Antistatic effects of ionic liquids for polyether-based polyurethanes

Akiko Tsurumaki [a,b], Saori Tajima [a,b], Takuya Iwata [a,b,c], Bruno Scrosati [a,d], Hiroyuki Ohno [a,b,*]

[a] Department of Biotechnology, Tokyo University of Agriculture and Technology, 2-24-16 Naka-cho, Koganei, Tokyo 184-8588, Japan
[b] Functional Ionic Liquid Laboratories, Graduate School of Engineering, Tokyo University of Agriculture and Technology, 2-24-16 Naka-cho, Koganei, Tokyo 184-8588, Japan
[c] Iwata & Co., Ltd., 1-2-11, Nishiki, Naka-ku, Nagoya, Aichi, 460-0003 Japan
[d] Istituto Italiano di Tecnologia, Via Morego, 30, 16163 Genova, Italy

ABSTRACT

Mobility of component anions of ionic liquids (ILs) was found to be a most effective factor to enhance antistatic properties of polyether-based polyurethanes (PUs). Then, the antistatic effects were discussed with Kamlet-Taft parameters (hydrogen bond acidity: α and basicity: β) of the added ILs. A strong correlation was found between β value and surface resistivity (Rs) of the PUs containing the ILs. On the contrary, α value was found to have a weak influence on the Rs. Since there was a weaker interaction between polyether chains and anions than cations, antistatic effects of the ILs were weaken by fixing the component anions into the PUs. This strongly suggests that effective antistatic effects are supported by the anion migration of ILs.

© 2015 Elsevier Ltd. All rights reserved.

1. Introduction

Polyurethanes have been recognized as important materials whose properties are tunable between rubber-like elasticity and plastic-like toughness. These can be controlled by changing the ratio of polyisocyanate to polyols, their plasticizing conditions, and other factors [1]. Polyether-based polyols are widely used among engineering and electronics fields to prepare elastic and flexible polyurethanes which can be used in a wide range of temperatures [2]. However, these polyether-based polyurethanes (PUs) are insulative and they cause electrostatic discharge (ESD) and damage of electronic devices which have contact with PUs. To apply these PUs in the electronics field, there is a strong requirement to prevent ESD of PUs.

In order to prevent ESD of PUs, their resistivity should be reduced, and antistatic agents have hitherto been added to polymer materials for this purpose. Materials showing surface resistivity (Rs) greater than $10^{12}\,\Omega\,sq^{-1}$ are generally classified as insulators [3], and the Rs of $10^{10}\,\Omega\,sq^{-1}$ is practically recognized as a preferable value to keep the antistatic effects [4]. There are two main possibilities to reduce Rs of polymers: one is based on the electronic conduction and the other is on the ionic conduction. Carbon black and inorganic fillers have been used as antistatic agents employing electronic conduction [5], while surfactants and intrinsically conductive polymers have been used as ones employing ionic conduction [6]. From the viewpoint of method to keep mechanical properties of polymer matrices, organic additives are used for organic matrices, and their added amount should be as smaller as possible. This should also be preferred to keep their properties such as transparency, morphology, and elasticity. Despite these advantages of organic additives, excellent antistatic effects are not achieved under dry conditions and considerable amount of additives are needed to form successive conduction pathways.

Ionic liquids (ILs) have been recognized as potential organic salts due to their low glass transition temperature (T_g) [7]. Since many ILs are highly dissociable and their T_g are quite low as compared to inorganic salts, ILs are expected to be excellent additives to prepare ion conductive polymers [8]. Based on this expectation, we have previously applied 1-butyl-3-methylimidazolium bis(trifluoromethanesulfonyl)imide ([C_4mim][Tf_2N]) as antistatic agents for the PUs [9]. The Rs of the PU films has been reduced from 2.1×10^{12} to $5.5 \times 10^{9}\,\Omega\,sq^{-1}$ under dry conditions when only 500 ppm of [C_4mim][Tf_2N] was added. These IL-doped PUs have been evaluated to be sufficient to avoid ESD. Smaller volume resistivity was found as compared to Rs suggesting ILs were considered to be dispersed and dissociated

* Corresponding author at: Department of Biotechnology, Tokyo University of Agriculture and Technology, 2-24-16 Naka-cho, Koganei, Tokyo 184-8588, Japan. Tel.: +81 42 388 7024; fax:+81 42 388 7024.
E-mail addresses: 50012831205@st.tuat.ac.jp (A. Tsurumaki), 50013641210@st.tuat.ac.jp (S. Tajima), t.iwata@iwata-cc.co.jp (T. Iwata), scrosati@cc.tuat.ac.jp (B. Scrosati), ohnoh@cc.tuat.ac.jp (H. Ohno).

into ions in the polyether domain of the PUs. The mobility of ions are considered to affect their antistatic effects. However, few studies have been made to discuss the relationship between mobility of ions and their antistatic effect in the PUs, and no strategy has been proposed yet to design novel antistatic agents based on ILs.

