Design of Electrophoretic Non-ionic Polyurethanes and the Applications

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Introduction

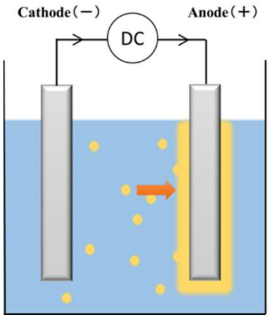


Figure 1. Schematic representation of EPD.

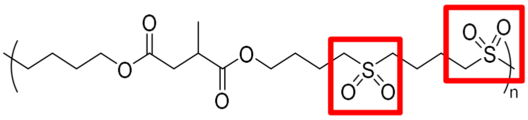


Figure 2. Chemical structure of poly(ester-sulfone) in which sulfonyl groups are marked in red.

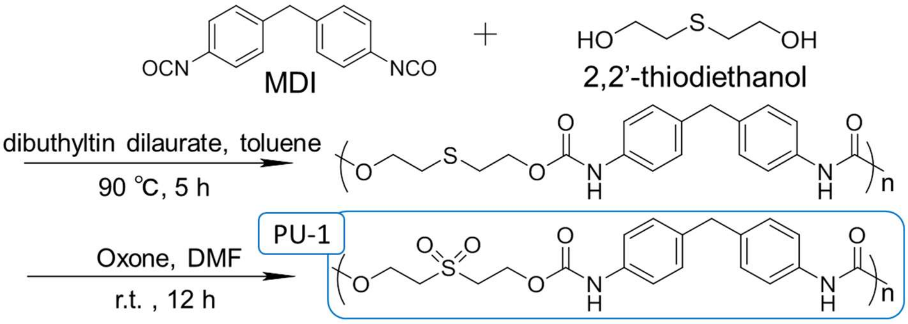
Polyurethane elastomers are ideal recycle materials, because cross-links in these materials are formed by physical interactions in appropriate engineered microdomains, crystallites, or hydrogen bonds.[1] Polyurethane elastomers are composed of alternating hard and soft segment and show versatile mechanical properties, which fascinate polymer chemists to apply for coating materials, too. During the past five years, our group has focused on sulfone-containing polymers for the investigation of the electrophoretic behavior of interesting non-ionic polymers.[2] Electrophoretic deposition (EPD) is a promising and facile technique for the fabrication of inorganic or organic or inorganic / organic composite films[3,4] onto electrodes. EPD is based on the controlled electric-field-induced deposition of charged particles or molecules in an orderly manner onto an electrode. The characteristics of EPD include the capability of film formation on a complex surface shape, easy control of thickness, and formation of a homogeneous layer. Recently, our group found that an aliphatic poly(ester-sulfone) prepared by thiol-ene click polymerization and subsequent oxidation showed anode-selective electrophoresis under EPD conditions.[2a] Anode-selective EPD coatings of bioactive glass (45S5Bioglass)[2a] and titanium dioxide (TiO_2)[2b] were also demonstrated. Furthermore, these observations and the interesting electrophoretic behavior of the sulfone-containing polyester prompted us to explore why the poly(ester-sulfone) is deposited onto the anode,[10f] and what part of its structure[10d,10e] is responsible for this unusual electrophoretic behavior. We now concluded that this anode selective EPD of non-ionic polymer is the first example in the world and discovered that sulfonyl group is essential for the EPD (Figure 2).

These research background prompted us to design electrophoretic non-ionic polyurethane containing sulfonyl group, aiming at smart coatings equipped with polyurethane's features. In this magazine, we introduce synthesis of non-ionic polyurethane containing sulfonyl group via polyaddition of methylene diphenyl 4,4'-diisocyanate (MDI) with 2,2'-thiodiethanol in the absence and presence of triethylene glycol as the soft segment and subsequent oxone oxidation. The strength of the coated polyurethane was evaluated both by pencil hardness and cross-cut tests.

Synthesis of Polyurethane 1 (PU-1) via Polyaddition of MDI and 2,2'-Thiodiethanol in the absence Triethylene glycol.

