



Fixation of ionic liquids into polyether-based polyurethane films to maintain long-term antistatic properties



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ABSTRACT

Ionic liquids (ILs) were fixed into polyether-based polyurethane (PU) films for sustainable antistatic properties. Preliminarily, ILs were screened in terms of efficiency of antistatic effect. Surface resistivity (ρ_s) for IL-doped PU films changed depending the anion species, and the smallest ρ_s was found for the PU films containing bis(trifluoromethanesulfonyl)imide ([TF₂N])⁻-type ILs. Then, [TF₂N]⁻-type ILs composed of ammonium cations having hydroxyl groups were fixed into the PUs through urethane bonds. The fixation of 1000 ppm of the ILs reduced the ρ_s of the PU films from 2.1×10^{12} to $2.1 \times 10^9 \Omega \text{ sq}^{-1}$. These IL-fixed PU films were revealed to possess high washing durability confirmed by negligible change of ρ_s before and after ultra-sonication treatment in methanol.

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1. Introduction

Polyurethanes have been recognised as important materials whose properties are tuneable between rubber-like elasticity and plastic-like toughness. These can be controlled by changing the ratio of polyisocyanate to polyols as components, plasticising conditions, and other factors [1]. Among engineering and electronics fields, there are strong requirements to design elastic and flexible polyurethanes which can be used in a wide range of temperature, and this attempt has been successfully carried out by using polyether polyols [2,3]. These polyether-based polyurethanes (PUs) have been applied as films and sheets for packaging and stuffing during production, packing, shipping, and materials for electronics devices. However, these PUs are insulating and they cause electrostatic discharge (ESD) damage of electronic devices such as precision instruments and office automation equipment. There is a strong demand to prevent ESD of PUs so that the electronic devices which have contact with PUs may not be suffered from ESD damage.

In order to prevent ESD of PUs, resistivity of PUs has to be reduced. Surface resistivity and volume resistivity are frequently used to evaluate ESD protective materials together with charge decay time and triboelectric properties. Materials showing surface resistivity (ρ_s) greater than $10^{12} \Omega \text{ sq}^{-1}$ are generally classified as insulators [4,5], and the ρ_s of $10^{10} \Omega \text{ sq}^{-1}$ is practically recognised as a preferable value to keep antistatic effect [6].

In order to reduce ρ_s , antistatic agents, such as carbon black, intrinsically conductive polymers, and surfactants have been added to polymers as ESD protective materials [7–10]. Antistatic effects of these agents are realised by electron or ion conduction mainly occurred through successive conduction paths formed by additives or moisture adsorbed on the polymer surfaces. In the area of polymer electrolytes, polyethers (e.g., poly(ethylene oxide); PEO) have long been recognised as potential matrices for ion conduction due to their low glass transition temperature (T_g) and high polarity. For the case of inorganic salts/PEO composites, ionic conductivity is enhanced with both dissociated ions produced by the large dipole moment on ether oxygens and ion motion accompanied with segmental motion of PEO [11,12]. Recently, ionic liquids (ILs) have been recognised as potential salts due to their low T_g [13], and ILs/PEO composites have been reported to generate large amounts of free ions compared to PEO composites with inorganic salts [14]. Since many ILs are highly dissociable and their T_g is quite low as compared with most inorganic salts, these ILs are expected to be excellent additives to prepare ion conductive polymers.

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Since the PUs examined here contain polyether networks, ILs should effectively act as antistatic agents in the PUs. Taking the low T_g of 1-butyl-3-methylimidazolium bis(trifluoromethanesulfonyl)imide ([C₄mim][Tf₂N]) into account, [C₄mim][Tf₂N] has recently been proposed as an antistatic agent for these PUs [15]. The ρ_s of the PU films has been reduced from 2.1×10^{12} to 9.4×10^{10} and $2.6 \times 10^9 \Omega \text{ sq}^{-1}$ by the addition of [C₄mim][Tf₂N] for 10 ppm and 1000 ppm, respectively. These IL-doped PUs have been evaluated to be sufficient to avoid ESD. However, the IL-doped PU films might suffer from bleed out of ILs when the films are washed under harsh conditions or the films are stored for long periods. In the present study, ILs have been fixed into the PU films with covalent bonds in order to preserve a long-term antistatic effect of the PU films.

