



# Synthesis and Characterization of Transparent Hydrophobic Sol-Gel Hard Coatings

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*Received August 25, 2005; Accepted October 31, 2005*

**Published online:** 21 April 2006

**Abstract.** It is challenging to make a transparent hydrophobic hard coating when soft hydrophobic additives are added into the coating system. Material non-homogeneity due to phase separation, non-durable hydrophobicity and deteriorated transparency are the main issues. In this paper, we describe a chemical formulation, which contains a pre-linked hydrophobic cluster and a silica hard matrix with silica hard fillers so that the hydrophobic property and hardness can be tuned separately and optimized. The transparency of the coating is found to be related to the effective modification of the reactive titanium tetraisopropoxide (TIP) precursor by ethyl acetoacetate (EacAc) and the right ratio between TIP and polydimethylsiloxane (PDMS) ( $\leq 0.5$ ). The water contact angle is increased to a maximum of  $133^\circ$  when 50 Vol% of PDMS is added into the silica matrix. The hardness of coating is proportional to silica filler content and curing temperature, and inversely proportional to PDMS Vol%. 30 Vol% silica filler in silica matrix and curing temperature at  $300^\circ\text{C}$  result in the best hardness in this study. Hardness at 50 Vol% PDMS dropped to 0.2 GPa from 0.85 GPa of pure silica coating. The Vol% of PDMS and silica filler will be further optimized in our next stage experiments.

**Keywords:** coating, sol-gel, hydrophobicity, PDMS, hardness

## 1. Introduction

Water repellent coatings have been achieved by different methods using hydrophobic additives, such as alkyl thiols, long chain alkyl silanes (C8–C12), fluoroalkylsilanes [1–3] or polydimethylsiloxane (PDMS) [4–7] etc. However, since all the hydrophobic additives are soft and tend to form a separate phase with the inorganic matrix, the durability of these coatings against wiper abrasion and outdoor weathering is low [2]. The main challenges of making a transparent hydrophobic hard coating are: (1) to maintain the hardness and abrasion resistance when sufficient amount of hydrophobic additives are added into the coating system, (2) to ensure

the hydrophobic additive is chemically incorporated into the material network, so that the hydrophobic property will be durable, (3) to prevent large inorganic precipitates to maintain the transparency. In our previous work, we used polytetrafluoroethylene (PTFE) [8] and C8 [9] as hydrophobic additives and colloidal silica as hard fillers in a silica based sol-gel coating system. The hydrophobicity in both cases was good, but the surface roughness was increased, and the light transmittance was greatly reduced. In this paper, we report a transparent smooth coating, in which the hydrophobic property and hardness can be tuned separately, whereby an optimum balance can be obtained. A hydroxyl-terminated PDMS (molecular structure as shown in Fig. 1), reacted with metal alkoxide (TIP), is used as the hydrophobic constituent owing to its low surface energy of  $16\text{--}21\text{ mNm}^{-1}$ .

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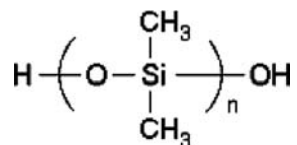


Figure 1. Structure of hydroxyl terminated polydimethylsiloxane.

The terminal hydroxyl groups of PDMS have the advantage of being able to participate in the condensation reaction so that PDMS is incorporated into the inorganic network. Although research work pertaining to mechanical properties of PDMS based hybrids has been reported [4, 5, 7, 10], as to date no paper has been found that characterizes the hardness of this hybrid system. In this paper, we use a suitable colloidal silica with particle size of 20 nm, that can be well distributed in the sol-gel matrix to increase the hardness of the coating. The TIP is modified and pre-linked with PDMS in certain ratio to maintain the coating's transparency.