Polymerization conditions were surveyed, an example follows. 2,2'-Thiodiethanol 2.06 mL (20 mmol), MDI 5.01 g (20 mmol), dibutyltin dilaurate (200μL) as the polymerization catalyst , and 86 mL of toluene were added to 200 mL round-bottomed flask with a magnetic stir bar under a nitrogen atmosphere. The mixture was stirred at 90 °C for 5 h, then we obtained white solid polymer, poly(MDI-*alt*-2,2'-thiodiethanol). The polymer was precipitated from *N,N*-dimethylformamide (DMF) by addition of excess acetone and dried under vacuum. In order to convert sulfide groups to sulfones, we oxidized the parent polymer using oxone as the oxidizing agent. The polymer (5.01 g, 13.4 mmol repeat unit) and oxone (4.08 g, 26.8 mmol) in DMF (100 mL) were added into a 200 mL round-bottom flask. After stirring at r.t. for 12 h, the mixture was filtered, and the solvent was evaporated under reduced pressure to give a pale-yellow solid that was then dissolved in DMF and precipitated by addition of 90 mL of H_2O/CH_3OH (9/1, v/v). Obtained polymer was a pale-yellow solid and named as PU1 (Scheme 1, PU-1, $M_n = 1.4 \times 10^4$, $M_w/M_n = 2.1$).

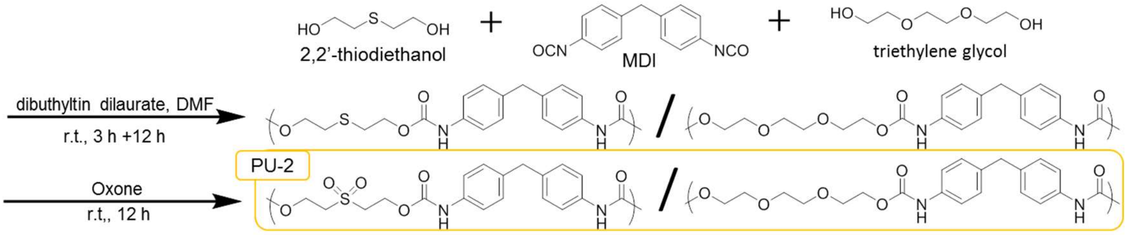
Scheme 1. Synthesis of PU-1



Synthesis of polyurethane 2 (PU-2) via Polyaddition of MDI and 2,2'-Thiodiethanol in the presence of Triethylene glycol.

Triethylene glycol 1.39 mL (10 mmol), MDI 5.01 g (20 mmol), dibutyltin dilaurate (200µL), and 86 mL of toluene were added to 200 mL round-bottomed flask with a magnetic stir bar under a nitrogen atmosphere. The mixture was stirred at r.t. for 3 h, then we added 2,2'-thiodiethanol 1.03 mL (10 mmol) and stirred them for 21 h. The polymer was precipitated from DMF by addition of diethyl ether and dried under vacuum. To convert sulfide groups in the polymer backbone to sulfones, we oxidized the polymer by oxone similar to PU-1. The parent polymer, poly(MDI-*alt*-2,2'-thiodiethanol)-*co*-poly(MDI-*alt*-triethylene glycol) (6.43 g, 9.57 mmol repeat unit) and oxone (2.91 g, 19.14 mmol) in DMF (70 mL) were added into a 100 mL round-bottom flask. After stirring at r.t. for 12 h, the mixture was filtered, and the solvent was evaporated under reduced pressure to give a pale-yellow solid that was then dissolved in DMF and precipitated by addition of 90 mL of H_2O/CH_3OH (9/1, v/v). Obtained polymer was a pale-yellow solid and named PU2 (Scheme 2, PU-2, $M_n = 1.2 \times 10^4$, $M_w/M_n = 1.7$)

Scheme 2. Synthesis of PU-2



Electrophoretic Deposition of PU-1 and PU -2.

PU-1and PU-2 formed colloidal suspensions in mixed solvents of DMF and ethanol and could be deposited onto a stainless-steel anode by EPD. The results are summarized in Table 1.