2. Experimental section

2.1. Materials

Scheme 1 shows structure of [Tf₂N]-type ILs containing such cations as (2-hydroxyethyl)trimethylammonium ([ch]), tris(2-hydroxyethyl)methylammonium ([thema]), and *N,N*-diethyl-*N*-methyl-*N*-(2-methoxyethyl)ammonium ([DEME]), as well as the PU films used in this study. Synthesis of ILs are mentioned in the Supplementary Information. Precursors of the PU films such as polymeric diphenylmethylenediiisocyanate, Sumidur 44V20 (PDI, >99.6%, from Sumika Bayer Urethane Chemical), trifunctional polyether polyols based on propylene-ethylene oxides 80/20 mol/mol (P(PO/EO), ≥99%, $M_w = 7,000$, from Asahi Glass), and dibutyltin dilaurate (DBTDL, ≥99%, from Kyodo Yakuhin) were purchased and used without further purification. DBTDL was diluted tenfold with of Exxsol™ D40 Fluid (99.9%, from ExxonMobil Chemical).

2.2. Preparation of PU films

We mixed 50.0 g of P(PO/EO), 3.59 g of PDI, and 0.9 g of DBTDL solution as a catalyst. This was further mixed homogeneously with MAZERUSTAR KK-102 (from KURABO Industries Ltd.), then the mixture was cast on a glass plate with a 0.1 mm spacer. The plate was heated to 80 °C for 30 min, and the network PU films were obtained as a thin film. Reactive ILs, having terminal hydroxyl group which is reactive with isocyanate, were proposed for the preparation of IL-fixed PU films, and IL-doped PU films were also prepared with un-reactive IL having no terminal hydroxyl group as a reference. The IL-doped and -fixed PU films were prepared by the same procedure as mentioned above but with P(PO/EO)-IL mixtures instead of pure P(PO/EO).

2.3. Electrochemical properties

The ρ_s was measured with a Modulab system (Solartron) at room temperature. Cells with a comb-shaped gold electrodes, with a four-pair-toothed formation with a 0.30 mm gap between electrodes, were used. From the IL-doped or IL-fixed PU films, a square with 5.0 mm per side was cut out for the measurement. The cut films were dried in a vacuum at room temperature for at least 3 h. These films were layered to a cell and tightly packed under N₂ atmosphere, then measurements were carried out in ambient atmosphere. Prior to the measurements, +5.0 V and -5.0 V were applied for 60 s to generate the same static environment on the film surfaces, then direct currents were measured by applying +5.0 V to the cell. The ρ_s was calculated with modified Ohm's Law (Eq. (1)), where V is the applied potential ($V = 5.0 \text{ V}$), l is the total length of electrodes ($l = 3.5 \text{ cm}$), I_s is the measured current intensity, and d is the distance between the electrodes ($d = 0.03 \text{ cm}$).

$$\rho_s = Vl/I_s d \quad (1)$$

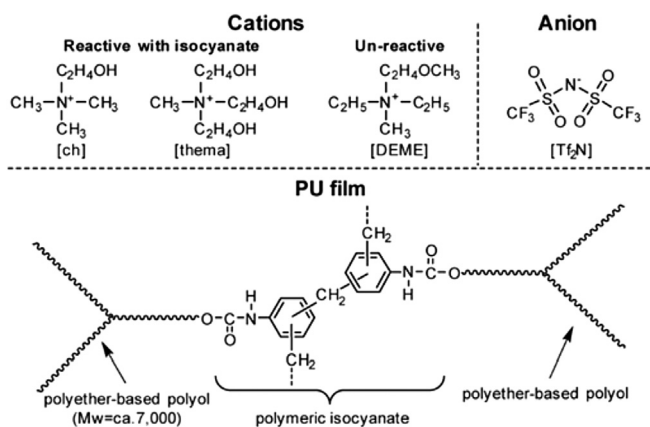
Ionic conductivity was measured using a Solartron 1260 Impedance Analyser at room temperature. The same cells for ρ_s measurement were used for this measurement. A signal of amplitude 5 mV was applied to the cell in the frequency range of 10^{-1} – 10^7 and 10^3 – 10^7 Hz, for IL-doped PU film and ILs, respectively. Conductivity was calculated according to the amplitude of a semicircle or intersection on the Z' axis of the Nyquist plot of the impedance. For the case of the ionic conductivity of IL-doped PU films (σ_{film}), the σ_{film} was calculated with the Eq. (2), where σ is measured conductivity.

