



Synthesis of sulfone-containing non-ionic polyurethanes for electrophoretic deposition coating

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Abstract

The desire to develop a sustainable society has recently inspired polymer chemists to explore functional polyurethane materials because of their versatile material shape and thermoplasticity. To develop further functionalities of polyurethane materials and manipulation methods, here, we report the synthesis and a new method for coating non-ionic polyurethanes containing sulfonyl groups with utilizing electrophoretic deposition. The polyurethanes were synthesized via polyaddition of methylenediphenyl 4,4'-diisocyanate (MDI) with 2,2'-thiodiethanol in the absence or presence of triethylene glycol (TEG) as the soft ternary segment of the polymer, followed by oxone oxidation. The electrophoretic behaviors of the polyurethanes toward a stainless-steel electrode were investigated, and the peeling resistance and scratch resistance of a polyurethane film coated on a plate were evaluated by cross-cut adhesion and pencil hardness tests, respectively. These tests revealed that incorporation of soft TEG segments at an appropriate fraction can enhance both peeling resistance and scratch resistance. We also tested the enhancement in the transparency of the coated films, which do not lose their favorable peeling resistance and scratch resistance in the process, by replacing the aromatic diisocyanate component (MDI) with an alicyclic diisocyanate, dicyclohexylmethane 4,4'-diisocyanate (HMDI).

Introduction

Polyurethane-based materials are widely used in our daily lives because of their versatile material shape, recyclability, and thermoplasticity [1–6]. The thermoplasticity is owed to cross-link domains, which are necessary for attaining sufficient materials toughness, are formed by physical interactions via hydrogen bonding in microdomains and crystallites [7, 8]. Polyurethane materials are usually composed of alternating hard and soft segments, and exhibit versatile mechanical properties, which provide polymer chemists with opportunities to apply them as elastomers [9, 10], paints, or coatings [11, 12]. Nevertheless, for further development of polyurethane-based materials and their functionalities, new methods for polyurethane manipulation must be established.

Over the past 5 years, we have focused on the development of non-ionic polymers with sulfonyl groups as exemplars for investigating their interesting electrophoretic behavior [13–18]. Electrophoretic deposition (EPD) is a unique technique for the fabrication of inorganic or inorganic/organic composite films onto electrodes [19, 20]. The method is based on the controlled electric-field-induced deposition of charged particles or molecules in an orderly manner onto an electrode (Fig. 1a). The advantages of EPD are the ability to form a thin film on a complex surface shape, easy control over film thickness, and the homogeneous nature of the deposited layer. Although utilization of EPD techniques for polymeric systems has been limited to charged particles that can be strongly migrated under an electric field [21, 22], we have demonstrated that non-ionic (non-charged) polymers can also show EPD behaviors by incorporating sulfonyl groups into the polymer chain. As a primary result, we found that an aliphatic poly(ester-sulfone), prepared by thiol-ene click polymerization and

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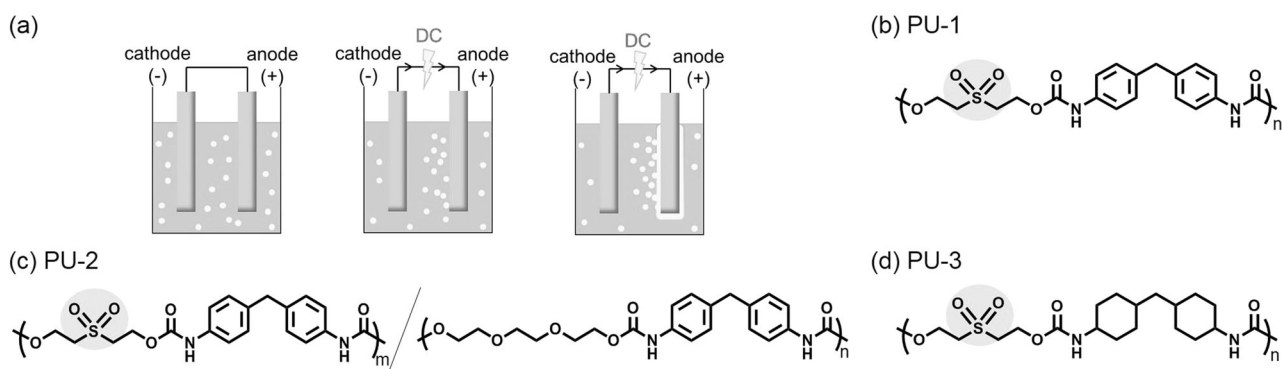


Fig. 1 **a** Schematic representation of the anode-selective EPD coating. Chemical structure of polyurethanes used in the present study: **b** PU-1, **c** PU-2, and **d** PU-3

subsequent oxidation, showed anode-selective electrophoresis [13]. Other molecular designs, including anode-selective EPD coatings of bioactive glass (45S5 Bioglass) [23] and titanium dioxide [24], were also demonstrated. These unique electrophoretic behaviors prompted us to address two questions: what structure is responsible for the unusual electrophoresis and why are the sulfone-incorporated polymers deposited onto the anode? We have concluded that such anode-selective EPD of the non-ionic polymers is induced by partial charge separation of protic solvents at the slip surface of the dispersions, where the charge separation is due to the dipole-ion interaction of negatively polarized sulfonyl groups and protic solvents [16]. Thus, the negative charges appear near the slip surface, bringing the particles to the anode.

