

Poly(methyl methacrylate) (PMMA)

Subjects: Polymer Science

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Poly (methyl methacrylate) (PMMA) is a thermoplastic synthetic polymer, which displays superior characteristics such as transparency, good tensile strength, and processability.

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1. Introduction

Poly (methyl methacrylate) (PMMA) is a transparent thermoplastic synthesized by emulsion polymerization, solution polymerization, and bulk polymerization from the MMA monomer ^[1]. This acrylate has high resistance to sunlight exposure and good optical properties, widely used to substitute and enhance the glass performance ^[2]. This polymeric compound is attractive; hence is stable, affordable, has been explored in multiple structural and forms—like sheets, films, tubular, even spherical composites—from nanotechnology to upper metrics/scales with variety being applied in all kinds of industries ^[3] ^[4]. One of the main advantages of PMMA is that it contains less potentially harmful subunits from the synthesis, like bisphenol-A, commonly found in other types of polymers such as polycarbonates, polysulfones, and epoxy resins ^[5]. It is a superior polymeric material for analytical separation, sensing ^[6], biomedical and medical applications due to biocompatibility ^[7]^[8], and is used for electrolysis ^[9], polymer conductivity, viscosity measurements ^[10]^[11], solar nano/micro concentrator lens for solar cells ^[12]^[13]^[14]. In practice, the PMMA surface properties can be tailored by surface modification through graft copolymerization ^[15] or by the incorporation of a surfactant into the polymer matrix ^[16].

2. ALD Coatings on PMMA Aided by Seed Layer

The literature above presented demonstrated that PMMA is a viable polymer material for ALD coating process. However, the requirement of a low deposition temperature due to its low T_g raises another limitation: the known ALD precursors for thin film formation at low temperatures are very limited. A solution can be the use of seed layers.

Wilson et al. reported on W deposition on polymers by ALD and their results showed that W nucleation was enhanced by a few previous cycles of Al_2O_3 by ALD. In this case, Al_2O_3 acts as a seed layer of nucleation on a variety of spin-coated polymers such as PMMA, polyvinyl chloride (PVC), polystyrene (PS), polypropylene (PP), and polycarbonate (PC). A growth per cycle (GPC) of 3.9 Å for W ALD at 80 °C has been attained, as shown in [Figure 1](#) ^[17].

