Effect of Graphene-Based Nanomaterials on Photocurable PLA Resin: Study of Curing Depth and Optimization of Exposure Time on LCD 3D Printing

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INTRODUCTION

The effect of different graphene-based nanomaterials (GBN) on the thermal curing of polymers has already been widely studied. Two tendencies were found[1,2]: (i) the presence of nanofillers accelerated the polymerization process by increasing thermal conductivity or catalyzing the reactions thanks to its oxygenated groups; (ii) nanofillers reduced the curing reaction rate due to the steric hindrance, or the increase in viscosity which hindered the mobility of the reactive species. Photocurable resins have gained great interest due to the population of 3D printing techniques based on UV polymerization. The effect of the GBN in the curing of this kind of resins have been hardly studied. These manufacturing techniques have gained a great attention for biomedical applications and some new biocompatible and bioactive resin formulations have been recently developed. GBN have been extensively used to improve mechanical properties of polymeric materials and also have demonstrated biological properties as antimicrobial activity or osteoconductivity. This work aims to study the effect that the addition of GBN to a photocurable resin, with biomedical applications, used for LCD 3D printing, have over the photopolymerization process and therefore, over the printing process.

Photopolymerization process is mainly governed by two parameters: the penetration depth of the curing light and the energy needed to polymerize. Jacob's working curve is widely used in literature as a basic procedure for testing and characterizing photocurable resins[1]. If curing depth is not large enough, delamination may occur. To avoid it, exposure time could be increased. However, over-curing could occur, leading to a detriment in printing accuracy.

In this work, the effect of GBN on curing depth was study and exposure time was optimized following the study reported by Barkane et al. [3].

EXPERIMENTAL METHODS

Materials: PLA resin was eResin PLA Bio-Photopolymer Resin White, supplied by Shenzhen eSUN Industrial Co., Ltd. (Shenzhen, China). Three different Graphene-Based Nanomaterials (GBN) were used in this study: Graphene (G) (Avanzare), Graphene Oxide (GO), and Graphite Nanoplatelets (GoxNP) (Nanoinnova).

Sample preparation: GBN were dispersed with ultrasonication by probe (US) combined with mechanical stirring (MS): 10' US + 60' MS + 10' US.

Jacobs' working curve: Liquid mixtures were exposed to UV light for different times. Cured surfaces were cleaned with IPA and thickness was measured. Jacobs' working curve is described by Eq. 1.

$$C_d = D_p \cdot ln\left[\frac{E_0}{E_c}\right] \quad (1)$$

Being C_d the cured depth, E_0 the energy of the light at the surface and E_c the "critical" energy to start the polymerization. D_p is the depth where the penetrating light intensity falls 1/e.

Optimal exposure time: Intensity of the peaks corresponding to C=O and C=C were measured with Tensor 27 Spectrophotometer (Bruker). $I_{C=O}/I_{C=C}$ was represented as a function of exposure time. A linear relationship is found, but the slope changed at a certain point. Optimal curing time can be calculated as the intersection point of the lines with different slope[3].

Thermal characterization: Samples with different exposure times were obtained by LCD printing and T_g was calculated by DSC 882e (Mettler Toledo).

RESULTS AND DISCUSSION

In all cases, the addition of GBN to PLA resin reduced E_c and D_p, affecting the photocuring process. The more notable effect on the D_p reduction was observed in the case of G, probable caused by a reduction on the light penetration due to its opaqueness against UV wavelength.

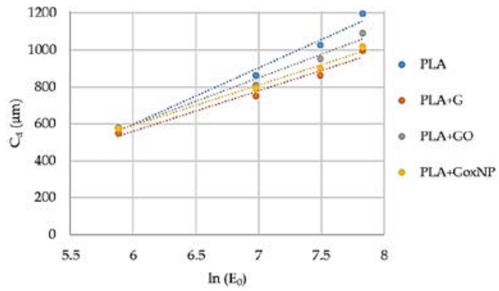

Figure 1. Jacobs' working curves

The reduction of E_c could be due to a catalytic effect of GBN. When optimal exposure time was studied, this catalytic effect was also found and the optimal time were reduced, especially in the case of GO.

Table 1. Optimal exposure time

	PLA	PLA +G	PLA +GO	PLA +GoxNP
Optimal time (s)	9.26	4.64	2.43	5.09

CONCLUSION

GBN catalyzed the polymerization of PLA thanks to its structure and oxygenated groups but also impact on the UV light penetration. This effect could modify the printing process and should be take into consideration to optimize the printability of this kind of materials.

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