In this report, we discuss the EPD coating of non-ionic polyurethanes containing sulfonyl groups with retaining the attractive features of polyurethane materials. First, we describe the EPD behaviors of non-ionic polyurethanes with sulfonyl groups, which were synthesized via polyaddition of methylenediphenyl 4,4'-diisocyanate (MDI) and 2,2'-thiodiethanol (TDE) in the absence (PU-1 in Fig. 1b) or presence of triethylene glycol (TEG) as a soft ternary segment (PU-2 in Fig. 1c), with subsequent oxone oxidation. By varying the fraction of soft TEG segments, we investigated the peeling resistance and scratch resistance of the coated polyurethane films based on cross-cut adhesion and pencil hardness tests, respectively. Solvent mixtures of dimethylformamide (DMF) and methanol (MeOH) of various volume ratios were used for polyurethane EPD, and the effects of the solubility of the polymers on the deposition amount were investigated. Finally, we tested the enhancement in the transparency of the coated films by replacing aromatic diisocyanate segments (MDI) with aliphatic diisocyanate segments (dicyclohexylmethane 4,4'-diisocyanate; HMDI) (PU-3 in Fig. 1d).

Experimental procedures

Materials

MDI, TEG, and TDE were purchased from Tokyo Chemical Industry Co. Ltd., Japan. HMDI, dibutyltin dilaurate (DBTDL), toluene, DMF, MeOH, and Oxone® were purchased from Wako Pure Chemical Industries, Ltd. All chemicals were used as received.

Polymer characterization

^1H NMR spectra were acquired at 27 °C using a Bruker Analytik DPX400 spectrometer (400 MHz). Tetramethylsilane was used as the internal standard (0 ppm). The number average molecular weight (M_n) and the polydispersity index (M_w/M_n) of the polymers were determined by size exclusion chromatography using a Tosoh DP8020 pump system, an RI (Tosoh RI-8020) detector, Shodex KD803+804 columns [eluent, 0.05% (w/v) LiBr/DMF; flow rate, 0.5 mL/min; temperature, 40 °C; Tosoh Corp.], and poly(methyl methacrylate) standards. Differential scanning calorimetry (DSC) was performed from 20 to 190 °C at 10 °C/min on a DSC210 calorimeter (Seiko Instruments Inc., Chiba, Japan). The instrument was calibrated with indium and tin. Each poly(urethane-sulfone) sample was placed in an aluminum pan in the calorimeter. The glass-transition temperature (T_g) was taken as the inflection point of the DSC heat-capacity jump. Dynamic light scattering (DLS) measurements were performed using a Zetasizer Nano ZS (Malvern Instruments, UK), where a solution with a constant concentration of 6 mg/mL was used. To determine the polymer particle size in the solution, the viscosity η values of mixture solvents were adopted from the literature and our past experiments.

Synthesis of polyurethane 1 (PU-1) via polyaddition of methylenediphenyl 4,4'-diisocyanate (MDI) and 2,2'-thiodiethanol (TDE) in the absence of triethylene glycol (TEG)

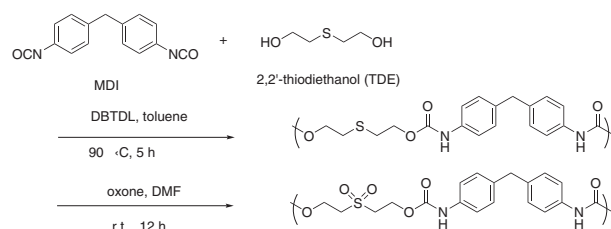
Polymerization conditions were surveyed as follows. In a sample test, 2.06 mL (20 mmol) of TDE, 5.01 g (20 mmol) of MDI, 200 μ L of DBTDL as the polymerization catalyst [25, 26], and 86 mL of toluene were added to a 200 mL round-bottom flask with a magnetic stir bar under a nitrogen atmosphere. The mixture was stirred at 90 °C for 5 h to obtain a solid white polymer, poly(MDI-*alt*-TDE). The polymer was precipitated from DMF solution into excess acetone, and the precipitates were dried under vacuum (quantitative yield). IR (KBr) cm^{-1} : 3326 (ν_{NH}), 2930 (ν_{CH}) 1707 [ν_{CO} (urethane)], 1535 [δ_{NH} (urethane)], 1414 (δ_{CH}). $^1\text{H-NMR}$ (400 MHz, DMSO- d_6): 9.60 (s, OC = ONH, 1H), 7.38–7.31 (m, 4H, aromatic), 7.12–7.06 (m, 4H, aromatic), 4.22 (t, $\text{CH}_2\text{CH}_2\text{S}$, 4H, 6.6 Hz), 3.78 (s, Ar- CH_2 -Ar, 2H), 2.84 (t, $\text{CH}_2\text{CH}_2\text{S}$, 4H, 6.5 Hz).