$$\sigma_{\text{film}} = \sigma d/l \quad (2)$$

3. Results and discussion

3.1. Relation between ρ_s and ionic conductivity

Preliminarily, ILs were screened for subsequent experiment in terms of efficiency of antistatic properties. We have suggested that ILs enhance antistatic properties by dissociating into ions and conducting through polyether networks of the PUs [15]. First, we analysed the relation between ionic conductivity of pure ILs (σ_{IL}) and ρ_s of IL-doped PU films. We have analysed ILs shown not only in Scheme 1 but also in Scheme S1 (six different [Tf₂N]-type ILs containing such cations as 1-butyl-3-methylimidazolium ([C₄mim]), 1-ethylpyridinium, 1-butyl-1-methylpyrrolidinium, *N,N,N*-tributyl-*N*-octylphosphonium, 1-butyl-2,3-dimethylimidazolium, and 1-ethyl-3-methylimidazolium. We also used six different imidazolium-type ILs such as 1,3-diallylimidazolium Br ([AAim]Br), [C₄mim]CH₃SO₃, [C₄mim](CH₃O)(H)PO₂, [C₄mim]BF₄, 1-ethyl-3-methylimidazolium bis(fluorosulfonyl)imide ([C₂mim][FSI]), and [C₄mim] tris(pentafluoroethyl)trifluorophosphate ([C₄mim][FAP]). As seen in Fig. 1(a), ILs with high ionic conductivity were favourable to reduce ρ_s of the films, however, a strong correlation between σ_{IL} and ρ_s was not observed. This may be due to the different compatibility, morphology, viscosity, and other properties of ILs in the PU films. Then we measured the σ_{film} . As shown in Fig. 1(b), the ρ_s was found to be the function of σ_{film} . The ρ_s of PU films doped with imidazolium-type ILs was found to be in order of [FAP], [FSI] < [Tf₂N] << BF₄ << (CH₃O)(H)PO₂, CH₃SO₃ < Br (triangular plots in Fig. 1(b)). In the case of Br salt, data with [AAim]Br, liquid state at room temperature, were used instead of those with [C₄mim]Br, solid state at room temperature, because [C₄mim]Br-doped PU films showed extremely low ionic conductivity which



Scheme 1. Structure of [Tf₂N]-type ILs and common structure of the PU films used in this study.

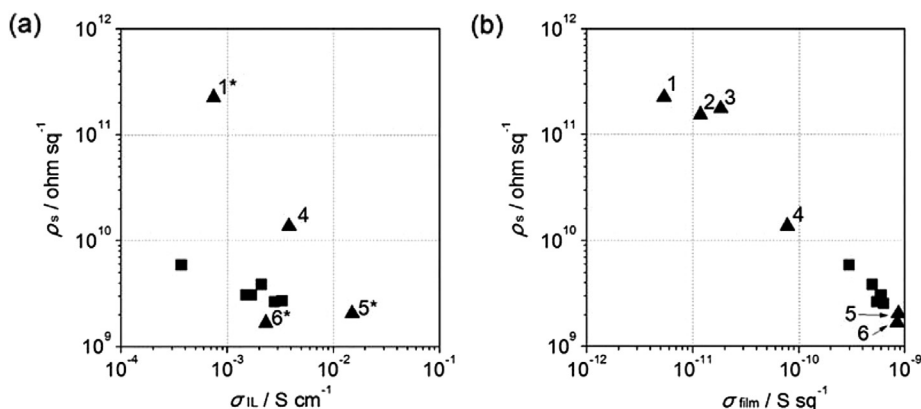


Fig. 1. Relation between ρ_s of the PU films containing 1000 ppm of ILs and (a) σ_{IL} and (b) σ_{film} at room temperature. Each number next to the triangular plots corresponds to 1: [AAim]Br, 2: [C₄mim]CH₃SO₃, 3: [C₄mim](CH₃O)(H)PO₂, 4: [C₄mim]BF₄, 5: [C₂mim][FSI], and 6: [C₄mim][FAP]. The square plots represent [Tf₂N]-type ILs. *Ionic conductivity data (at 25 °C) are available in Refs. [16–18], unless the data for [C₄mim][FAP] were taken at 20 °C [19].

