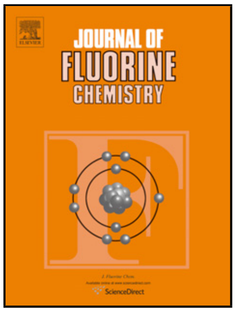

Title: The Surface Properties and Corrosion Resistance of Fluorinated Polyurethane Coatings

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The Surface Properties and Corrosion Resistance of Fluorinated Polyurethane Coatings

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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.

Keywords: fluorinated polyglycol; fluorinated polyurethane coating; hydrophobic; corrosion resistance

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.

2. Experimental

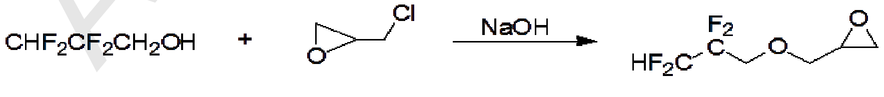
2.1 Materials

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, dibutyl tin 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 billion 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.

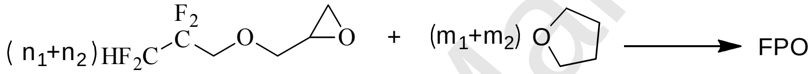


Scheme. 1. Reaction scheme of FO.

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—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 5-6 times to neutrality. After vacuum dehydration for 2-3 h, a colorless, transparent, and sticky fluorinated glycol was collected (Scheme. 2.).



Scheme. 2. Reaction scheme of FPO

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 dibutyltindilaurate. 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.

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 to 600 cm^{-1}.

Bruker DMX400^{1}H-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℃. 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:

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

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

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.

2.6.3 Water resistance test

The FPU coating on the tin is applied and cured. Then, two-thirds of the tinplate samples were placed in a water bath at 25°C for 24 h. Finally, they were removed and dried by filter paper to observe whether the coating surface modified changes such as blistering, loss, and rust.

2.6.4 Anti-corrosion test

The FPU coating and PU coating were cured and placed simultaneously in a closed F-90 resistant to salt spray machine. The salt concentration was 50±10 g/L; salt settlement was 1 mL/h; spray chamber temperature was 35±2°C for 72 h. After a predetermined period, the samples were removed from the chamber, rinsed with clean water to remove the remaining solution on the surface of the testing samples and then immediately studied for blistering, rust and cracking. Finally, scanning electron microscopy (SEM; model QuantaFEG450) was used to observe the surface morphology.

3. Results and discussion

In this paper, an important reactant was FPO, which was synthesized by FO and THF in a controlled cationic ring-opening copolymerization reaction. What's more, FO was obtained through the preparation of ECH and TFP. Thus, the structural confirmations of FO and FPO were characterized by FT-IR, ^{1}H-NMR, and ^{13}C-NMR (Figs. 1 and 2).

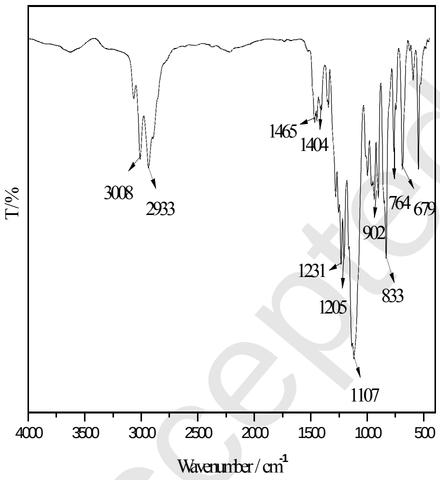


Fig. 1. FT-IR spectra of FO.

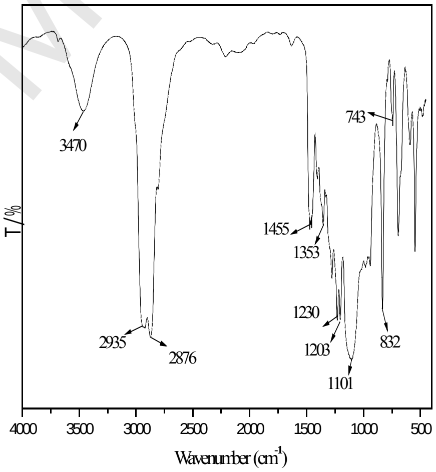


Fig. 3. FT-IR spectra of FPO.

