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The surface properties and corrosion resistance of fluorinated polyurethane coatings

Xia Wang *, Jiaojiao Hu, Ying Li *, Jinrui Zhang, Yuanyuan Ding

School of Materials Science and Engineering, University of Shanghai for Science and Technology, Shanghai 200093, China

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ABSTRACT

Fluorine-containing epoxy (FO) compounds were synthesized through a one-step process from 2,2,3,3-tetrafluoro-1-propanol (TFP) and epichlorohydrin (ECH). Cationic polymerization was adopted to prepare fluorinated polyglycol with controllable molecular weight. The structure of FO and FPO were studied by FTIR, NMR and GPC and a two-component fluorinated polyurethane coating was synthesized using FPO and methyl diphenylenediisocyanate (MDI) with a room temperature curing method. We characterized the contact angle of the surface of the coating. The water resistance and resistance to salt spray as well as SEM imaging of the film surface indicates that hydrophobicity, water resistance, and corrosion resistance are improved due to surface migration of the fluorine element.

1. Introduction

Corrosion is material deterioration due to reactions between the material and the environment. According to the American Association of Corrosion Engineers (NACE), annual losses caused by corrosion account for 3–5% of GDP [1–3]. Therefore, finding the right way to prevent material corrosion has profound importance. In many corrosion prevention schemes, the use of anti-corrosion coatings is proposed due to their cost and convenience [4]. Of these, polyurethane coatings are a very versatile class. They are second only to alkyd painting [5]. Because of a large number of hydrogen bonds, large intermolecular forces, and chemical stability, polyurethane anti-corrosion coatings have excellent chemical resistance [6–8]. However, single polyurethane coating cannot sustain very harsh corrosive environments such as high salt spray, high heat, chemicals, sewage, and other harsh conditions. These prevent its widespread deployment [9].

For high-solid fluorinated heavy-duty polyurethane coatings, fluorinated blocks were introduced into the molecular chains of polyurethane elastomer (PU) [10–13]. The resulting fluorinated polyurethane elastomers (FPU) not only maintain most of the outstanding properties of PU such as high strength, high toughness, and high damping properties, but also offer improved solvent and chemical resistance, a lower surface tension, and a low coefficient of friction [14–16]. This results in wide applications in the areas of heavy duty coatings, which have important theoretical and practical significance.

In this work, solvent-based fluorinated polyurethane coatings were prepared by controlling the introduction of the fluorine-containing segment to modulate the surface enrichment effect of the fluorinated segment [17–19]. For environmental reasons, this paper uses cyclohexanone, butyl acetate—a xylene mixed solvent system to minimize the amount of xylene. Via solubility parameter principles, the molar ratio of cyclohexanone, butyl acetate, and xylene is 1:1:1. To further enhance the corrosion resistance of FPU coating, we also added two anticorrosive pigments—aluminum tripolyphosphate and mica flakes. The common feature of aluminum tripolyphosphate and mica flakes is that they are flake pigments, and they easily form a "labyrinth effect" in the painting that can improve impermeability. They form solid complexion on the surface of the metal and also complex hydroxyl and carboxy groups in the coating. Consequently, the adhesion of the coating has been improved. In this work, the NCO/OH molar ratio is set to 1.05:1. This is because the water in environment and on the surface of the substrate has a negative influence on –OH and –NCO reactions. Finally, the surface properties, water resistance and salt spray corrosion of FPU coatings were studied. The results indicate that the surface migration of fluorine gives the fluorinated polyurethane coatings excellent chemical stability, salt spray resistance, and low surface energy.

* Corresponding authors at: School of Materials Science and Engineering, University of Shanghai for Science and Technology, 516 Jungong Road, Shanghai 200093, China. Tel.: +86 21 55274069; fax: +86 21 55270632.
E-mail address: liying@usst.edu.cn (X. Wang).

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2. Experimental

2.1. Materials

Tetrafluoropropanol (TFP) and diphenyl-methane-diisocyanate (MDI) were purchased from Sigma (USA). The fluorinated epoxy compound (FO), fluorinated polyether polyol (FPO) were prepared according to the literature. The 1,2-epichlorohydrin, cyclohexane, tetrahydrofuran, sodium hydroxide, methylenechloride, ethylene glycol, a boron trifluoride diethyl ether, dibutyltin dilaurate, cyclohexanone, butyl acetate, and ditoluene were purchased from China Medicine, Shanghai Chemical Reagent Corporation. The mica flakes and aluminum tripolyphosphate were supplied by Shijiazhuang tuomalin minerals Co. Ltd. The billi- on positive anti-corrosion Material Co. Ltd. in the new Music City.