To convert sulfides to sulfones, we oxidized the parent polymer using oxone as the oxidizing agent. The polymer (5.01 g, 13.4 mmol repeating unit) and the oxone (4.08 g, 26.8 mmol) in DMF (100 mL) were added to a 200 mL round-bottom flask. After stirring at room temperature (r.t.) for 12 h, the mixture was filtered, and the solvent was evaporated under reduced pressure to yield a pale-yellow solid. The obtained solid was then dissolved in DMF and precipitated into 90 mL of $\text{H}_2\text{O}/\text{DMF}$ (9/1, v/v) for purification. The polymer obtained was a pale-yellow solid (quantitative yield) coded as PU-1 (Scheme 1, PU-1, $M_n = 1.4 \times 10^4$, $M_w/M_n = 2.1$).

IR (KBr) cm^{-1} : 3328 (ν_{NH}), 2930 (ν_{CH}) 1707 [ν_{CO} (urethane)], 1535 [δ_{NH} (urethane)], 1414 ($\delta_{\text{C-H}}$). 1285 [$\nu_{\text{S=O}}$ (sulfone)], 1120 [$\nu_{\text{S=O}}$ (sulfone)]. $^1\text{H-NMR}$ (400 MHz, DMSO- d_6): 9.65 (s, OC = ONH, 2H), 7.38–7.31 (m, 4H, aromatic), 7.12–7.06 (m, 4H, aromatic), 4.44 (t, $\text{CH}_2\text{CH}_2\text{SO}_2$, 4H, 5.6 Hz), 3.78 (s, Ar- CH_2 -Ar, 2H), 3.61 (t, $\text{CH}_2\text{CH}_2\text{SO}_2$, 4H, 5.6 Hz) (see also Figure S1).

Synthesis of polyurethane 2 (PU-2) via polyaddition of MDI and TDE in the presence of TEG

To a 200 mL round-bottomed flask with a magnetic stir bar, 1.39 mL (10 mmol) of TEG, 5.01 g (20 mmol) of MDI, 200 μ L of DBTDL, and 86 mL of DMF were added under a nitrogen atmosphere. The mixture was stirred at r.t. for 3 h, and 1.03 mL (10 mmol) of TDE was then added as the ternary ingredient and stirred for 24 h. The polymer was precipitated from DMF solution into diethyl ether, and the precipitates were dried under vacuum (quantitative yield). IR (KBr) cm^{-1} : 3314 (ν_{NH}), 2951 (ν_{CH}), 1717 [ν_{CO} (urethane)], 1541 [δ_{NH} (urethane)], 1413 (δ_{CH}), 1078 [ν_{CO}



Scheme 1 Synthesis of poly(urethane-sulfone) (PU-1)

(ether)]. $^1\text{H-NMR}$ (400 MHz, DMSO- d_6): 9.61 and 9.57 (2s, OC = ONH, 4H), 7.38–7.31 (m, aromatic, 8H), 7.12–7.06 (m, aromatic, 8H), 4.21 (t, $\text{CH}_2\text{CH}_2\text{S}$, 4H, 6.6 Hz), 4.17 (t, C = $\text{OOCCH}_2\text{CH}_2\text{O}$, 4H, 4.4 Hz), 3.78 (s, Ar- CH_2 -Ar, 4H), 3.63 (t, C = $\text{OOCCH}_2\text{CH}_2\text{O}$, 4H, 4.4 Hz), 3.56 (s, $\text{OCH}_2\text{CH}_2\text{O}$, 4H), 2.85 (t, $\text{CH}_2\text{CH}_2\text{S}$, 4H, 6.6 Hz).

