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A novel UV/sunlight-curable anti-smudge coating system for various substrates

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HIGHLIGHTS

- An anti-smudge coating system can be cured by sunlight exposure or UV irradiation.
- 35 s of UV irradiation is enough for exceptional anti-smudge performance.
- The coating can also be applied onto heat-sensitive substrates and rough surfaces.
- The coating provides substrates with striking self-cleaning and protective properties.
- The coating solution can be used to fabricate colorful anti-smudge products.

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ABSTRACT

In this paper, a novel anti-smudge coating cured by natural sunlight exposure or 35 s of UV irradiation was prepared. The coating shows highly transparency and it can be used in various substrates, including heat-sensitive materials. Besides, this coating repels against water, ink, cooking oil, crude oil, artificial fingerprint liquid, and protects substrates against strong acid, strong base, salt solution and organic solvent, indicative of striking self-cleaning and protective properties. And this coating can be used to fabricate anti-smudge products in various colors without compromising its anti-smudge properties. Optional curing strategies and rapid UV-curing property make this novel coating can be used in the special area.

1. Introduction

Anti-smudge coatings, typically consisting of low-surface-tension components, are highly repellent against water- and oil-borne contaminants, so that they are able to maintain surfaces clean after contact with contaminants [1,2]. These coatings are strongly desirable, and their widespread applications will facilitate our daily life to a certain extent. They inhibit stain formation on the skyscraper windows, reduce friction and sludge deposition on the crude oil transport pipelines, prevent oil smoke from accumulation and spread onto kitchen hoods, protect metals from being corroded, thus help us to save a lot of time and money.

Generally, two approaches are used to prepare anti-smudge coatings. The first one is to create hierarchical rough surface with low surface energy. Rough surface, which can be fabricated through numerous methods, such as using nanoparticles [3–12], etching [13–16], electrospinning [17,18], lithographing [19], template-assisted deposition [20], followed by subsequent low-surface-energy treatment, have been employed to prepare rough anti-smudge coating. On these coatings, oil and water droplets exhibit high contact angle and readily roll off without wetting their surfaces [21,22], while their intricate and fragile textures inherently weaken mechanical strength [23–25] and optical clarity [26], which will limit their practical applications. Another approach is to produce smooth anti-smudge coating, on which contact angle of test liquid may not be high but low sliding angle can be achieved [27,28]. More strikingly, these smooth coatings not only inhibit smudge deposition and facilitate smudge removal, but also work beyond the challenges typically encountered with the rough one, such as poor durability and transparency as mentioned above. These advantageous features promote the application of smooth anti-smudge coating.

Aside from surface textures, anti-smudge properties are also dependent on low surface energy provided by fluorinated components or PDMS-containing components that have been grafted onto polymer matrix. Though fluorinated compounds, such as 1H,1H,2H,2H-heptadecafluorodecyl polyhedral oligomeric silsequioxane [29],

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1H,1H,2H,2H-perfluorodecyltriethoxysilane [30], triethoxy (tridecafluorooctyl) silane [31], and perfluorocarboxylic acid [32], are the preferred choice for the preparation of anti-smudge coating, they are toxic and detrimental to our health [33]. Besides, the potential of these fluorinated compounds to enter the food chain and to undergo bioaccumulation in wildlife has raised environmental concerns [34]. Furthermore, high cost limits their commercial application. Instead, covalently grafting of PDMS-containing component onto the polymer matrix for the preparation of anti-smudge coating is relatively economical and more environmentally-friendly. It is noteworthy that Liu et al. employed PDMS-containing compounds to modify polyurethane-based and epoxy-based coatings to fabricate fluorine-free anti-smudge coatings, and the resultant coatings were robust and transparent [27,28]. Outstanding anti-smudge properties and reasonable cost make these PDMS-containing anti-smudge coatings more suitable for practical applications.

Although many anti-smudge coatings with exceptional performance have been made [2,27,28,35,36], thermal curing at high temperature is still an indispensable part for their preparation. Even heat curing is convenient for many applications, it would be a problem for heat-sensitive substrates [37], especially for thermoplastics. Besides, it is noteworthy that, in practice, in the case of the treatment of bulky materials, space and equipment limitations should be taken into consideration. Thus, an anti-smudge coating that can be cured at room temperature and even cured without the assistance of certain equipment is highly desirable.

Herein, for the first time, we have prepared a versatile anti-smudge coating cured at room temperature via either natural sunlight exposure or UV irradiation, which will exhibit superior anti-smudge performance on the surface of various substrates, even on the surface of heat-sensitive materials. This coating consists of poly(dimethyl siloxane) (PDMS) to provide low surface energy, pentaerythritol triacrylate (PETA) to enhance crosslinking, 3-isocyanatomethyl-3,5,5-trimethylcyclohexyl isocyanate (IPDI) to form multi-functional monomers. This coating cured by sunlight exposure or 35 s of UV irradiation, and it is highly transparent and repellent of water, ink, cooking oil, crude oil, strong acid, strong base, salt solution and organic solvent, demonstrating its excellent self-cleaning and protective properties.

