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# Effects of oxygen on interfacial strength of incremental forming of materials by photopolymerization

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ABSTRACT

Photopolymerization is one of the most widely used methods for additive manufacturing and microfabrication of polymer structures. However, the mechanical properties of these materials, formed incrementally or layer-by-layer by photopolymerization, remain unclear. One critical issue is the strength of the interfaces between adjacent layers. During free radical photopolymerization, these interfaces are exposed to atmospheric oxygen, which is detrimental to the polymerization reaction due to radical inhibition. The influence of oxygen on the interfacial properties, however, is still not well understood. This paper investigates the effect of oxygen on the mechanical behavior of interfaces. In order to facilitate mechanical tests, the interfacial strength is investigated using a part-by-part method that mimics the conventional layer-by-layer photopolymerization process. The experiments found that oxygen enhances the interfacial strength by improving interfacial bridging macromolecular links. A theoretical model is developed to capture the interfacial evolution. Numerical studies further illustrate the role of several processing parameters such as curing condition and resin component.



## 1. Introduction

Photopolymerization is widely used in coatings, adhesives, dentistry, and microfabrication [1,2]. It is also one of the most popular methods used in polymer additive manufacturing (or 3D printing) [3], as photopolymerization can cure a resin in less than ten seconds, a layer-buildup speed that meets critical requirements of 3D printing. A typical photopolymerization resin contains monomer solutions and photoinitiators. Once irradiated by light, photoinitiators cleave into primary radicals and subsequently propagate by reacting with double bonds in monomers (see Fig. 1(a) for illustration) to form a network. During this process, oxygen reacts with primary or propagating radicals to form less active peroxyl radicals. [4]. The reaction is shown schematically in Fig. 1(b). The effects of oxygen have been investigated in, for example, the work of Decker et al. [5,6] and Bowman et al. [7,8]. In general, they are more pronounced near the surface where oxygen is abundant. As pointed out by Bowman et al. [8], oxygen inhibition is undesirable in most cases: it prevents photopolymerization in thin films and creates tacky surface layers for thick films. According to Jariwala et al. [9], oxygen inhibition may also influence the shape stability of 3D printed products. Several strategies were proposed by researchers to prevent this effect, including curing in an oxygen free environment, changing irradiation wavelength, optimizing initiator concentration and implementing different chemical modifications. Detailed discussions can be found in the review of Ligon et al. [10]. But in some conditions, oxygen inhibition can be useful. Dendukuri et al. [11] showed that the tacky lubrication layer created by oxygen was essential in microfluidic fabrication of photocrosslinked particles. Jeong et al. [12] utilized oxygen-induced partial curing to fabricate hierarchical microstructures. Guvendiren et al. [13] applied the effect of oxygen in surface patterning. Our previous work [14] showed that oxygen could regulate the deformation of thin films of light active polymers. Recently, Tumbleston et al. [15] utilized the effect of oxygen to create "dead zone" interfaces in 3D printing, which accelerated the printing speed by several orders of magnitude.

The strength of the polymer interface is one of the most important concerns in applications of photopolymerization-based 3-D printing, which create structures in a layer-by-layer manner. In such applications, light irradiation is used to cure one layer of resin to a 2D pattern according to the cross-section of the 3D