## 2. Experiments

### 2.1. Materials

The coating system consists of the following components and raw materials:

- hydrophobic additive: hydroxyl-terminated PDMS, average molecular weight 550, viscosity 25 cSt.
- metal alkoxide as linker for the PDMS: Titanium tetraisopropoxide (TIP)
- modifier for TIP to reduce the hydrolysis and condensation reaction rate: ethyl acetoacetate (EAcAc),
- sol-gel matrix to provide the primary strength of the coating: Methyl-triethoxysilane (MTES) and Tetraethyl orthosilicate (TEOS),
- silica nano-filler: 20 nm colloidal particles suspended in iso-butanol (pH 7),
- catalysts: acetic acid (HAc) or hydrochloric acid (HCl),
- solvents: Ethanol (EtOH) and 1-Propanol (PrOH).

All materials are purchased from leading chemical suppliers without further purification.

### 2.2. Synthesis Procedures

**2.2.1. Formulation of TIP/PDMS Solution.** We intend to achieve a stable and clear solution containing TIP and PDMS, in order to incorporate it as a cluster into silica coating matrix. First we used acetic acid as the catalyst for the hydrolysis of TIP/PDMS mixture. HAc was first added into TIP in different molar ratios from 0.125 to 2. PDMS was dissolved in 1-propanol and mixed with the TIP/HAc solution in TIP:PDMS molar ratios from 0.5 to 10. To this mixture, water was added for hydrolysis in molar ratio of

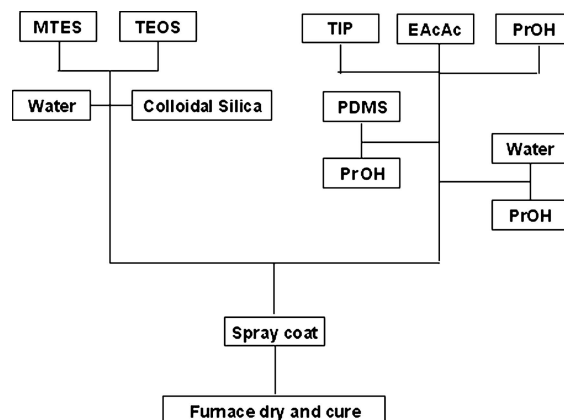


Figure 2. Chemical formulation procedures.

$\text{H}_2\text{O}:(\text{TIP} + \text{PDMS}) = 4:1$ . We sprayed these solutions onto glass slides to check the transparency, and found the formation of white precipitates on glass with all the solutions.

In our second experiment, we used EAcAc as the chemical modifier to replace the HAc. We found that only TIP:PDMS molar ratio of 0.5 resulted in transparent coating. From these experiments, we defined our TIP:EAcAc:PDMS: $\text{H}_2\text{O}$  molar ratio of 1:2:2:2. The chemical formulation procedures are described in Fig. 2 and summarized as follows: TIP is first modified and stabilized by EAcAc in 1-propanol. PDMS is dissolved in 1-propanol, then added to the TIP solution, stirred for 30 min, then DI water is added into the TIP/PDMS mixture to hydrolyze and link the TIP and PDMS.

**2.2.2. Formulation of MTES/TEOS Solution and Final Solution.** A stock solution of MTES and TEOS is prepared by hydrolysing these precursors in water followed by an addition of colloidal silica. The molar ratios of the components are: MTES:TEOS: $\text{H}_2\text{O}$  = 1:0.016:4.4. The colloidal silica is acidified by HCl to pH4, and added at 13 Vol% and 30 Vol% with respect to the volume of the cured solid coating. This is calculated based on the total mass of MTES, TEOS, TIP, PDMS and colloidal silica with eliminating the mass of the alcohol side groups contained in MTES, TEOS and TIP. Weight% of each component can then be calculated. The density of the cured coating was measured on a thick film of a similar silica based sol-gel coating and used as a standard value ( $1.4 \text{ g/cm}^3$ ) for all the coatings in this paper. Therefore, the vol% of each component can be calculated. Both colloidal silica Vol% and PDMS Vol% mentioned in this paper are calculated by this method.

The TIP/PDMS mixture is added to the MTES/TEOS stock solution in various ratios to form the final solutions to study the hydrophobicity and hardness. The procedures are summarized in Fig. 2.

