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# Hard-coating materials for poly(methyl methacrylate) from glycidoxypropyltrimethoxysilane-modified silatrane via a sol–gel process

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## Abstract

Hard-coating suspensions for improving the scratch resistance of poly(methyl methacrylate) (PMMA) surfaces have been developed by a sol–gel processing method of silatrane in the presence of 3-glycidoxypropyl-trimethoxysilane (GPTS) using 1 M HCl as a catalyst. Poly(methyl methacrylate) substrates were dipped into the coating solutions and dried at 60 °C for half an hour before being cured at 120 °C for 2 h. The addition of GPTS to silatrane suspensions enabled the formation of dense and transparent thin-film with smooth surface on the substrates. The scratch resistance of the coated surface was found to increase with increasing GPTS to silatrane ratio. Both the curing time and curing temperature were found to affect the scratch resistance and adhesion properties of the coating layer.

*Keywords:* Silicate coating; Scratch resistance; Sol–gel process; Poly(methyl methacrylate); Silatrane

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## 1. Introduction

Nowadays, many types of plastics are used as optical materials due to their lightness in weight, ease of mass production, and inexpensiveness. Among these, poly (methyl methacrylate) (PMMA) and polycarbonate (PC) are well-known materials for making sheets or articles of excellent optical and mechanical properties. One of the major drawbacks limiting their uses is the poor scratch resistance. To overcome such a problem, many different kinds of hard-coating media, such as melamine-, acrylic-, and urethane-based chemicals, have been developed and used [1–3].

Organic–inorganic hybrid composites have been used as effective hard-coating materials, which show excellent advantages of both organic and inorganic precursors. These composites are based mainly on the use of metal alkoxide and organosiloxane via sol–gel processing, which has been known to be one of the practical methods for preparing metal oxide thin-films as coating materials for glasses [4], metals [5], and organic polymers [6]. Thin-film coating of metal oxide based on sol–gel process offers an important advantage over other techniques in its relatively low-temperature processing conditions.

A number of published works have been focussing on improving the scratch resistance and mechanical strength of sol–gel-derived, low-refractive index silica thin-films. Lee and Jo [7] used condensed matters from mixtures of colloidal silica and methyltriethoxysilane (MTES) as hard-coating materials for PMMA. They found that the optimal amount of MTES for the hard-coating formula was 100 wt.% to the colloidal silica. The addition of tetramethylammonium formate, a curing catalyst, helped enhance the adhesion between the coating layer and the PMMA substrates as well as reduce the curing time. Li et al. [8,9] have developed many abrasion-resistant coatings based mainly on sol–gel reactions of aluminum, titanium, zirconium, or silicon alkoxide mixed with an organic compound

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containing two or more triethoxysilyl groups, from which the abrasion resistance of coated substrates was found to markedly improve.

Piboonchaisit et al. [10] reported a synthetic route for a silicon alkoxide structure, called “silatrane,” which was found to have a remarkable stability in moist atmosphere. This advantage has made silatrane a good candidate for preparing silicon dioxide network via sol–gel transition, which was later reported in a subsequent work by Charoenpinijkarn et al. [11] as being successful.

In the present contribution, silatrane was used as a precursor for preparing hard-coating suspensions specific for improving the scratch resistance of PMMA surfaces. The effects of ingredient compositions and curing conditions (i.e. curing temperature and curing time) on the adhesion between the coating layer and the PMMA substrates and the scratch resistance of the coated surface were thoroughly investigated.