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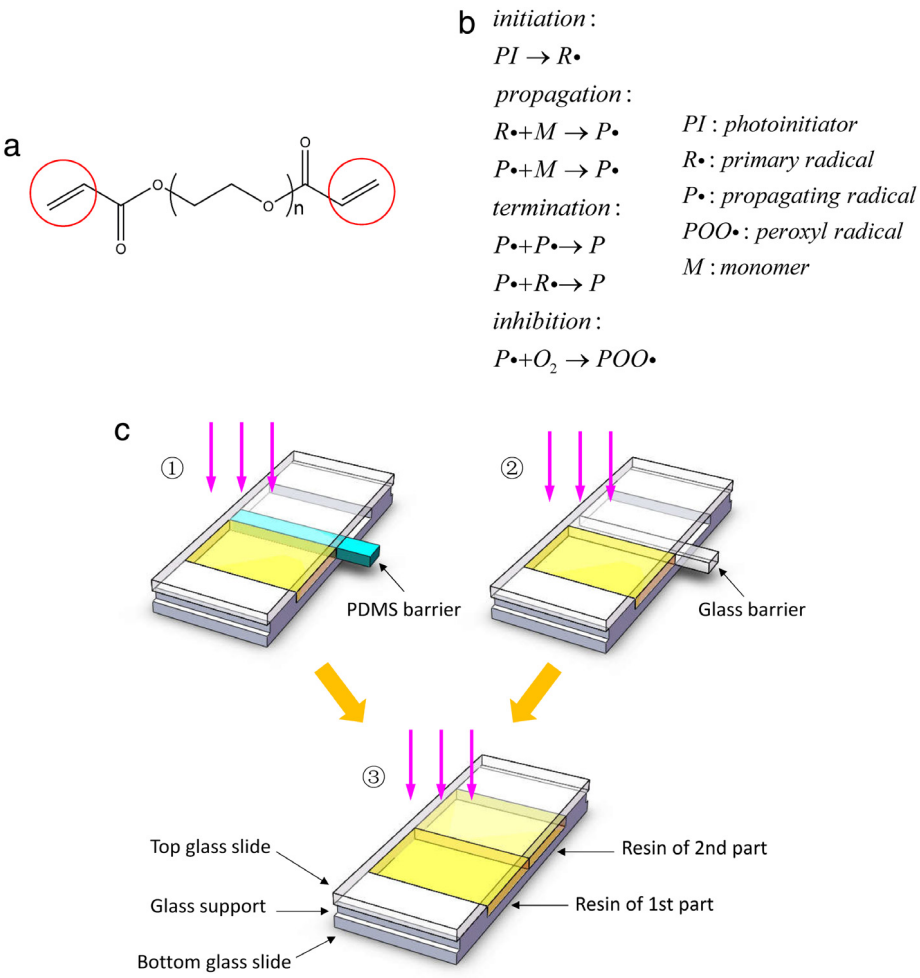


**Fig. 1.** Photopolymerization process. (a) Chemical structure of photo curable PEG-DA. (b) Reaction mechanism in photopolymerization. (c) Schematic graphs of sample preparations. ① Curing of the first part by inserting a PDMS barrier. ② Curing of the first part by inserting a glass barrier. ③ Curing of the whole structure after the addition of a second part.

part. Subsequently a second layer resin is added on the top of the first and is then cured in the same manner. When this process is open to air, the chemical reactions of curing the top surface of the first layer will be inhibited by oxygen, which subsequently affects the properties of the interface between the first and the second layers. According to some researchers, for example Jeong et al. [16], the oxygen-inhibited partial curing of the surface is actually beneficial to interfacial bonding of layer-by-layer structures. A similar phenomenon is also observed in dental composites, which also involve this layer-by-layer structure. However, published studies related to dental applications mainly deal with small molecule monomers [17], which are different from those long chain crosslinkers used in 3-D printing. In addition, current results on the interfacial strength of dental composites are contradictory. Many researchers showed that oxygen inhibition is desirable to increase the interfacial strength [17–19], but some others found that oxygen seems to play no role [20]. It is apparent that many questions remain to be answered regarding the role of oxygen on interfacial strength. In addition, to our best knowledge, comprehensive studies that can provide quantitative information for 3D printing are scarce and most of them are just qualitative.

In this work, the role of oxygen on interfacial strength during incremental photopolymerization was investigated. We carried out experiments on interfacial bonding under different photopolymerization processing parameters to investigate the effect of oxygen on interfacial strength. Realizing the challenge in conducting mechanical experiments on the single interface that is formed in the layer-by-layer photopolymerization method, we used an alternative approach, or the part-by-part incremental photopolymerization method. This method could facilitate mechanical characterization without significantly changing the nature of the interfaces. Based on experimental results, an interfacial model was developed to capture the evolution of interfacial strength under oxygen inhibition. Parametric studies were also conducted in order to investigate the role of oxygen for different conditions.

## 2. Experiments

### 2.1. Materials and sample preparations

The resin used in this work was a mixture of 99.28 wt% PEG-DA (Poly(ethylene glycol) (700) diacrylate; Sigma Aldrich, St. Louis, MO, USA), 0.67 wt% photoinitiator Irgacure 819 (Phenylbis (2,4,6-trimethylbenzoyl)phosphine oxide; Sigma Aldrich) and 0.05 wt% photoabsorber Sudan I (Sigma Aldrich). The phtoabsorber was added to slow down the reaction so that we could control the speed more precisely. In 3D printing, the layer-by-layer method involves hundreds to thousands of layers with a layer thickness smaller than 0.1 mm, making it a significant challenge to study individual interfaces. Here, we designed a part-by-part curing process that would maintain a similar interface but could be easily employed for mechanical tests. The fabrication process is shown schematically in Fig. 1(c). Samples were cured between two glass slides with

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