2. Experimental

2.1. Materials

3-Isocyanatomethyl-3,5,5-trimethylcyclohexyl isocyanate (IPDI, > 99.0%) was purchased from Aldrich and used as received. Hydroxyl-terminated poly (dimethysiloxane) (PDMS-A, Mn = 930 g mol^{-1}) and mono-di-hydroxyl-terminated poly(dimethysiloxane) (PDMS-B, Mn = 3176 g mol^{-1}) were kindly supplied from Shin-Etsu Chemical Co., Ltd. Pentaerythritol triacrylate (PETA) was purchased from Jiangsu Sanmu Group Co., Ltd. Methoxy-2-propyl acetate (99.0%, Aladdin) was distilled under reduced pressure before use. Dibutyltin dilaurate (97.5%, J&K), 2-hydroxy-2-methylpropiophenone (97.0%, Aldrich), 4-methoxyphenol (97.0%, Aldrich) were used as received. Hexadecane was of analytical reagent grade, and was supplied from Tianjin Damao Chemical Reagent Factory. Dow Corning 184 was purchased from Dow Corning Corporation. ABS plates (95 mm × 44 mm × 2 mm) and PS plates (110 mm × 55 mm × 2 mm) were kindly supplied from Dongguan Santong Materials Technology Co., Ltd. Glass plates (76 mm × 25 mm × 1 mm) were purchased from Yancheng Feizhou Bose Plastic Co., Ltd. Aluminum plates (150 mm × 76 mm × 0.42 mm), stainless steel plates (100 mm × 100 mm × 0.3 mm), and tin plates (120 mm × 25 mm × 0.29 mm) were purchased from local hardware stores. Wood (beech wood) plates (100 mm × 60 mm × 6 mm) were kindly supplied by local wood processing factory. Tile plates (73 mm × 32 mm × 9 mm) were purchased from local ceramic tile shop. Powder-free disposable nitrile gloves (M) were purchased from AMMEX Corporation. Polystyrene foam (135 mm × 87 mm × 3 mm), stone plates (80 mm × 54 mm × 15 mm), paper sheets (297 mm × 210 mm × 0.87 mm), cotton fabrics (1000 mm × 1000 mm × 0.48 mm, cut into several pieces (45 mm × 41 mm × 0.48 mm) before use) were purchased from local stores.

2.2. Preparation of coating solution

IPDI (4.00 g), PDMS-A (5.86 g), PDMS-B (8.57 g) were mixed thoroughly in a 100 mL flask under magnetic stirring. Then the flask was heated to 85 °C, and dibutyltin dilaurate (0.03 g) was added into the above mixture. The reaction proceeded at 85 °C for 4 h. Afterwards, calculated amount of PETA (9.00 g), 4-methoxylphenol (0.03 g) and methoxy-2-propyl acetate (6.00 g) were added into the flask to prepare coating precursor. The reaction was continued at 80 °C till the complete consumption of isocyanate groups, which was determined according to ASTM D1638. Then, additional PETA (hardener, 27.50 g) and 2-hydroxy-2-methylpropiophenone (3.84 g) were mixed together with the above coating precursor at room temperature to form desirable coating solution.

2.3. Coating treatment

Coating solution was painted onto various substrates, such as glass plate, tin plate, wood plate, paper, and dried at room temperature for about 10 min. After that, coated substrates were exposed to 2 kw UV lamp (the wavelength of UV lamp is 365 nm, and the UV intensity is 134 mW/cm^2) irradiation for 35 s except the samples that required for the investigation of the curing kinetics. As for cotton fabric swatches, samples were immersed into a coating solution (diluted with acetone into the solid content of 7.0 wt%) for 1 h, then dried at room temperature for 5 min and cured using UV lamp for 35 s. In the case of the sunlight-curable samples, substrates treated with coating solution were placed onto a flat glass plate (500 mm × 500 mm × 8 mm) and stayed for about 15 min. Then the flat glass plate with the coated substrates above was moved horizontally from a lab without sunlight to a vacant and flat place to let the coated substrates bask in the natural sunlight (coated side faced the sun) for 2–3 h. Time period for sunlight exposure was from 11:00 a.m. to 3:00 p.m., and the temperature was 28 ± 1 °C.

2.4. Anti-smudge property tests

Ink contraction and removal behavior, dirt-removal test, self-cleaning test, anti-fingerprint test and protective property test were used to demonstrate the anti-smudge properties of the coatings. To show practical application of anti-smudge coating, tests were implemented on the surface of specific substrates. For example, self-cleaning test of cooking oil was demonstrated on kitchen tile, anti-fingerprint test was carried out on the screen of smartphone.

2.5. Hardness test

Hardness of the coatings was scored by pencil test according to ASTM D3363. Pencils with different harness from 9B to 9H were firstly sharpened and flattened by rubbing on an abrasive paper vertically to form a flat and circular cross section. Then, beginning with the hardest one, the pencil was pressed against the coating surface at a 45° angle and proceed down softer pencils until a pencil left no scratch on the coating surface. The hardness of the pencil that created no scratch on coating was the scratch hardness of the tested coating.

2.6. Other characterizations

Contact angles (CA) were measured by a JC2000A contact angle measuring instrument using test droplets of 5 μL in volume. Sliding angles (SA) were measured by a Dataphysics OCA40 Micro instrument