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The role of surface energy reducing agent in the formation of self-induced nanoscale surface features and wetting behavior of polyurethane coatings

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ABSTRACT

The effect of surface energy reducing agent (SERA) on the surface chemistry and physics of the polyurethane (PU) coatings containing 0–10 mol% of SERA was studied. The coatings were carefully analyzed by differential scanning calorimeter, infrared spectroscope, field-emission scanning electron microscope, atomic force microscope and contact angle measurement system. Results indicated that at different concentrations of additive, the SERA segments took different strategies to minimize their interface area with other segments which affected their population on the coating surface. The concentration gradient of SERA segments on the surface of PU led to the creation of a local lateral pressure. The local lateral pressure along with the relative content of solvent showed a synergic effect on the formation of self-induced nanoscale surface features. Contact angle measurements revealed that the role of SERA segments in enhancing the hydrophobicity of PU coatings through creation of specific physical features was more pronounced than through chemical modification of the surface.

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1. Introduction

In recent years, hydrophobic coatings have attracted the researchers' attention due to their some interesting properties and applications. Anti-corrosion, anti-fouling and anti-icing are some advantages of these coatings which can increase the longevity of equipment and tools [1–4]. To obtain a non-wetting surface, different approaches have been proposed among which hydrophobic polymer coatings may be preferred due to the simplicity, high potential of application and relatively low cost [5,6]. Studies have long shown that lowering the surface free energy through chemical and/or physical modifications favors the water repelling properties of the polymer coatings [7–15].

In the physical modification approach, the optimum surface texture to obtain high degrees of hydrophobicity is a specific roughness pattern usually in the form of micro/nano features which enables the entrapment of air molecules in the valleys [5,7–11]. To chemically modify the polymer coatings and reduce the intrinsic surface polarity and affinity with water, hydrophobic materials including fluorocarbons, hydrocarbons and silicones are used [12–16]. Since having a good adhesion to the substrate is also needed, the polarity should not be completely destroyed. The issue can be resolved by just modifying the outermost atomic or molecular layer of the coatings using low surface energy materials. On the other hand, a more long-lasting hydrophobic property can be achieved using the surface energy reducing additives with the ability of participating in a chemical reaction with the functional groups of the main polymer.

Butruk et al. [12] studied the hydrophobic behavior of PU coatings modified by polydimethylsiloxane (PDMS) and octafluoropentanol compounds. A two-step dip coating method was used to covalently bond the free isocyanate groups with hydroxyl groups of the modifying agents. Results showed a 50 degree improvement in hydrophobicity of the coatings. Dong et al. [13] used two different types of initiators to synthesize diblock fluoroacrylate copolymers. Surface studies of the samples revealed that the fluorinated initiator reduced the surface free energy more than the non-fluorinated one. In another research conducted by Naseh et al. [14], the silicone polyacrylate and hydroxyl-functional PDMS were used to reduce the gum adhesion to the surface of automotive acrylic/melamine coatings. It was found that the use of additives reduced the surface free energy and enhanced the mechanical properties of the clear coats. In a similar study Lumiflon FE-4400, a fluoropolymer emulsion, was used at various concentrations to modify two-part

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Table 1
Chemical composition of the coating solutions.

Solution No.	SERA content (mol.%)	SERA content (wt.%)	Acrylic content (wt.%)	Hardener content (wt.%)	Total solvent content (wt.%)
1	0	0	65	35	35
2	2	13	56	31	40
3	3	19	52	29	42
4	4	24	49	27	44
5	5	28	46	26	46
6	6	32	43	25	48
7	10	45	33	21	53
8	0	0	65	35	46

water-based military PU topcoats. Results showed the increase of water contact angle in a linear fashion with the increase of fluorine concentration on the surface [15]. Wu et al. [16] introduced PDMS as a low surface energy material to prepare hydrophobic water-borne PU coatings. A high degree of hydrophobicity was achieved by the formation of a specific pattern on the water-borne PU films. The patterns were attributed to the increase of phase separation with the increase of PDMS content.

Although, the results from the previous reports pointed out that SERAs significantly enhanced the hydrophobic behavior of polymer coatings, the mechanism of this enhancement has not been well studied.

Here, the effectiveness mechanism of a typical SERA on the surface morphology and hydrophobicity of two-pack PU is investigated. In this regard, various concentrations of a hydroxyl functionalized silicone modified polyacrylate additive are used and the surface chemistry and physics of the modified PU coatings are thoroughly and precisely studied. For this purpose, various techniques including differential scanning calorimetry, infrared spectroscopy, field-emission scanning electron microscopy, atomic force microscopy and contact angle measurement system are used.