To convert sulfide groups in the polymer backbone to sulfones, we oxidized the polymer by oxone similarly to the synthesis of PU-1. The parent polymer, poly(MDI-*alt*-TDE)-*co*-poly(MDI-*alt*-TEG) (6.43 g, 9.57 mmol repeat unit), and oxone (2.91 g, 19.14 mmol) in DMF (70 mL) were added to 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 yield a pale-yellow solid. The solid was then dissolved in DMF and precipitated into 90 mL of $\text{H}_2\text{O}/\text{DMF}$ (9/1, v/v). The polymer obtained was a pale-yellow solid (quantitative yield) coded as PU-2 (Scheme 2, PU-2, $M_n = 1.2 \times 10^4$, $M_w/M_n = 1.7$). IR (KBr) cm^{-1} : 3315 (ν_{NH}), 2929 (ν_{CH}), 1717 [ν_{CO} (urethane)], 1541 [δ_{NH} (urethane)], 1416 (δ_{CH}), 1126 [$\nu_{\text{S=O}}$ (sulfone)], 1072 [ν_{CO} (ether)]. $^1\text{H-NMR}$ (400 MHz, DMSO- d_6): 9.60 (s, OC = ONH, 4H), 7.38–7.31 (m, aromatic, 8H), 7.12–7.06 (m, aromatic, 8H), 4.44 (t, $\text{CH}_2\text{CH}_2\text{SO}_2$, 4H, 5.5 Hz), 4.17 (t, C = $\text{OOCCH}_2\text{CH}_2\text{O}$, 4H, 4.3 Hz), 3.78 (s, Ar- CH_2 -Ar, 4H), 3.65–3.59 ($\text{CH}_2\text{CH}_2\text{SO}_2$, 4H), 3.63 (t, C = $\text{OOCCH}_2\text{CH}_2\text{O}$, 4H, 4.4 Hz), 3.56 (s, $\text{OCH}_2\text{CH}_2\text{O}$, 4H) (see also Figure S2).

Electrophoretic deposition procedure

The polyurethanes (24 mg) were first stirred in 1.7 mL of DMF to obtain a homogeneous solution. Then, 2.3 mL of MeOH, a non-solvent for the polyurethanes, was added to the solution to yield a dispersion containing polymer particles. To deposit each polymer onto stainless-steel electrodes via EPD, the distance between the electrodes was set to 6.5 mm. The deposition time was set to 90 s and the applied voltage was done to 200 V unless noted otherwise. The depositions were carried out on $0.2 \times 10 \times 40 \text{ mm}^3$ stainless-steel (SUS 301) electrodes obtained from the Japan Metal Service (Saitama, Japan). A cross-section of the coated films was visualized via scanning electron microscopy (SEM) (dual-stage JSM-6010LA; JEOL Ltd., Tokyo, Japan).

Scheme 2 Synthesis of poly(urethane-sulfone) containing TEG unit (PU-2)