In the spectrum, there are stretching vibration absorption peaks of C-O (1107 and 764 cm^{-1}), C-F (1231 and 1205 cm^{-1}) [20], three-ring (1404 and 833 cm^{-1}) and methyl (3008 and 2933 cm^{-1}). Through the analysis of the infrared spectrum, fluorine was introduced into the epoxy chloropropane. It retained the three-ring structure. In addition, the ^{1}H-NMR spectrum of FO（Fig.2.） was also observed.

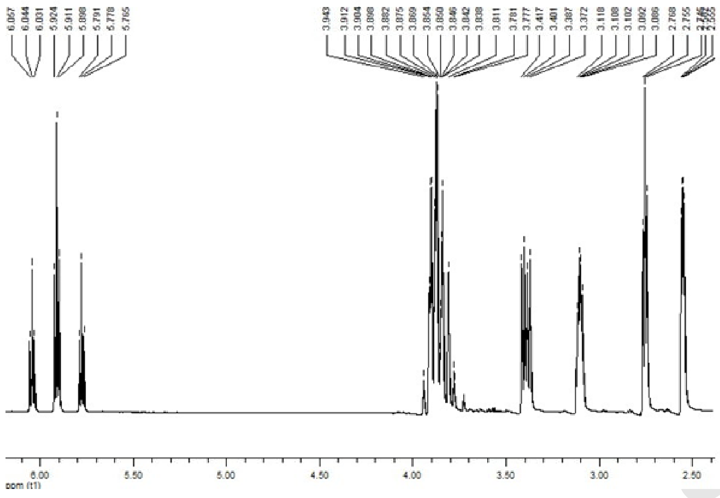


Fig. 2. ^{1}H-NMR spectra of FO

The 1H-NMR spectra of FO is shown in fig. 2. It is evident that the peak appears at 5.76-6.06 ppm, which is assigned to the proton in -CF2H. The peaks at 3.81-3.89 ppm are attributed to –CH2 in OCH2CF2H, and the peaks assigned to the protons of -OCH2CH appear at 2.54-2.77 ppm. Besides, the peaks at 3.77 ppm corresponding to the CH in the epoxy group are also observed in the 1H-NMR spectra of FO.

Fig. 3. presents the FTIR spectrum of FPO. There was an O–H stretching vibration absorption peak at 3470 cm^{-1}, and C-H stretching vibration absorption peak at 2935 and 2876 cm^{-1}; its bending vibration absorption peak was observed at 1455 cm^{-1}. This proved that –OH and -CH_2 were in the compounds. The peak at 1203, 1230, and 1353 cm^{-1} were assigned to the C–O stretching vibration absorption and O-H plane bending, vibration, and absorption. This indicates that the compound belongs to a primary alcohol. A C-C frame stretching peak was observed at 693 and 743 cm^{-1} which shows that the compound contains -$(CH_2)_n$. The value of n is not less than 4. From the spectrum, we conclude that that the stronger characteristic absorption bands locating at 1101 cm^{-1} can be attributed to stretching vibrations of C-F.

The fluorine-containing group was completely consumed in the reaction, which can also conclude in ^{13}C-NMR of FPO. It is evident that the peak appears at 27 and 70 ppm, which is assigned to THF. Two peaks at 65-80 ppm and 105-120 ppm are relative to the fluorinated epoxy compound. Thus, we conclude that the fluorinated polyether polyol is polymerization of fluorinated epoxy compound and tetrahydrofuran. Besides, the peaks of ^{13}C-NMR assigned to the random copolymer of polyether polyol mainly appear at 70-80 ppm [21]. This is the same as ^{13}C-NMR of the random copolymer of polyether polyol shown here.

3.1 Contact angle

Variation of roughness, and chemical composition can change the water contact angle. Samples' surfaces prepared in this paper are smooth that have no defects and bubbles, and are placed under constant temperature and humidity of the environment, so the surfaces which we take to CA measurement are the same batch, the same lab environment. This paper uses three different molecular weights of FPO (1300, 1500, and 2000 g/mol) for the FPU coatings. These are termed: FPU (FPO1300), FPU (FPO1500), and FPU (FPO2000). The coating of different surfaces was measured with contact angles and surface energy (Table 1) by the contact angle meter.

Table 1. Surface properties of the FPU $^{\#}$coatings.