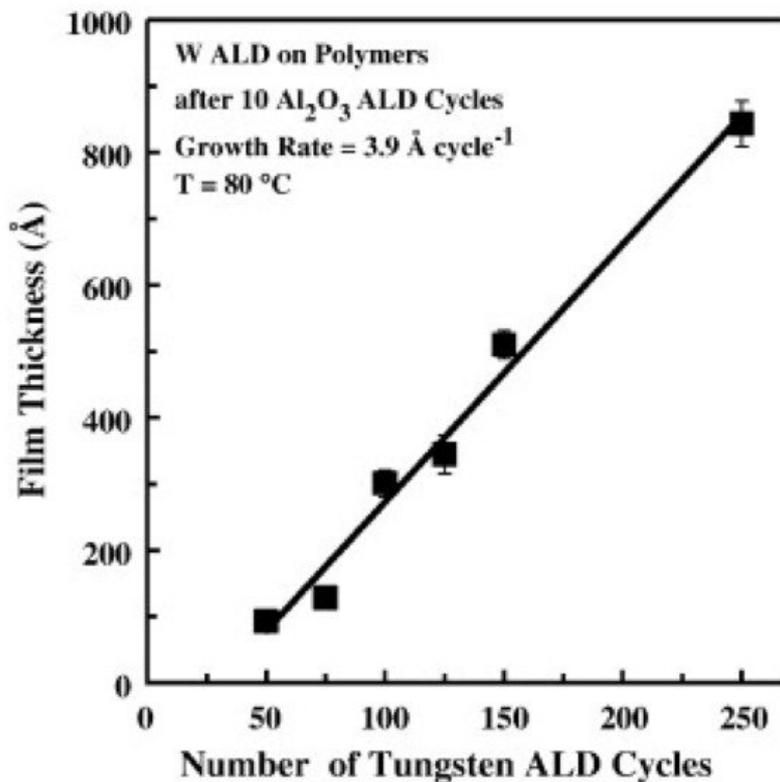


Figure 1. Profilometry measurements of W ALD film thickness on different polymers vs. the number of W ALD cycles. Al_2O_3 ALD was used as a seed layer (10 ALD cycles) (reprinted from [17], Copyright (2008), with permission from Elsevier).

Minton et al. followed the same strategy in terms of using Al_2O_3 ALD seed layer prior to TiO_2 ALD, because TiO_2 did not nucleate well on the PMMA surface. Their results showed that the uncoated PMMA lost a considerable part of its mass, when exposed in vacuum to UV radiation and the bilayers formed with 20 cycles of Al_2O_3 and 100 or 200 cycles of TiO_2 were efficient in preserving PMMA (Figure 2) [18].

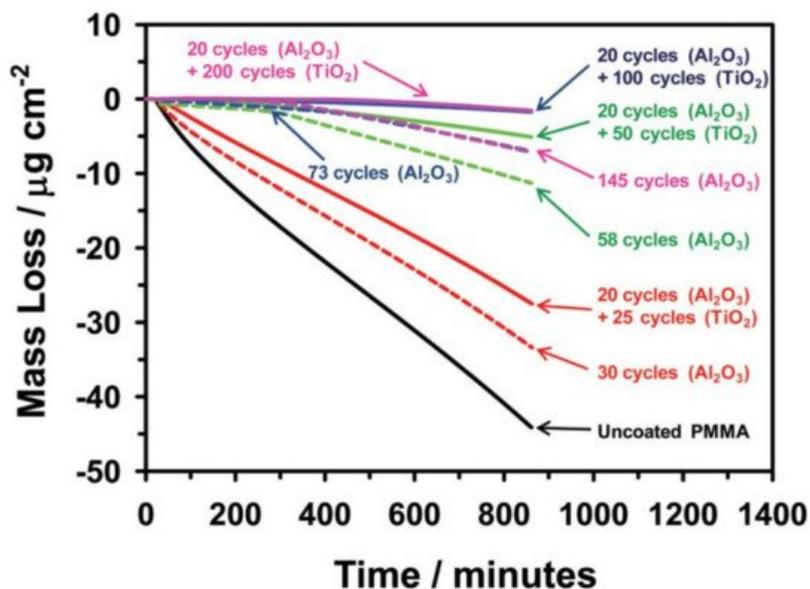


Figure 2. Mass loss of uncoated and coated PMMA with Al_2O_3 and $\text{Al}_2\text{O}_3/\text{TiO}_2$ when exposed to vacuum UV radiation over time (reprinted with permission from [18], Copyright (2010) American Chemical Society).

Kemell et al. also explored the ability of ALD coatings of Al_2O_3 and TiO_2 on PMMA films, among other polymer films, like polyether ether ketone (PEEK), polytetrafluoroethylene (PTFE), and ethylene tetrafluoroethylene (ETFE) [19]. The deposition temperature range was from 80 to 250 °C, enabling the synthesis of amorphous and crystalline metal oxides. Firstly, amorphous Al_2O_3 was deposited at 150–250 °C followed by TiO_2 deposited at 100 °C. For the case of TiO_2 deposition on Al_2O_3 -coated PMMA at 250 °C, polycrystalline anatase TiO_2 films were obtained, as shown in Figure 3. These results highlight the importance of Al_2O_3 seed layer, or interlayer, prior to TiO_2 . In fact, TiO_2 deposition on bare PMMA was attempted also at 250 °C, but virtually no growth was observed, revealing that TiO_2 does not nucleate well on

PMMA. Interestingly, the authors did not point out any constraints of the polymer's thermal stability when deposition at 250 °C, in particular regarding PMMA stability.