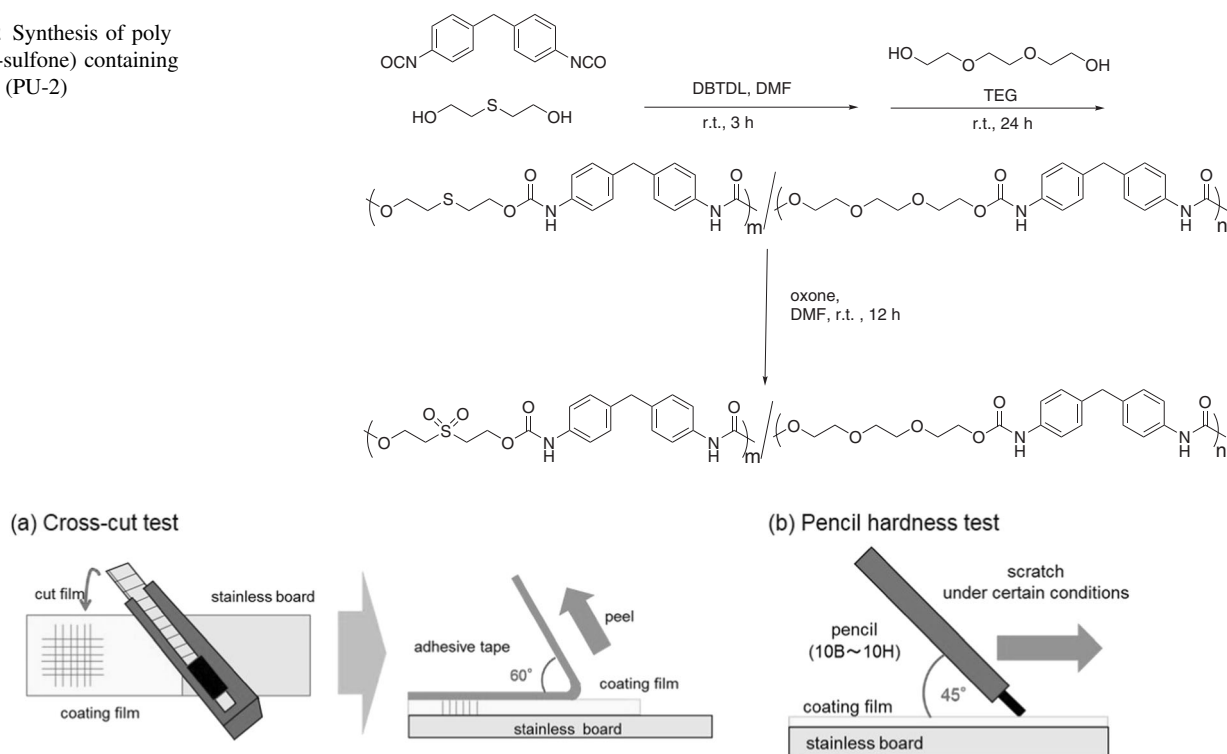


Fig. 2 Measurement protocols for **a** cross-cut test and **b** pencil hardness test

Cross-cut adhesion test

A cross-cut adhesion test (JIS K5600-5-6; ISO 2409:2007) was performed using CROSS CUT GUIDE 1.0 (CCI - 1) and polyester adhesive tape (Tape 8705B) purchased from COTEC Co. Ltd., Japan. According to ISO 2409:2007, the resistance of the EPD coatings to separation from substrates by peeling was evaluated using a right-angle lattice pattern cut into the coating, penetrating to the substrate (Fig. 2a) [27]. The property measured by this empirical test procedure depends on the adhesion of the coating to the substrate—in this case, the adhesion of the poly(urethane-sulfone) film to the stainless-steel electrode.

Pencil hardness test

A pencil hardness test (JIS K5600-5-4, ISO15184) was performed using a Wolff-Wilborn (KT-VF2391) apparatus, purchased from COTEC Co. Ltd., Japan, and pencils, purchased from MITSUBISHI PENCIL CO., LTD. The test was performed following the ISO15184 procedure; ISO 15184:2012 specifies a method for determining the scratch resistance of a film by pushing pencils of known hardness onto the film (Fig. 2b). The test was performed on a single EPD coating of poly(urethane-sulfone). This rapid test is useful for simply comparing the scratch resistance of coatings [28], which provides relative ratings based on pencil hardness (2H

> H > HB > F > B > 2B) for a series of poly(urethane-sulfone) coatings.

Results and discussion

Electrophoretic deposition of PU-1 and PU -2

The poly(urethane-sulfone)s PU-1 (Scheme 1, $M_n = 1.4 \times 10^4$, $M_w/M_n = 2.1$) and PU-2 (Scheme 2, $M_n = 1.47 \times 10^4$, $M_w/M_n = 1.97$, TEG content in total diol = 50 mol%) were synthesized by polyaddition and ternary polyaddition, respectively, using DBTDL as the catalyst for the step polymerization. Both of the synthesized poly(urethane-sulfone)s formed colloidal suspensions in a mixed solvent of DMF and MeOH (1.7 mL/2.3 mL), from which they were deposited onto a stainless-steel anode by EPD. The results are summarized in Fig. 3 and Table 1.

As shown in Fig. 3, we succeeded in the anode-selective EPD of both non-ionic aromatic polyurethanes, PU-1 and PU-2; the deposition amounts, summarized in Table 1, are comparable to those obtained in our previous work involving electrophoretic non-ionic poly(ester-sulfones) [16]. The difference in deposition amount between the two samples should be due to the difference in solubility against DMF/MeOH (1.7 mL/2.3 mL); the effects of the solvent on the EPD behavior are further discussed later. Visual observation indicated that the PU-2 coating formed a more

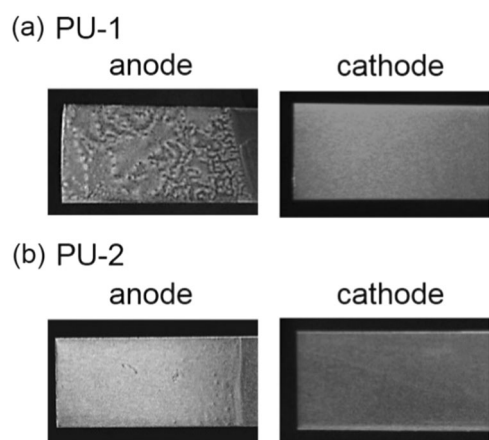


Fig. 3 Appearance of EPD coating with **a** PU-1 and **b** PU-2 on anodes and cathodes

Table 1 EPD results for poly(urethane-sulfone)s PU-1 and PU-2

Polymer	Deposition (mg/cm ²)	Class of cross-cut adhesion	Pencil hardness
PU-1	2.78	4	2B
PU-2	1.37	1	2H

Note: The distance between the electrodes was 6.5 mm, and the deposition time was 90 s. The applied voltage was 200 V, where the initial current was 12 or 45 mA. The solvent used for the EPD was DMF/MeOH (1.7 mL/2.3 mL)

uniform and smoother surface than PU-1, thanks to the use of TEG as the soft segment.

