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Fluorine-free low surface energy organic coating for anti-stain applications

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ABSTRACT

Perfluorinated polymer material are widely used in various industries for their excellent amphiphobic properties while there is significant environmental concern on them recently. So US Environmental Protection Agency (EPA) regulations require new fluorine-free materials for anti-stain applications in leather, paper, textile, masonry, and homecare industries. Silicone materials are hydrophobic in nature but traditionally believed to be oleophilic. In this paper, it is demonstrated that by molecular design and tuning of surface energy, better oleophobicity could be obtained from silicone materials. For good amphiphobicity and instead of using fluoro-containg materials, tris-trimethylsily(M_3T) unit was introduced into the polyacrylate as the functional side chain, to form M_3T-containing copolyacrylate, the base polymer for the anti-stain application. By applying M_3T copolyacrylate, fluorine-free silicone based material to masonry and fabrics, good anti-stain performance was achieved. The lowest surface energy of the silicone based copolymer is about 13 mN/M which is close to fluorine polymer. Research work has been done systematically on the effects of the ratio of M_3T unit in the copolyacrylate, copolyacrylate concentration in coating formulation, copolyacrylate molecular weight, and solvents on coating anti-stain performance. Good anti-stain performance has been obtained on the treated substrate, while the copolyacrylate with molecular weight of 80,000 and concentration of 20 wt%, With increase of tris-trimethylsilypropyl methacrylate (M_3T) ratio, the coating critic surface energy decreased, better anti-stain performance was achieved.

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1. Introduction

Currently, fluorinated materials dominate the anti-stain applications for masonry, textile, leather and paper products because of its excellent hydrophobicity and oleophobicity [1–11]. There have been extensive studies in the scientific community on the reason why fluorinated materials could offer amphiphobicity [12–19]. It is believed that electronegativity of fluorine atom plays an important role and in a perfluorinated molecule, the fluorine atoms form a "protective sheath" against chemical attack. In perfluorinated polymers, low interchain forces, close pack of perfluorinated side chains of polymers and rigidity of the chains contribute to low surface energy and amphiphobicity.

However, US Environmental Protection Agency (EPA) issued tighter regulations on fluoropolymers used in these applications, which could release materials such as perfluoroalkyl carboxylates, or perfluoroalkyl sulfonates into the environment. These materials remain in the environment and ecosystem, suspected as "highly toxic" [20–22]. Accordingly, the identification of fluorinated materials with shorter four to six carbon perfluoroalkyl chain products [23–29] that are not considered bioaccumulative or non-fluorinated products that can avoid environmental and health concerns become of increasingly commercial interests and scientific interests [30]. However, many of the key performances of fluoropolymer decrease sharply when fluorinated chains become shorter. On the other hand, they still remain persistent in the environment with their longer chain homologues, and still could be an environmental issue and health concern. In order to address those concerns, a non-fluorinate chemistry would be desired solution for the anti-stain application. How to design the molecular structure with non-fluorinated chemistry to achieve amphiphobicity and low surface energy is the most effective way to address those concerns.

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Table 1
Relationship between surface composition and critical surface tension.

Surface composition	Critical surface tension (mN/m)
$-CF_3$	6
$-CF_2H$	15
$-CF_2$	18
$-CH_2CF_3$	20
$-CF_2CFH$	22
$-CF_2CH_2$	25
$-CFHCH_2$	28

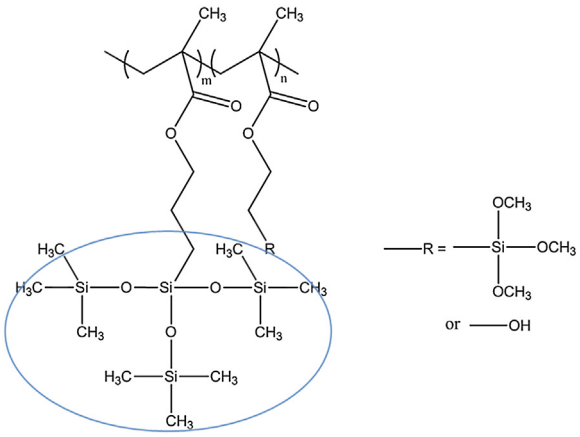

Fig. 1. Chemical structure of M_3T unit.

Based on previous research, it is understood that the influencing factors for the surface energy of the fluorinated polymer or oil/water repellency include length of perfluoro (PF) chain, alignment of the PF chain, distribution of PF at surface, rigidity of chain and roughness of surface. The relationship between critical surface tension and surface composition of fluoro materials is shown in Table 1, it indicates that surface energy can be tuned by manipulating molecular structure and surface composition of materials.