### 2.3. Coating and Curing Processes

Coating is applied to glass substrates by a spraying process. The air spray gun is a LVMP (low volume medium pressure) gun, which makes higher transfer efficiency and better atomization with less air consumption. This is necessary to ensure fine spray droplets and maintain a uniform transparent coating. The coated glass is dried in oven at 80°C for 40 min, then cured at 100°, 150°, 200°, 250° and 300°C respectively for 90 min.

### 2.4. Coating Characterizations

Coatings' hydrophobicity is measured using the VCA Optima contact angle machine. The image of the water drop was obtained when a pre-determined amount of water (50  $\mu$ l) is dropped on the surface under test. The program then analyses the image of the drop and gives the contact angle.

In order to measure the coating thickness, a corner of the specimen is masked by scotch type, which is peeled off after coating. The height difference between coated and uncoated surfaces is measured by Taylor-Hobson profilometer.

Coating hardness is evaluated by both Vicker's micro-hardness and nano-indentations. A 10 gf load is used for HV measurement. The nano-indenter is a diamond Berkovich type with tip radius of 50–100 nm. The indentation depth is controlled to be at most 10% of the coating thickness to reduce the influence from the substrate.

## 3. Results and Discussion

### 3.1. Coating's Transparency

When HAC was used as the catalyst for TIP hydrolyses, the coating transparency was poor due to the uncontrolled growth of titanium dioxide precipitates. The contact angle was lowered from 99° to 65° with increasing TIP/PDMS ratio from 0.5 to 10. Only when EAcAc is used as a ligand for TIP and molar ratio of TIP/PDMS is reduced to 0.5, a transparent coating can be obtained. Meanwhile, water contact angle of 110° is obtained. Figure 3 shows the photographs of the HAC catalysed translucent coating and EAcAc modified transparent coating. MTES/TEOS solution is not yet added for these samples. This result defines the optimum chemical formula for TIP/PDMS combination, in which the PDMS is pre-linked to TiO<sub>2</sub> nano-structures and remains stable in the silica matrix. The TIP/PDMS ratio of 0.5 is different from Yamada's result where transparent coatings were obtained in the TIP/PDMS ratios from 1 to 10. The reasons could be that our coating is sprayed on glass substrate, where air atomisation is required, which introduces additional chance of forming large titanium dioxide pre-



Figure 3. Photographs of HAC catalysed (HAC:TIP:PDMS = 0.125:1:2) translucent (a) and EAcAc modified (TIP:EAcAc:PDMS = 1:2:2) transparent (b) glass slides using only the TIP/PDMS solutions (no MTES/TEOS nor silica filler is added). Coatings are cured at 200°C for 90 min.

cipitates. Therefore, more PDMS to surround the TIP is needed.

### 3.2. Hydrophobicity

Since the TIP/PDMS cluster is soft, it is used as hydrophobic additive in a harder silica matrix. Therefore, the MTES/TEOS coating solution is made, which contains silica matrix as well as silica nano-fillers chemically bonded with the silica matrix. The combination of this hard matrix with the hydrophobic TIP/PDMS cluster provides the possibility to optimize the hydrophobic property and the coating hardness at the same time. Because there are hydroxyl groups on PDMS and hydrolysed TIP in the solution, both of the components can further react with hydrolysed MTES/TEOS and condense together. This design makes a uniform bonding of all the components resulting in a uniform and durable microstructure. Figure 4 shows the water contact angle in relation to PDMS Vol%. A maximum contact angle of 133° is obtained with 50 Vol% PDMS, with a curing temperature of 200°C and curing time 90 min. The slight decrease of contact angle at 60 Vol% PDMS may be due to the effect of surface morphology or roughness. Similar trend was also reported in our previous paper [11], the contact angle did decrease in the low roughness regime. The increased surface roughness may be related to the non-uniform distribution of PDMS since there are less silica matrix (40 Vol% only) to surround the TIP/PDMS clusters. The influence of surface roughness or morphology on contact angle has been investigated by many researchers using both theoretical models and experimental methods [11–13]. Many factors must be considered and more experiments