cannot be detected accurately with our equipment. Since [C₄mim]CH₃SO₃ which is solid at room temperature gave better properties (#2 in Fig. 1(b)) than [AAim]Br, dissociation rate as well as the structure of component ions of ILs are suggested to affect ρ_s of IL-doped PU films. Among these ILs, the [Tf₂N]-type ILs showed similar properties of 10^{-9} S sq⁻¹ and 10^9 Ω sq⁻¹ for σ_{film} and ρ_s , respectively (square plots in Fig. 2(b)). A remarkable difference of the efficiency of antistatic effect was not observed for [Tf₂N]-type ILs. Taking the effect of anion species into account, the ILs containing [Tf₂N] anions have been proposed to reduce ρ_s of the IL-doped PU films.

3.2. Washing durability of antistatic effects of the PU films containing ILs

Fig. 2 shows the effect of methanol washing on the ρ_s of [C₄mim][Tf₂N]-doped PU films. The ρ_s without any agitations is also depicted as a reference. The ρ_s for the pure PU film was found to be 2.1×10^{12} Ω sq⁻¹ and was reduced to 6.2×10^7 Ω sq⁻¹ by adding

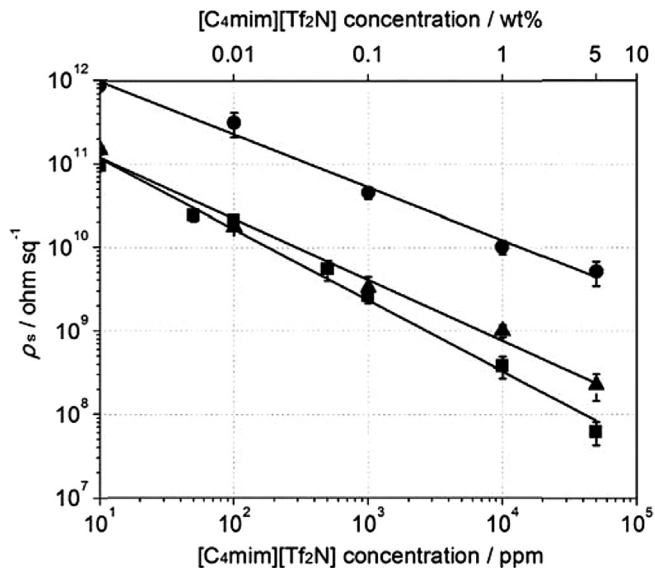


Fig. 2. Effect of methanol washing on ρ_s of the PU films containing [C₄mim][Tf₂N] after 10 s rinsing (▲) and 10 min ultra-sonication (●). The square plots (■) represent ρ_s of the PU films without any agitations (as reference).

5 wt% of [C₄mim][Tf₂N]. These values were almost retained after 10 s methanol rinsing of the PU films. However, the ρ_s drastically increased after 10 min ultra-sonication treatment (at 35 W) of the films, and the larger increment was found at higher [C₄mim][Tf₂N] concentration. For example, the PU films containing 5 wt% of [C₄mim][Tf₂N] showed the ρ_s which was increased hundred times as compared to the original value. These results strongly suggest the requirement of fixation of ILs to PU films in order to improve antistatic properties for long-term and against harsh washing.