Except fluoro materials, silicone and olefin are materials with the very low critical surface tension. but silicone is commonly oleophobic material and critical surface tension of these materials is about 20 mN/M. In order to change silicone materials to repel oil, the critical surface tension needs to be the lower, even below surface tension of oil. Generally speaking fluorination on the surface of silicone can reduce the critical surface tension [31–34]. In this paper, the critical surface tension decreased by manipulating molecular structure without fluorination. Tris-trimethylsily(M_3T) unit was introduced into the polyacrylate as the functional side chain to form M_3T-containing copolyacrylate shown in Fig. 1, R is the curing group to form high crosslinked polymer film. Side chain of Tris-trimethylsily(M_3T) unit has three repeats of Si-$(CH_3)_3$ group which gain good alignment on film surface after curing and they are like umbrella to repel water and oil, at the same time high crosslinked polyacrylates backbone provides the barrier property for oil and water. This paper demonstrated the low surface energy and good anti-stain performance of the tris-trimethylsilypropyl (M_3T) containing methacrylate copolymer. Also, the effects of the ratio of M_3T unit in the copolyacrylate, copoly-acrylate concentration in coating formulation, copolyacrylate molecular weight, and solvents on coating anti-stain performance were also systematically studied in this paper.

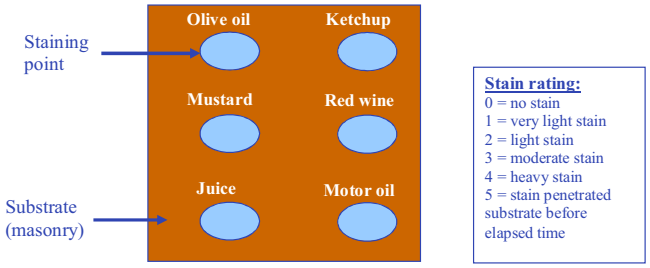

Fig. 2. A Schematic diagram of staining test on masonry.

2. Experimental method

2.1. Copolymer synthesis

Tris-trimethylsilypropyl containing methacrylate copolymers were synthesized by solvent polymerization using AIBN as initiator. A typical process for the solvent polymerization of two component copolymer was described as follows: 20.0 g (47.3 mmol) M_3T, different amount of TMOSPMA (e.g. 1.17 g, 4.7 mmol), 1% (molar ratio of total monomer) AIBN and 110 mL toluene were charged into a 250 mL two-neck round bottom flask, and stirred with magnetic stirrer. Then, the mixture was degassed using freeze-thaw cycles and finally charged with Argon. After the temperature of the mixture was raised to room temperature, the mixture was stirred at 70 °C and reacted for 48 h. Before use, the copolymer was dried and dissolved in white spirit (a mixture of aliphatic and alicyclic C7–C12 hydrocarbons, clear liquid used as a common organic solvent in painting). The other two components copolymer (M_3T-HEMA) and three components copolymer (M_3T-TMOSPMA-PMA) were synthesized by the same process.

2.2. Coating formulation

The synthesized copolymers were diluted to required concentration by solvents, and mixed with catalyst or curing agent, then dipped clean substrates (e.g., marble, terracotta, granite and textile) into above solutions for about 3 min, or used a thumb-powered manual sprayer (e-Tool® F-2 spray gun, air consumption: 3 kg/cm^2) to apply the solutions on substrates. In all cases the coated substrates were allowed to dry at room temperature overnight followed by a typical curing process in isocynate cured system: 100 °C for 6 h, and for moisture cured system: 50 °C for 8 h and 130 °C for 20 h.

2.3. Coating performance evaluation and characterization

2.3.1. Anti-stain performance evaluation on masonry

The evaluation method of anti-stain performance on masonry was developed in the lab. The staining of the coated masonry (e.g., marble, terracotta, granite) was performed as following: for the low viscosity liquids (olive oil, motor oil, juice and red wine), 50 μL of liquids were dropped on the substrate surface via a pipette; and approximately 0.2 mL of ketchup and mustard were applied to the surface by injector. For a typical process of staining, please see Fig. 2. The staining agents were allowed to remain on the surface for 5 h. After cleaned by tap water, the substrates were dried by paper towel and allowed to stay at room temperature overnight until completely dry. The anti-stain performance was evaluated by 6 level ratings: 0 indicates no stain residue remains, while a rating of 5 denotes a heavy staining mark and obviously visual penetration of staining agents.

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