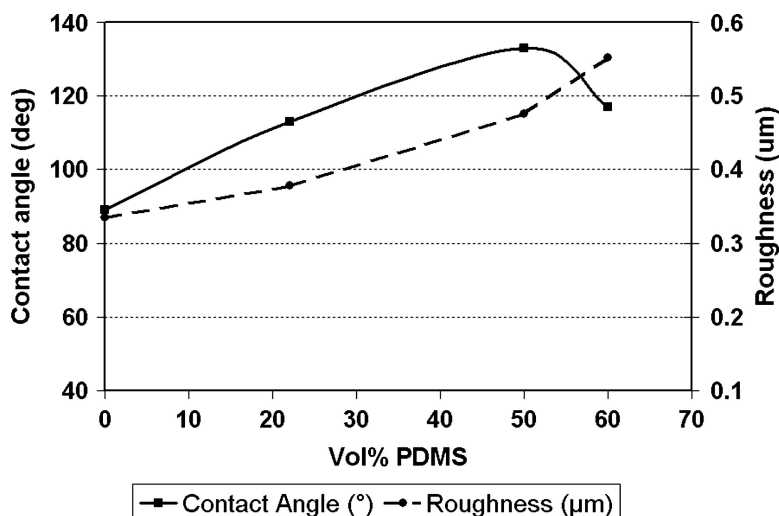


Figure 4. Contact angle in relation to PDMS Vol% and roughness showing a maximum of 133° at 50 Vol% PDMS. Coatings are cured at 200°C for 90 min. Colloidal silica is at 30 Vol%.

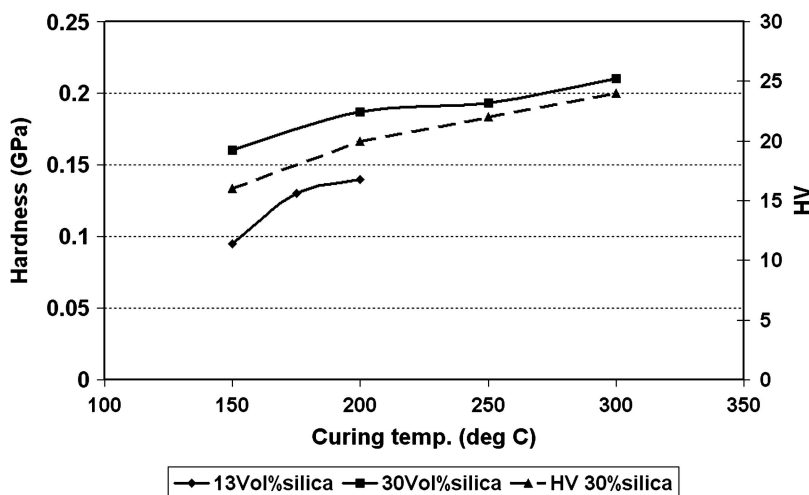


Figure 5. Coating hardness in relation to curing temperature at 13 Vol% silica and 30 Vol% silica respectively. PDMS content is 50 Vol% for all the samples. Curing time was kept the same at 90 min for all the samples.

are required. We will study this phenomenon further in our future experiments.

### 3.3. Coating Hardness

Coating's hardness depends on three factors: (1) the fraction of colloidal silica filler in the sol-gel matrix, (2) the curing temperature which affects the density of the coating and (3) the PDMS fraction. Figure 5 shows the hardness by Nano-indentation in relation to curing temperature and colloidal silica volume fraction, with PDMS 50 Vol%. For comparison purpose, Vicker's hardness (HV) of 30 Vol% silica is plotted in the second Y-axis. The coating thickness has been kept constant at  $9 \pm 1 \mu\text{m}$ . It is seen from the picture that coating hardness increases with increasing curing temperature due to higher degree of condensation of both MTMS/TEOS matrix and TIP/PDMS cluster. The

evaporation of PDMS small molecules also causes the increase of coating hardness, especially at higher temperatures, since the soft phase of PDMS is reduced. 30 Vol% colloidal silica results in higher hardness at all curing temperatures comparing to 13 Vol% silica. HV values show the same trend as the hardness by nano-indentation.