## 2. Experimental details

### 2.1. Materials

In silatrane synthesis, fumed silica ($SiO_2$, 99.8%; Sigma-Aldrich, USA) and triethanolamine (TEA; Carlo Erba, Italy) were used as reactants; ethylene glycol (EG; J.T.Baker, USA) was used as both the solvent and a possible reactant, and acetonitrile [Labscan (Asia), Thailand] was used to cleanse the silatrane products and was distilled prior to use. In the preparation of the hard-coating suspensions, the synthesized silatrane and poly(vinyl alcohol) (PVA; Sigma-Aldrich, USA) or 3-methacryloxypropyl-trimethoxysilane (MPTS; Acros Organics, USA) or 3-glycidoxypropyl-trimethoxysilane (GPTS; Acros Organics, USA) were used as reactants; HCl (BDH Laboratory Supplies, UK) was used as the acid catalyst; diethylenetriamine (DETA; Facai Group (2000), Thailand) or 3-aminopropyl-triethoxysilane (APS; Fluka, Switzerland) was used as a curing agent; and isopropanol (IPA; Labscan (Asia), Thailand) was used as a solvent. Lastly, PMMA substrates were prepared by cutting a 3-mm-thick sheet into specimens of 1.5 cm×7 cm.

### 2.2. Preparation of silatrane

Silatrane [tris(silatranyloxy-ethyl)amine or $Si(TEA)_2$] was synthesized directly from inexpensive and abundant raw materials, $SiO_2$ and TEA, via the oxide one-pot synthesis (OOPS) [10]. A mixture of 0.125 mol of TEA, 0.1 mol of $SiO_2$, and 100 ml of EG was first heated at 200 °C under nitrogen atmosphere. The reaction was completed within 10 h, and the mixture was slowly cooled down to room temperature before distilling the mixture to get rid of the excess EG under vacuum (i.e. 8 mm Hg) at 110 °C for another 6 h. The white solid precipitate was washed three times with dried acetonitrile to remove unreacted TEA and EG. The silatrane products were dried in a vacuum desiccator overnight prior to being characterized to confirm their successful synthesis.

### 2.3. Preparation of hard-coating solutions

Prior to the successful preparation of hard-coating suspensions for PMMA, there were a number of fail trials, which are worth noting. In the first fail trial, suspensions of silatrane and PVA were prepared by mixing 1 g of silatrane with 10 ml of solutions of PVA in water with the concentration ranging from 4% to 6% w/v (based on the weight of PVA per volume of water). Potassium hydroxide (KOH)-etched PMMA was then dip-coated in these suspensions, pre-cured at 60 °C for 30 min, and then cured at 120 °C for 2 h. Even though the coating layer was transparent, it was soluble in water.

In the second fail trial, partially hydrolyzed silatrane suspension was prepared by dissolving an amount of silatrane in IPA, using 1 M HCl as the catalyst. Various amounts of MPTS were then added to the silatrane suspension and stirred for 24 h. The weight ratio between MPTS and silatrane was varied between 1 and 10 (i.e. 1, 3, 5, 7, and 10, respectively). KOH-etched PMMA was then dip-coated in these solutions, pre-cured at 60 °C for 30 min, and then cured at 120 °C for 2 h. The resulting coating layer appeared to be yellow in color and the as-prepared pre-curing suspensions tended to phase-separate rather easily.

In the third fail attempt, GPTS was used to prepare the pre-curing suspensions of silatrane instead of MPTS. Before dip-coating PMMA in the suspensions, DETA in various amounts ranging from 1 to 5 wt.% (based on weight of DETA per total weight of the pre-cured suspensions) were added to the pre-curing suspensions. Coated PMMA specimens were pre-cured at 60 °C for 30 min and later cured at 120 °C for 2 h. It was found that the coating layer was improperly cured.

In the fourth, successful attempt, APS was used as the curing agent instead of DETA. It was found that, among the various amount of APS added (i.e. from 1 to 5 wt.%), 3 wt.% was the best in giving the resulting curing or hard-coating suspensions in the conditions appropriate for dip-coating for a long enough time (i.e. long enough gelation period). The resulting coating layer was found to be transparent, but the adhesion between the coating layer and the PMMA substrates was not good, as the coating layer could be peeled off from the substrate surface rather easily. To improve the interfacial adhesion between the coating layer and the PMMA surface, plasma etching was utilized along with chemical etching in a KOH solution.

Based on the aforementioned preliminary studies, the successful method for preparing the hard-coating suspensions can be capitulated as follows. First, partially hydrolyzed silatrane suspension was prepared by dissolving a known amount of silatrane in 1 M HCl solution and was later diluted by the addition of IPA. HCl was used as the