Coating system	Contact angle (°)	Surface energy (mN/m)
FPU (FPO1300)	130.0	6.86
FPU (FPO1500)	126.7	8.30
FPU (FPO2000)	110.7	16.69

PU (HPO1300)*	103.8	20.76

Theoretical body fluorine content is 14.34%.

* Using the same method of FPO synthesis to prepare HPO with 1300 g/mol molecular weight and further prepared with PU coating.

Fluorinated polyurethane (FPU) showed significantly higher contact angle values versus the polyurethane (PU). Table 1 shows the PU (HPO1300) after the introduction of fluorine coating, its contact angle changes from 103.8 ° to 130.0 °. This clearly indicates the generation of a more hydrophobic surface as a result of introducing the fluorinated groups. Because of low surface energy of fluorine atoms, it can migrate to the surface of the material spontaneously. Fluorinated groups exhibit hydrophobic and unique low surface energy. In general, a lower surface free energy component is enriched on the surface to minimize the polymer-air surface tension. It is believed that the lower surface energy of fluorine atoms provides a thermodynamic driving force for the migration of fluorine to the free surface. We observed that the contact angle increased with decreasing molecular weight of FPO in Table 1. The smaller molecular weight of FPO is the shorter molecular chain. Thus, the interaction between the molecular chains is reduced, and it is easier for fluorinated side chains to migrate to the surface. Fluorine migrates to the top of surface and creates a low surface energy on the upper surface. This results in a higher contact angle and lower surface energy, and thus the coatings have improved hydrophobicity.

3.2 Water resistance

The fluorinated polyurethane coatings are applied on tinplate to cure resulting in

FPU coating samples. In the test, two-thirds of the tinplate samples were placed into a water bath at 25°C for 24 h. They were imaged after removal and drying with filter paper (Fig. 4).

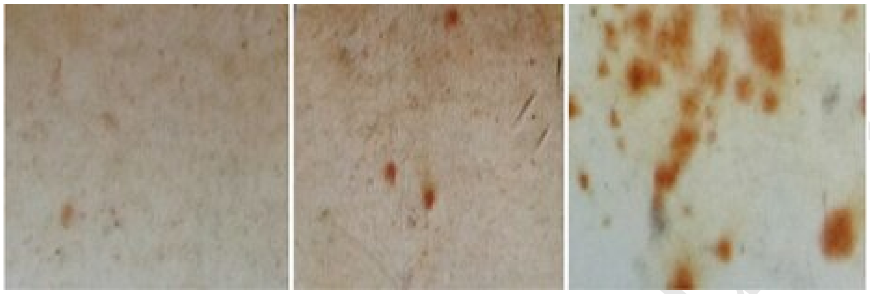


Fig. 4. Surfaces of FPU coatings after the water resistance test.

Here, A, B, and C represent FPU (FPO1300), FPU (FPO1500), and FPU (FPO2000) coating systems, respectively.

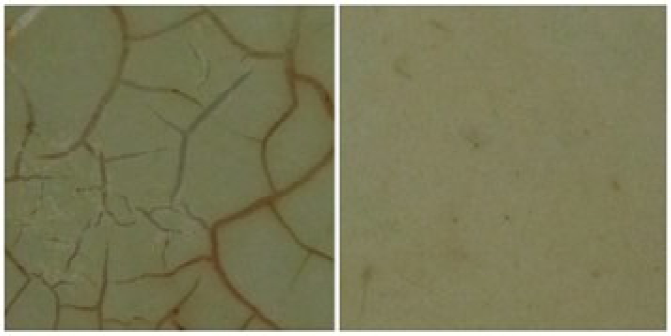
After the water resistance test, FPU (FPO2000) films have serious rust spots (Fig. 3C.). The FPU (FPO1300) film rusted only slightly (Fig. 3A.). This can be explained according to Table 1. Comparing FPU (FPO1500) and FPU (FPO2000), FPU (FPO1300) underwater contact angle is the largest. Thus, it had the lowest surface energy. For hydrophobic properties, FPU (FPO1300) is the best. FPU (FPO1300) has higher water penetration than FPU (FPO1500) and FPU (FPO2000) coating, FPU (FPO1500) in the second best.

3.3 Anti-corrosion test

Stain testing has little influence on the performance of the surface of the FPU coating (Table 2). This reflects that the surface enrichment of F improves the chemical resistance. Furthermore, the effect of F on FPU coating corrosion resistance is also fully reflected in the state of the surface coating after being subjected to the salt spray test (Fig.5.). Figure 5 shows the surface state of the FPU (FPO1300) and PU (HPO1300) coating after the salt spray test. The FPU (FPO1300) coating's surface did not change after the salt spray test, but the PU (HPO1300) film has a serious crack.