Since the load applied in HV measurement is higher than that in nano-indentation, the indentation into the coating is deeper, thereby, the tendency of influence from substrate is higher. In this case, the coating thickness would have effect on the hardness values. Whereas in the nano-indentation, the influence from substrate is almost eliminated since the indentation depth is only one tenth of the coating thickness. Therefore, nano-indentation is highly recommended in the study of thin coatings. Vicker's hardness can be used for hardness comparison between the samples where other parameters are kept the same.

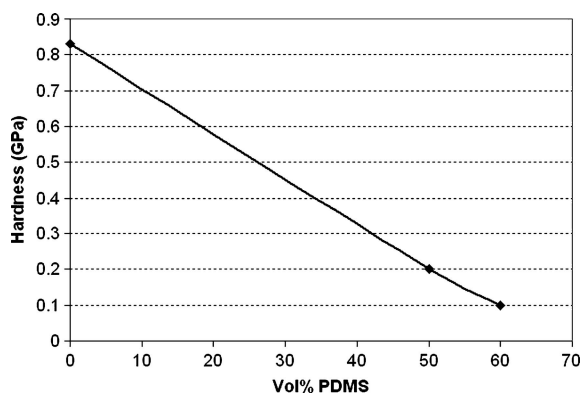


Figure 6. Effect of PDMS content on coating hardness, colloidal silica at 30 Vol%, cured at 250°C for 90 min. Further refining of composition at lower PDMS content will be carried out.

The influence of PDMS content on overall coating hardness is tremendous as shown in Fig. 6. 50 Vol% PDMS reduces the hardness from 0.84 GPa to 0.2 GPa, and further to 0.1 GPa at 60 Vol% PDMS. This is expected since the PDMS itself is an elastomeric material. It is clear that the addition of organic component such as PDMS has a very adverse effect on hardness particularly for higher content. However, there are still room for improvement.

We will further refine the chemical composition by reducing the PDMS content and increasing the silica nano-filler. Surface morphology may be modified by special nano-fillers for further improvement of hydrophobicity. We will also analyse the coating's microstructure, wear properties and durability.

#### 4. Conclusion

We have synthesized a transparent hydrophobic hard coating by sol-gel method. To ensure high transparency, TIP is modified and stabilized by EAcAc in 1-Propanol before mixing with hydroxyl terminated PDMS in the same solvent environment. They are then hydrolysed by water to form hydrophobic clusters. The maximum molar ratio of TIP/PDMS is 0.5 for a transparent coating. The water contact angle is increased to a maximum of 133° when 50 Vol% of PDMS is added into the silica matrix. No further improvement of contact angle by higher PDMS (60 Vol%)

due to the effect of increased roughness and changed surface morphology, which may be caused by the non-uniform distribution of PDMS/TIP cluster in the limited silica matrix (only 40 Vol%). The coating matrix material is formulated by hydrolysing MTMS and TEOS in an acidic system with addition of silica nano-fillers. The hardness of coating increases with silica filler content and curing temperature, and is inversely proportional to PDMS Vol%. 30 Vol% silica filler in silica matrix and curing temperature at 300°C result in the best hardness in this study. Higher PDMS content (50–60 Vol%) reduces the hardness tremendously. Hardness at 50 Vol% PDMS dropped to 0.2 GPa from 0.85 GPa of the pure silica matrix. The TIP/PDMS hydrophobic cluster and the MTMS/TEOS/filler matrix provide a possibility that hydrophobic property and coating hardness can be tuned separately and optimized at the same time. Further optimization on silica filler and PDMS content and material characterization will be carried out in our next study.

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