To clarify the effects of TEG segments on the coating properties, we performed the cross-cut adhesion test, which is regarded as a qualitative method for evaluating the peeling resistance [27]. After cutting a cross on the coating, we placed an adhesive tape on the coated film and subsequently peeled the tape as shown in Fig. 2a. The tests showed that PU-1 was easily peeled and classified as class 4, while PU-2 was difficult to peel and was classified as 1 (Figure 4). The results demonstrate that the EPD coating became more peeling-resistant by introducing TEG units as the soft segment (Table 1). Next, we performed pencil hardness tests, in which the coated samples were scratched with a pencil of known hardness (2H > H > HB > F > B > 2B) [28]. The PU-1 coating was damaged by a pencil hardness of 2B, while the PU-2 coating required a pencil hardness of 2H to be scratched. In other words, the scratch resistance of the EPD coating was also improved by introducing TEG as the soft segment. This improvement in scratch resistance should be related to the energy dissipated by incorporating soft segments. The rigid films were hard but more fragile, and thus could be scratched by a softer pencil. In contrast, the film containing soft segments, that is, the PU-2 film, was softer (i.e., more flexible). This softness

(a) Classification in cross-cut adhesion test

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

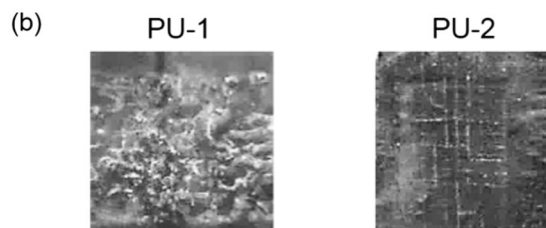


Fig. 4 **a** Classification via cross-cut adhesion test. **b** Appearance of the coated films after cross-cut adhesion test for PU-1 (class 4) and PU-2 (class 1)

Table 2 Characterization of poly(urethane-sulfone) synthesized by ternary polyaddition of MDI and TDE in the presence of TEG as ternary units

codes	[TDE]:[TEG] ^a	$M_n^b \times 10^{-4}$	M_w/M_n^b	T_g (°C) ^c
terPU-1	13:87 (20:80)	1.60	1.69	35, 72
terPU-2 ^d	45:55 (50:50)	1.47	1.97	39, 88
terPU-3	53:47 (60:40)	1.57	1.37	38, 76
terPU-4	76:24 (80:20)	1.30	1.43	35, 107

^aMolar ratios between TDE and TEG ([TDE]:[TEG]) in the synthesized PU, which were determined by ¹H NMR in DMSO-*d*₆. The ratios in parentheses represent the feed molar ratios

^bDetermined by GPC measurement in DMF/LiBr. The number average molecular weight (M_n) and polydispersity (M_w/M_n) were estimated using poly(methyl methacrylate) standards

^cGlass-transition temperature (T_g) determined by DSC (heating rate 10 °C/min), where the lower T_g was derived from poly(urethane-TEG) and the higher one was derived from poly(urethane-sulfone) segments

^dterPU-2 corresponds to PU-2 in the above section

provided energy dissipation in the pencil hardness tests, and thus, the PU-2 coating was sustained against a harder pencil, unlike the PU-1 coating.

We then investigated the effects of the TEG fraction in the polyurethane EPD-coated films on the peeling and scratch resistances. In the present system, it is easy to tune the fraction of TEG in the chains by varying the feed ratio between TDE and TEG, while keeping the reactive group ratio between NCO and OH groups unity. Thus, as shown in Table 2, the ratio of TDE to TEG in the synthesized polyurethanes was nearly the same as the feed ratio, and the M_n values were approximately 15,000. According to the DSC measurements, PU-2 with various TEG fractions showed two glass-transition temperatures (T_g s) (see Table 2), while PU-1 showed only one T_g at 68 °C. This finding may reflect the multiblock nature of the polymers,

Table 3 EPD results for poly(urethane-sulfone)s with various TEG contents

Polymer	Deposition (mg/cm ²)	Class of cross-cut adhesion	Pencil hardness
terPU-1	3.28	2	B
terPU-2	1.37	1	2H
terPU-3	1.75	0	H
terPU-4	2.89	1	H