In this study, we have proposed IL-fixed PU films instead of IL-doped PU films as novel antistatic PU films. For the preparation of IL-fixed PU films, [ch][Tf₂N] containing cations having a terminal hydroxyl group per cation unit was used, and 1000 ppm of [ch][Tf₂N] was mixed with polyether-based polyols prior to plasticisation for the PU films. Terminal hydroxyl groups are expected to form urethane bonds with isocyanate. In order to check the effect of terminal hydroxyl groups in cation structure, [DEME][Tf₂N] having no hydroxyl group on cation was also used in this investigation as reference. Fixation of [ch][Tf₂N] into the PU films led to low ρ_s as compared to the pure PU films, and the ρ_s for [ch][Tf₂N]-fixed PU films was found to be equivalent with that of [DEME][Tf₂N]-doped PU films (see Fig. 3, far left plot). Also, we investigated ρ_s of these films after methanol rinsing for 3 s and after ultra-sonication treatment in methanol for 1, 5, 10, and 15 min (Fig. 3). There were negligible changes on the ρ_s before and after 3 s methanol rinsing for both [DEME][Tf₂N]-doped and [ch][Tf₂N]-fixed PU films (Fig. 3, the second left plots). However, after 10 min ultra-sonication treatment of these films, ρ_s for [DEME][Tf₂N]-doped PU films jumped up from 10^9 to 10^{11} Ω sq⁻¹ nevertheless [ch][Tf₂N]-fixed PU films retained ρ_s in the order of 10^9 Ω sq⁻¹. This was kept even after 15 min ultra-sonication treatment. This indicates that [ch] cations were successfully fixed into the PU films via covalent bonds with isocyanate and that this fixation has potential to maintain the antistatic effect. The same durability was observed when [thema][Tf₂N] having three hydroxyl groups per cation unit was fixed into the PU films for 1000 ppm (reverse triangular plot in Fig. 3). We also analysed changes of ρ_s for the films containing 5 wt% of [ch][Tf₂N]. The ρ_s for this film was found to be 1.5×10^8 Ω sq⁻¹ without any agitations. This value slightly increased to 6.4×10^8 Ω sq⁻¹ after 15 min ultra-sonication treatment. However, the increased values were still comparable with the ρ_s for the films containing 5 wt% of [C₄mim][Tf₂N] without agitations and several tenth of that measured after 10 min ultra-sonication treatment (see Fig. 2). The IL-fixed PU films prepared here possessed high washing durability which was confirmed by negligible change of ρ_s before and after

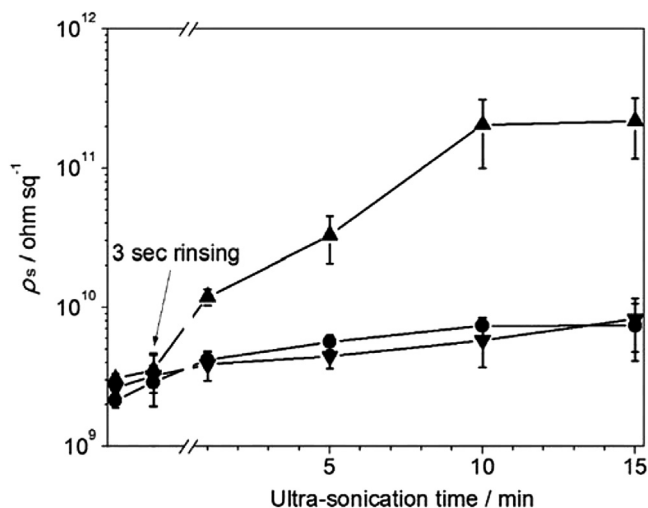


Fig. 3. The ρ_s of the PU films containing [DEME][Tf₂N] (doped; ▲), [ch][Tf₂N] (fixed; ●) and [thema][Tf₂N] (fixed; ▼) after methanol rinsing for 3 s and after ultra-sonication treatment in methanol for 1, 5, 10, and 15 min.

ultra-sonication treatment of the films in methanol. As a result, we have confirmed effectiveness of the fixation of ILs to the PU films to improve long-term antistatic properties.

4. Conclusion

The ρ_s of the PU films was effectively reduced by adding [Tf₂N]-type ILs. For sustainable antistatic properties, ILs composed of cations having hydroxyl groups were fixed into PU films via urethane bonds. Fixation of 1000 ppm of [ch][Tf₂N] into the PUs reduced ρ_s from 2.1×10^{12} to $2.1 \times 10^9 \Omega \text{ sq}^{-1}$, and the reduced ρ_s was found to be comparable with that of IL-doped PU films. However, after 10 min ultra-sonication treatment of these films in methanol, ρ_s for IL-doped PU films jumped up from 10^9 to $10^{11} \Omega \text{ sq}^{-1}$ nevertheless IL-fixed PU films retained the ρ_s in the order of $10^9 \Omega \text{ sq}^{-1}$. Fixation of the ILs into PU films via urethane bonds were concluded to be effective to maintain antistatic properties of the PU films for long-term.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at <http://dx.doi.org/10.1016/j.polymer.2014.03.028>.

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