Table 1. Result of EPD

Polymer	Solvent (v / v)	State	Deposition (mg / cm^2)	Initial current (mA)
PU-1	DMF / MeOH (1.7 / 2.3)		2.78	50
PU-2	DMF / MeOH (1.7 / 2.3)		2.53	45

The distance between the electrodes was 6.5 mm and the deposition time was 90 s at a voltage of 200 V.

As shown in Table 1, we succeeded in anode-selective EPD of non-ionic polyurethane and an expected amount of deposition was confirmed in comparison with previous work.[2] It seems that coating of PU-2 formed more smooth and uniform surface than PU-1.

Pencil Hardness Test.

We first evaluated coating hardness by pencil hardness test (JIS K5600-5-4). As shown in Figure 3, we scratch coating by a pencil known hardness. Coatig of PU-1 was dameged by a pencil hardness of 2B, on the other hand, coating of PU-2 by pencil hardness of 2H. We confirmed that strenghth of EPD coating was improved by introducing triethylene glycol as the soft segment.

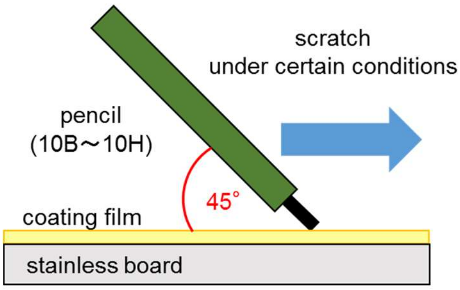


Figure 3. Image of pencil hardness test.

Cross Cut Test.

We also investigated resistance of peeling from metal substrate by cross cut test (JIS K5600-5-6). It is a qualitative method for evaluation of the peeling strength, in which after cutting cross on coating, we put an adhesive tape on the coating film, subsequently peel the tape as shown in Figure 4. As a result of this test, PU-1 was easily peeled and classified in 4 and, on the other hand, PU-2 was classified in 1 (see Figures 5 and 6). We confirmed that EPD coating become stronger by introducing triethylene glycol as the soft segment.

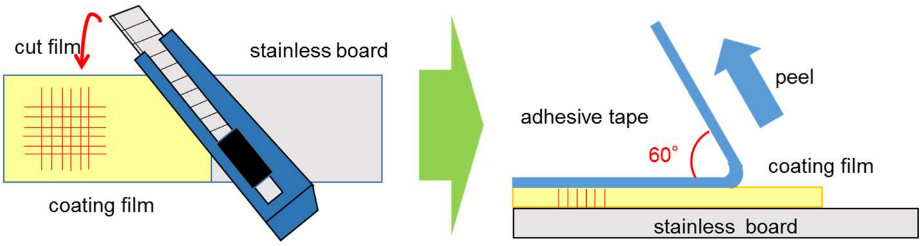
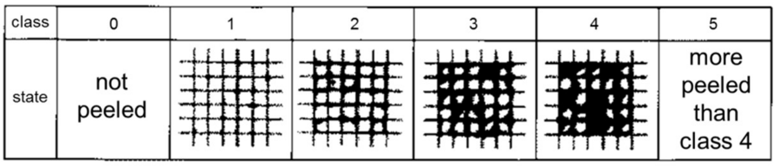


Figure 4. Image of cross-cut test.



class	0	1	2	3	4	5
state	not peeled					more peeled than class 4

Figure 5. Evaluation of cross-cut test.

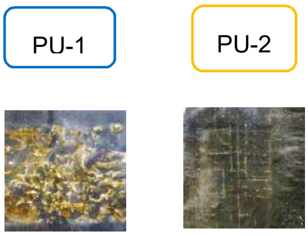


Figure 6. Results of cross-cut test [PU-1 (left) and PU-2 (right)].

Conclusion

We successfully synthesize non-ionic polyurethane and we could observe the anode selective EPD. The strength of the polyurethane-based coating film was improved by adding triethylene glycol as the ternary monomer. These fundamental results should provide new guideline for smart coating using polyurethane elastomers.

References

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