Note: The distance between the electrodes was 6.5 mm, and the deposition time was 90 s. The applied voltage was 200 or 300 V. The solvent used for the EPD was DMF/MeOH (1.7/2.3 by volume)

which is reasonable by considering the present synthesis procedure (see again Scheme 2). Considering the softness (i.e., flexibility) of the TEG segments and the T_g of PU-1, the lower T_g is attributed to poly(urethane-TEG) segments, and the higher T_g is attributed to poly(urethane-sulfone) segments. It should be noted that the T_g of the poly(urethane-sulfone) block segments increased after the incorporation of the TEG segments, surpassing that of the original PU-1 without any TEG segments. This finding indicates that the segmental relaxation of the poly(urethane-sulfone) blocks is restricted by linking with other blocks, as reported in the literature [29, 30]. In addition, the higher T_g derived from poly(urethane-sulfone) segments showed a decreasing tendency with an increase in the fraction of poly(urethane-TEG) segments. This trend was observed because, in the present synthesis method, the lengths of successive poly(urethane-sulfone) segments were shortened by incorporating a larger fraction of TEG monomers and segmental relaxation occurred at a lower temperature for shorter segments.

Table 3 summarizes the scratch resistance of EPD-coated polyurethanes with various TEG fractions. For comparison, we prepared a film with a deposition amount greater than 1.35 mg/cm² and a thickness of approximately 20 μ m (see SEM image in Figure S3). In the cross-cut tests, improved peeling strength was observed in all TEG-incorporated coatings, compared with poly(urethane-sulfone) with no TEG units, i.e., PU-1 (these data are compared in Tables 1 and 3). The pencil hardness tests also showed a similar tendency; that is, the introduction of TEG units increased the scratch resistance (H to 2H) relative to that of PU-1 (2B). Among the samples, the sample containing 55 mol% TEG (terPU-2), which in fact corresponds to PU-2 described in the previous section, showed the best coating properties, with the highest peeling and scratch resistances. These results are important because the incorporation of an excessive amount of soft segments reduces the strength of the coated films, and there is an optimal soft segment fraction that yields the most favorable coating properties.

Electrophoretic deposition of PU-2 films at different DMF/MeOH ratios

As indicated in the Introduction, the solvents used for EPD must have a strong influence on the deposition amount, although the influence has not been investigated in detail for EPD systems featuring non-ionic polymers. In the present system, the PU-2 films were soluble in DMF but insoluble in MeOH; therefore, the turbidity of the dispersions increased with MeOH content (Fig. 5a). Interestingly, however, DLS measurements revealed that the particle size in the solvents containing various DMF/MeOH ratios was nearly independent (\sim 90 nm) of the DMF/MeOH ratio (see Fig. 5b). Instead of the particle size increasing, the actual scattering light intensity systematically increased with MeOH content, as shown in Fig. 5c. Based on these data, we presume that particle size (i.e., the number of chains in the aggregated particles) was scarcely affected by the ratio of DMF/MeOH within the present range, while the number of particles floating in solution increased with the MeOH ratio, which eventually caused the solution to become turbid. The deposition amount from various solutions under the same EPD conditions, i.e., the same polymer concentration (6 mg/mL), total solution volume (4 mL), deposition time (90 s), and applied voltage (200 V), followed the tendency observed for the scattering light intensity (Fig. 5c). This result is understandable because each individual chain *dissolved* in the solvent, which has little influence on the scattering intensity, would not contribute to form slip surfaces in the solution (see also the schematic explanation in SI, Figure S4). To date, we have reported on the tunability of the deposition amount via solution concentration [23] and applied voltage [27], and the above-mentioned data demonstrate that the deposition amount could be tuned by the miscibility between polymers and solvents used for EPD.

Effect of aromaticity on EPD

Finally, we investigated the influence of aromaticity in the poly(urethane-sulfone) on the EPD behavior, which prompted us to synthesize an aliphatic poly(urethane-sulfide), i.e., poly(HMDI-*alt*-TDE), followed by oxone oxidation to afford the corresponding aliphatic poly(urethane-sulfone) (PU-3; M_n of 1.68×10^4 and M_w/M_n of 1.37), which possessed a structure similar to that of PU-1 (Scheme 3). The synthesized aliphatic poly(ester-sulfone) was colorless and transparent, making it quite different from the aromatic poly(urethane-sulfone) (PU-1) (see Fig. 6a, b).