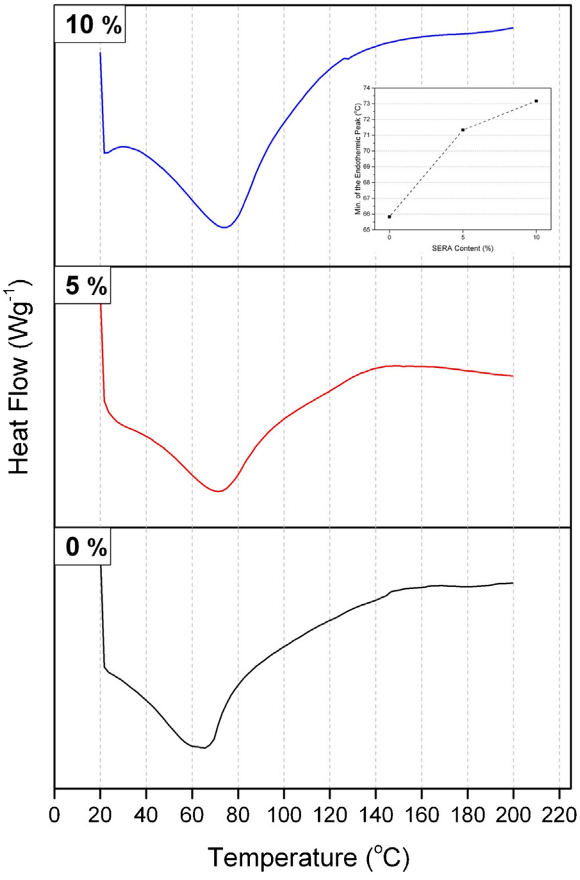

Fig. 1. The DSC curves of coating solutions containing 0, 5 and 10 mol% of SERA and the inset shows variation of minimum of the endothermic peak versus SERA content.

2. Experimental procedure

2.1. Materials

Hydroxyl-functional acrylic resin (Tacryl 1210N) and aliphatic polyisocyanate (Desmodure N75) were supplied by Taak Resin Co. and Bayer Co., respectively. An OH-functional silicone modified polyacrylate (BYK-SILCLEAN 3700) was obtained from BYK Altana group and used as SERA. Xylene from Merck chemicals was chosen as the solvent.

2.2. Preparation of the SERA-modified PU coatings

Coating solutions with NCO:OH of 1:1 (mol/mol) containing different amounts of SERA ranging from 0 to 10 mol% were prepared and the chemical compositions are listed in Table 1. For the comparison, a coating solution containing equal amount of solvent with solution no. 5 but without SERA was also prepared. After mixing of acrylic polyol and SERA under moderate magnetic stirring at the ambient temperature, the hardener was added to the mixture of resin and additive. The mixture stirring continued until a homogenous mixture was obtained. The coating solutions were then applied on the pre-cleaned glass slides using a quadruple film applicator with gap height of 300 μm followed by curing at the ambient temperature (25 ± 3 °C) and relative humidity of 29% for 10 days. Deionized water and acetone were used to clean glass slides before applying the films.

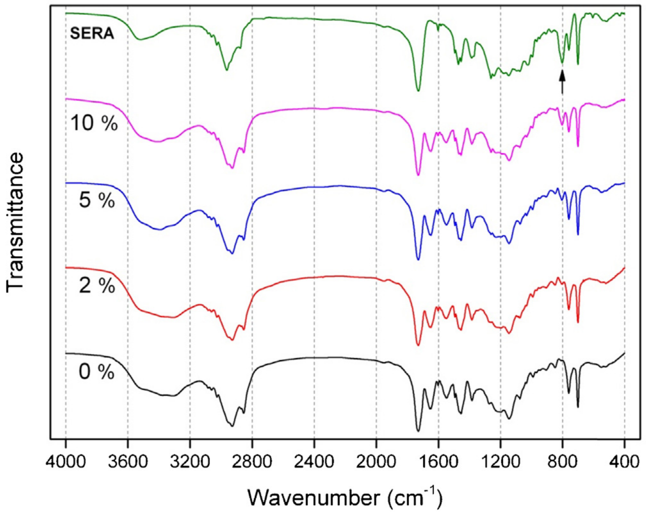

Fig. 2. FTIR spectra of the SERA precursor and the coatings containing 0, 2, 5 and 10 mol% of SERA.

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