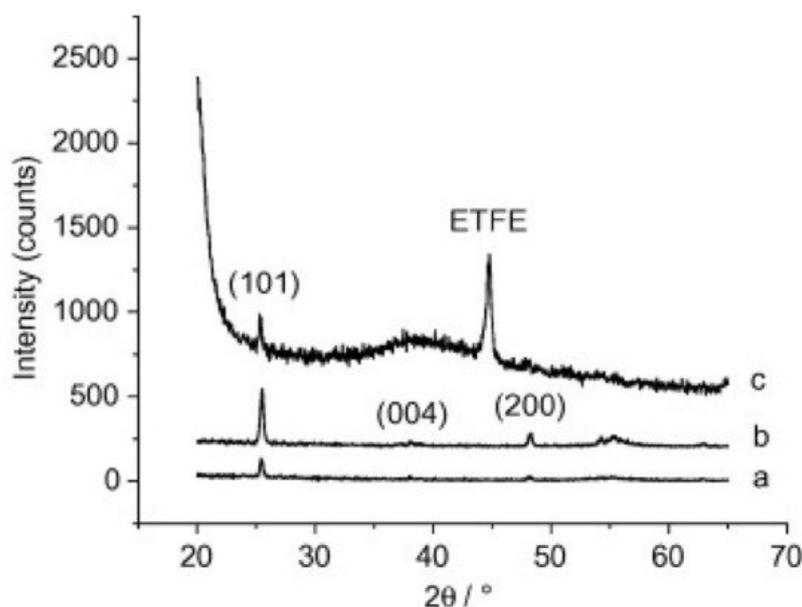


Figure 3. XRD patterns of anatase TiO₂ films in substrates made of (a) Si at 200 °C, (b) PMMA at 250 °C, and (c) ETFE at 200 °C. Si substrate was used as a reference, for comparison purpose (reprinted from [19] Copyright (2008), with permission from Elsevier).

An identical approach was performed by Napari et al. Authors reported on the influence of the deposition of an Al₂O₃ seed layer to the ZnO film growth, morphology, and crystallinity, on PMMA commercial plates and spin-coated PMMA films on Si substrate. The Al₂O₃ seed layer provides a pathway for blocking the DEZ precursor into the PMMA subsurface and improves the ZnO growth with some degree of hexagonal crystal orientation at low deposition temperature viz 35 °. The ZnO surface wetting properties were altered upon UV illumination. As a consequence, this photoinduced changes on the wettability find applications in microfluidics, where thin functional coatings on patterned polymer platforms can be used to manipulate the fluid flows [20]. This work is a promising alternative for lab-on-a-chip technologies development and microfluidics platforms.

In brief, the seed layer or interlayer approach on polymers can be seen as an in-situ two-step ALD process, consisting of the deposition of a few nanometer seed-like layer, at a lower temperature step, followed by a second process for the more refractory metal oxides. The choice of Al₂O₃ ALD from TMA and H₂O precursors is a viable pathway to seeding layer on polymers because Al₂O₃ ALD can be conducted at temperatures as low as 35 °C, conjugated with the TMA positive characteristics like its high volatility and reactivity towards different co-reactants at low temperatures. Based on the above studies, the majority of published work for ALD on polymers addresses Al₂O₃ ALD from TMA and H₂O cycles, stressing out the versatility of this ALD process either as coating and/or seed layer, being also a method to study the influence of the polymer substrate properties on the nucleation and growth of metal oxides. Similar to Al₂O₃, ZnO ALD can also be performed on polymers by taking advantage of the DEZ high volatility and reactivity at low temperatures. It is clear that the modification of a polymer substrate that shows high reactivity towards a given ALD process is crucial to ensure high-density nucleation towards a homogeneous and uniform thin film.

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