Figure 6c shows that it was possible to prepare a transparent film (4.5 mg/cm²) of the aliphatic poly(urethane-sulfone) by EPD. The peeling resistance of the deposited film, as evaluated by the adhesion test, was classified as

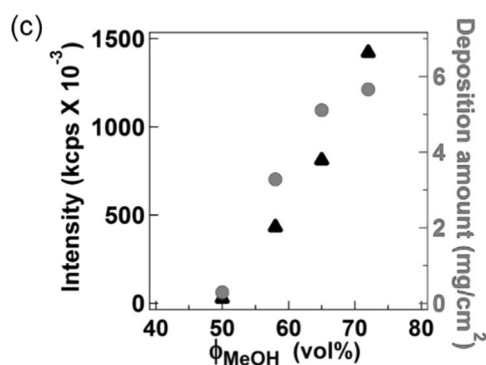
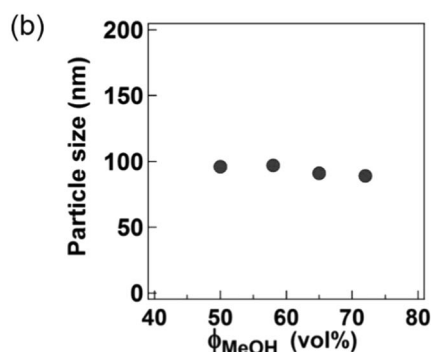
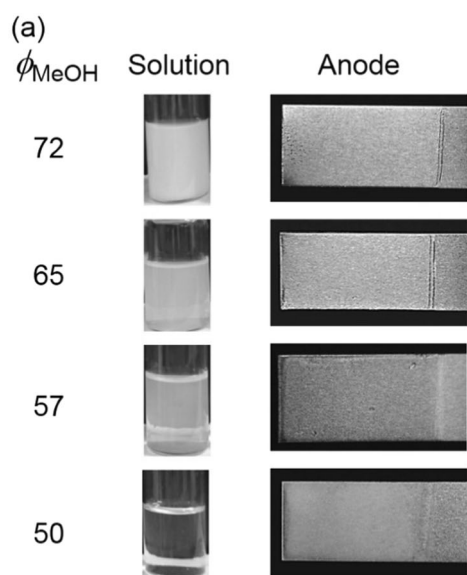
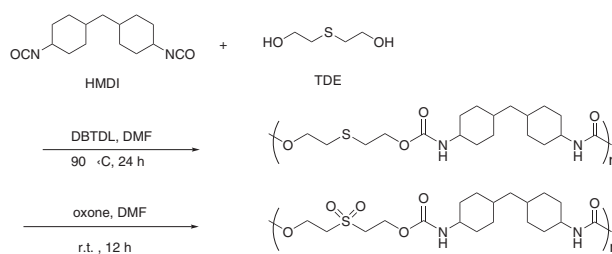


Fig. 5 **a** Appearance of PU-2 (terPU-1) dispersion solution and EPD coating film on the anode depending on MeOH (=MeOH/(DMF + MeOH), by vol%). **b** Relationship between particle size and MeOH. **c** Dependence of MeOH on scattering intensity measured by DLS and deposition amount on anode in EPD

class 2 (Fig. 6c), making it stronger than the aromatic poly(urethane-sulfone) PU-1 (classified as 4). The results indicate that the presence of an aromatic ring in the poly(urethane-sulfone) has little influence on EPD behavior, and the introduction of a soft aliphatic ring structure (HDMI unit), instead of the incorporation of soft TEG segments, is also an effective procedure for improving the peeling resistance.



Scheme 3 Synthesis of aliphatic poly(urethane-sulfone) (PU-3)

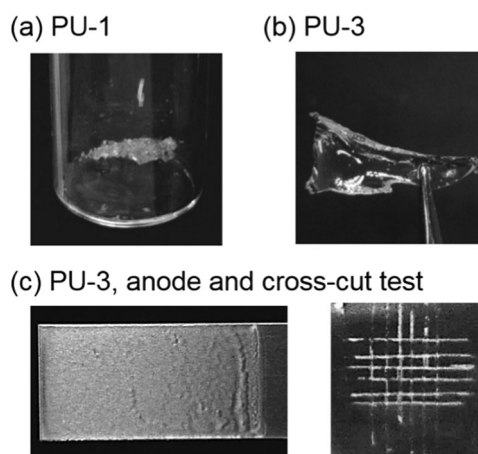


Fig. 6 Appearance of as-synthesized **a** PU-1 and **b** PU-3. **c** Anode appearance of PU-3 after EPD and cross-cut test

Conclusion

We synthesized several non-ionic polyurethanes containing sulfonyl groups to establish a noble manipulation technique for polyurethane materials. Selective deposition on a stainless-steel anode was successful, regardless of the types of diisocyanate components and diol components used, as long as sulfonyl groups were incorporated. The peeling resistance and scratch resistance of the polyurethane-based coating films was improved by adding soft TEG units as the ternary component. We also demonstrated that the miscibility between polyurethanes and solvents used for EPD was a factor enabling the tuning of the deposition amount. We also found that the use of alicyclic diisocyanate is a useful method for enhancing the coating transparency without losing the good peeling resistance of the films. These fundamental results should provide new insights into the development of smart coatings using polyurethane materials.

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Compliance with ethical standards

Conflict of interest The authors declare that they have no conflict of interest.

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