Table 2. Impacts of salt spray on the surface properties of fluorinated polyurethane coatings.

Coating system	Contact angle (°)		Surface energy (mN/m)	
	Before test	After test	Before test	After test
FPU (FPO1300)	130.0	128.3	6.86	7.93
FPU (FPO1500)	126.7	122.4	8.30	10.38
FPU (FPO2000)	110.7	102.5	16.69	21.53

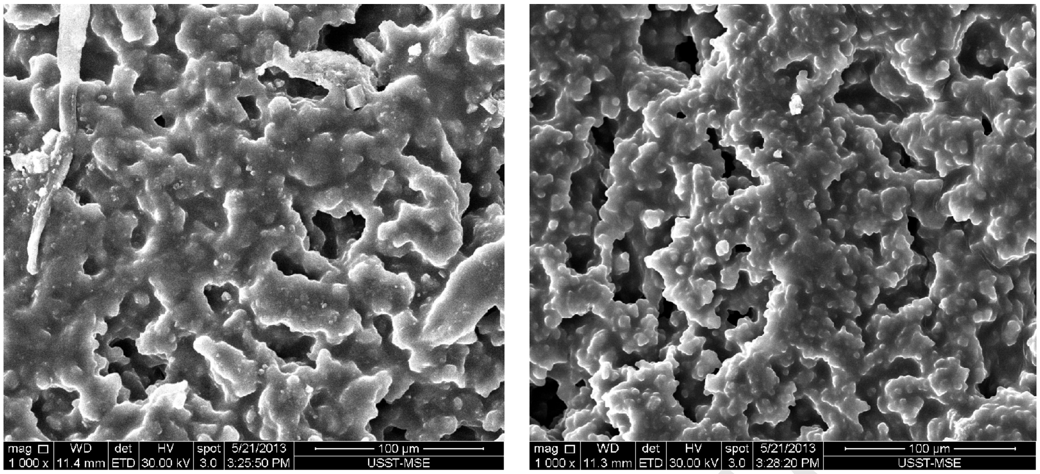


PU (HPO1300) FPU (FPO1300)

Fig. 5. The surface of PU (HPO1300) and FPU (FPO1300) after the anti-corrosion test.

To further analyze the protective effect of the F element on the FPU coating, FPU (FPO2000) coating's surface morphology before and after the salt spray test was also observed by SEM (Fig. 6.). It shows that the surface morphology of the coating has not obviously changed. This proves that due to the protective effect of the F element on the surface, there is no structural damage caused by the corrosion test after 72 h. The FPU

(FPO2000) coating still has a complete state.



A B

Fig. 6. SEM images of FPU (FPO2000) coating's surface

(A, B represent SEM photographs of FPU (FPO2000) coating's surface before and after anti-corrosion test).

4. Conclusions

In this paper, FO was one-step synthesized 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 structures of FO and FPO were characterized by FTIR and NMR. Finally, a two-component fluorinated polyurethane coating was successfully prepared by using FPO and methyl diphenylenediisocyanate (MDI) with a room temperature curing method. The incorporation of fluorinated polyether glycol in the polyurethane showed a significant effect on the hydrophobic and anti-corrosion resistance of PU. The contact angle of PU (HPO1300) was 103.8 °. This increased to 130.0 ° when introducing fluorine into the coating. The salt spray test suggested that FPU (FPO1300) coating surface changed little, while PU (HPO1300) coating surface had severe cracking. These results indicate that there was an obvious migration of fluorinated groups to the surface of the fluorinated polyurethane films. Furthermore, the fluorinated polyurethane had outstanding anti-corrosion resistance versus the conventional PU. Also the contact angle of the coating, water resistance, and resistance to salt spray performance illustrates that along with the lower molecular weight FPO, the resulting FPU coatings have better hydrophobic, water resistance, and anti-corrosion performance.

Acknowledgements

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1. Fluorine migrates to the top of surface and creates a low surface energy.
2. Fluorinated polyurethane showed higher contact angle versus polyurethane.
3. FPU coating has outstanding anti-corrosion resistance versus PU coating.
4. The lower molecular weight FPO, the FPU coatings have better water resistance.

22.

***Graphical Abstract - Pictogram**