2.2. Synthesis of fluorinated epoxy compounds (FO)

The molar ratio of epichlorohydrin and tetrafluoropropanol is 7:1. FPO was prepared by a two-step solution polymerization method. The synthesis process is described as follows: excess ECH and cyclohexane (as water-carrying agent) were added in a three-neck glass flask equipped with a magnetic rotor and water separator. This was placed in a constant temperature oil bath. When the solvent began to reflux, the 40% sodium hydroxide and TFP were slowly added into glass flask. The solution was stirred for 6 h at 100 °C. The reaction was stopped upon reaching an anhydrous state. The resulting product was subjected to distillation under reduced pressure to obtain the pure fluorinated epoxy compound. The reaction formula and synthesis of the fluorinated epoxy is shown in Scheme 1.

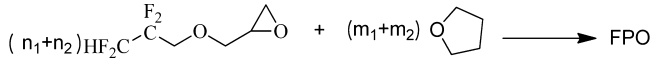
2.3. Synthesis of fluorinated polyether polyol (FPO)

This study used a controlled cationic polymerization method to synthesize fluorinated polyether polyol. The molar ratio of fluorinated epoxy compound and tetrahydrofuran was between 1.5:1 and 1:1.5.

The methylene chloride and tetrahydrofuran were first added into a reactor equipped with a stirrer and a thermometer in a three-necked flask at 0 °C under nitrogen. Cationic copolymerization of FO with THF was performed by slowly adding FO to the reaction mixture containing bulk THF, EG, and BF_3OEt_2. After 6 h, distilled water was added and stirred for 5 min to stop the reaction. The product was then washed with distilled water five to six times to neutrality. After vacuum dehydration for 2–3 h, a colorless, transparent, and sticky fluorinated glycol was collected (Scheme 2).

2.4. Film preparation

The fluorinated polyurethane coating was prepared by two components. One component was prepared by mixing 15 parts of fluorine-containing polyether polyol (FPO) and 0.01 parts of dibutyltin dilaurate. These were added sequentially to a three-necked flask equipped with a stirring bar and then stirred for 30 min. The other component was prepared by mixing 10 parts of MDI, 5 parts of aluminum tripolyphosphate and mica flakes that were stirred to dissolution in the mixed solvent system. To remove moisture, the anticorrosive pigments and mixed solvents were dehydrated before use. The two mixed components in the three-neck flask were stirred 8–10 min. The samples were coated on to tinplate sheets after grinding the mixed material to a fineness of 40–50 μm. The applied wet coatings were hardened after 24-h of curing at room temperature.



Scheme 2. Reaction scheme of FPO.

2.5. Preparation of comparative polyurethane coating

The contrast coating in this paper is a polyurethane coating. It has the same formulation and preparation as fluorinated polyurethane coatings except there is replacement of the raw materials. The tetrafluoropropanol was replaced with *n*-propanol. The epoxy compound and the polyether polyol were prepared first followed by the polyurethane coating.

2.6. Characterization

2.6.1. FT-IR, NMR, and GPC

An Fourier transform infrared (FT-IR, America Perkin Elmer Instrument Co. Ltd., China) was used to identify FO and FPO structures. The samples for FT-IR analysis were prepared by solution casting of 1% (w/v) polymer in THF directly onto KBr plates and dried at 70 °C. Four scans were averaged for each sample in the range of 4000–600 cm^{-1}.

Bruker DMX400 ^1H NMR and Bruker AV 300 ^{13}C NMR at 400 MHz were used to further determine the FO and FPO structure, respectively, using deuterated chloroform ($CDCl_3$) as the solvent.

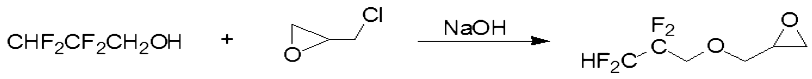
The average molar mass of the polyether polyol (hereinafter referred to as molecular weight) was determined by gel permeation chromatography (GPC; Perkin Elmer). Tetrahydrofuran was the eluent, polystyrene (PS) was the standard sample, flow rate was 1 mL/min at 35 °C. The theoretical molecular weight of the polyether polyol was dominated by controlling the amount of the initiator ethylene glycol (EG) and the catalyst boron trifluoride diethyl ether, which was calculated as follows:

$$\frac{[m(\mathrm{FO}) + m(\mathrm{THF})]}{n(\mathrm{EG})} = M \tag{1.1}$$

$$V\,(\text{EG orboron trifluoride diethyl ether}) = \frac{m\,(\text{EG or boron trifluoride diethyl ether})}{\rho} \tag{1.2}$$

2.6.2. Contact angle

Contact angle (CA, DSA30, KRUSS) measurements were used as a measure of the hydrophobicity of the material surface. The contact angles were measured by the sessile drop method using telescoping goniometers at room temperature. Then, 5−10 μL of distilled water was pumped from a micro-syringe onto the surface of the FPU films, and an image was captured by a telescope fitted with a video camera. All results were expressed as the average value of at least five independent measurements. These were collected within the first 10 s after application of droplets.



Scheme 1. Reaction scheme of FO.