PERMEABILITY TUNING OF 3D PRINTED AZO-BASED MEMBRANES

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Three-Dimensional Printing (3DP) has assumed a central role in recent years both in academic and industrial fields. The progressive printers' price knocks off, the high flexibility, the considerable saving of raw materials are only few advantages, but the lack of available 3D printable materials is the main drawback of these techniques.¹ To overcome this limitation, functional dyes have been used to enlarge the palette of available polymers, giving innovative properties to the final object. Materials able to change chemical, mechanical or optical properties, modulating the colour under an external stimulus, such as light, temperature or mechanical stresses, are examples of these appealing research on functional polymers.²



Figure 1. a) Scaffold of synthetized azodyes with different halogens in the ortho position respect to the azo group. b) Schematic representation of permeometer device.

Here we have synthetized and characterized azodye-functionalized polymethacrylates for Digital Light Processing (DLP). The introduction of small amount of dye-monomers into the liquid formulation produced noticeable changes in gas permeability properties of the 3DP polymeric membranes, owing to the ortho halogen group (Figure 1a). We tested CO₂, O₂ and H₂O permeability (Figure 1b), noting an increase in the transmission rate (T_r) for the first two gases compared to the membrane without dyes and, at the same time, a reduction in water permeability. Moreover, an instant rise in the CO₂ T_r can be obtained under green laser irradiation (532 nm), while no remarkable effects are obtained for other gases.

^[1] Layani, M.; Wang, X.; Magdassi, S. Novel Materials for 3D Printing by Photopolymerization. *Advanced Materials* **2018**, *30* (41), 1706344.

^[2] Gastaldi, M.; Cardano, F.; Zanetti, M.; Viscardi, G.; Barolo, C.; Bordiga, S.; Magdassi, S.; Fin, A.; Roppolo, I. Functional Dyes in Polymeric 3D Printing: Applications and Perspectives. ACS Materials Lett. 2020, 1–17.