oxide incorporated 3D printed polycaprolactone scaffolds. *Mater. Sci. Eng. C* **2019**, *102*, 1–11, doi:10.1016/j.msec.2019.04.026.

11. dos Santos, M.N.; Opelt, C. V.; Lafratta, F.H.; Lepienski, C.M.; Pezzin, S.H.; Coelho, L.A.F. Thermal and mechanical properties of a nanocomposite of a photocurable epoxy-acrylate resin and multiwalled carbon nanotubes. *Mater. Sci. Eng. A* **2011**, *528*, 4318–4324, doi:10.1016/j.msea.2011.02.036.

12. Mu, Q.; Wang, L.; Dunn, C.K.; Kuang, X.; Duan, F.; Zhang, Z.; Qi, H.J.; Wang, T. Digital light processing 3D printing of conductive complex structures. *Addit. Manuf.* **2017**, *18*, 74–83, doi:10.1016/j.addma.2017.08.011.

13. Weng, Z.; Zhou, Y.; Lin, W.; Senthil, T.; Wu, L. Structure-property relationship of nano enhanced stereolithography resin for desktop SLA 3D printer. *Compos. Part A Appl. Sci. Manuf.* **2016**, *88*, 234–242, doi:10.1016/j.compositesa.2016.05.035.

14. Manapat, J.Z.; Mangadlao, J.D.; Tiu, B.D.B.; Tritchler, G.C.; Advincula, R.C. High-Strength Stereolithographic 3D Printed Nanocomposites: Graphene Oxide Metastability. *ACS Appl. Mater. Interfaces* **2017**, *9*, 10085–10093, doi:10.1021/acsami.6b16174.

15. Liang, H.; Bu, Y.; Zhang, Y.; Zhang, J. Graphene oxide as efficient high-concentration formaldehyde scavenger and reutilization in supercapacitor. *J. Colloid Interface Sci.* **2015**, *444*, 109–114, doi:10.1016/j.jcis.2014.12.063.

16. Xia, W.; Xue, H.; Wang, J.; Wang, T.; Song, L.; Guo, H.; Fan, X.; Gong, H.; He, J. Functionlized graphene serving as free radical scavenger and corrosion protection in gamma-irradiated epoxy composites. *Carbon N. Y.* **2016**, *101*, 315–323, doi:10.1016/j.carbon.2016.02.004.

17. Miller, S.G.; Bauer, J.L.; Maryanski, M.J.; Heimann, P.J.; Barlow, J.P.; Gosau, J.M.; Allred, R.E. Characterization of epoxy functionalized graphite nanoparticles and the physical properties of epoxy matrix nanocomposites. *Compos. Sci. Technol.* **2010**, *70*, 1120–1125, doi:10.1016/j.compscitech.2010.02.023.