2. Experimental section

2.1. Materials

Fig. 1 shows structure of ILs and zwitterion (ZI) used in this study. Abbreviation and preparation for all salts are summarized in the Supplementary Information.

In this study, linear PU was used to evaluate the solubility to ILs and network PUs were used to evaluate the conductivity of the PU films (Fig. 2). Precursors such as diphenylmethane-4,4′-diisocyanate, Millionate® MT (MDI, from Nihon Polyurethane Co., Ltd.), poly(propylene glycol) (PPG, average Mw is 4,000, from Asahi Glass Co., Ltd.), polymeric diphenylmethylene diisocyanate, Sumidur 44V20 (PDI, from Sumika Bayer Urethane Chemical Co., Ltd.), trifunctional polyether polyols based on propylene-ethylene oxides 80/20 mol/mol (P(PO/EO), Mw = 7,000, from Asahi Glass Co., Ltd.), and dibutyltin dilaurate (DBTDL, from Kyodo Yakuhin Co., Ltd.) were purchased and used without further purification. DBTDL was diluted tenfold with Exxsol™ D40 Fluid (from Exxon Mobil Chemical).

A linear PU was prepared with 8.0 g of MDI, 110.5 g of PPG, and 2.0 g of the DBTDL solution as a catalyst. The mixture was stirred at 80 °C for 60 min under N_2 atmosphere, and the linear PU was obtained as a sticky liquid.

The PU films were prepared with 50.0 g of P(PO/EO), 3.59 g of PDI, and 0.9 g of DBTDL solution. This mixture was further mixed homogeneously by MAZERUSTAR KK-102 (from KURABO Industries Ltd.), then cast on a glass plate with a 0.1 mm spacer. The plate was heated to 80 °C for 30 min, and the network PUs were obtained as a thin film (thickness = 0.1 ± 0.05 mm). ILs having hydroxyl groups, which were reactive with isocyanate, were used for preparation of IL-fixed PU films, and ILs without hydroxyl groups were used for IL-doped PU films. IL-fixed and IL-doped PUs were prepared by the same procedure of the pure PU films by using with P(PO/EO)-dried IL mixtures instead of pure P(PO/EO). The same procedure was applied for the preparation of ZI-doped PUs.

Poly(ethylene oxide) (PEO) based films were prepared by solution casting procedure. Initially, ILs were diluted tenfold with methanol. For 0.30 g of PEO (average Mv = 1,000,000, from Sigma–Aldrich) was added to 5.0 g of methanol, and the solution was mixed at 50 °C for 1 h. To the resulting solution, 3.0 mg of the IL solution was added and mixed for 10 min. The mixture was cast on a 5 cm diameter petri dish at 60 °C. To evaporate methanol, the Petri dish was heated at 60 °C for 30 min, heated at 80 °C for 10 min, and gradually cooled to room temperature.

2.2. Solubility of the linear PU in ILs

The linear PU was freeze dried prior to solubility measurement. Dried ILs and the linear PU were mixed with a ratio of 10.0/1.0 by weight. The mixed solutions were stirred at 25 °C for 24 h, and also 60 °C for 1 h if the PU was not homogeneously dissolved. Their solubility was checked visually by naked eyes at each temperature. All procedures were carried out under N_2 atmosphere.

2.3. Measurement of Kamlet-Taft Parameters

Kamlet-Taft parameters, α: hydrogen bond acidity and β: hydrogen bond basicity (Et(30) and π^* are not discussed in this study), are often used to estimate solubility of polymers in ILs [10]. Three different dyes, N,N-diethyl-4-nitroaniline (NN, from Wako Pure Chemical Industries, Ltd.), 4-nitroaniline (4N, from Tokyo Chem. Ind. Co.), and Reichardt' dye 33 (Rei from Fluka) were used. The dry methanol solution, 0.3 mL containing 0.03 g of corresponding dyes were added to ILs. Methanol was then removed by vacuum drying at 60 °C for 6 h. For the solvatochromic measurements, the IL solution containing dyes were placed in quartz cells with light path length of 0.1 mm, and their visible spectra were recorded with Shimadzu UV 2550 (from Shimadzu Corp.). The Kamlet-Taft parameters (π^*, α, and β values) were calculated according to the following equations (Eqs. (1)–(5)):
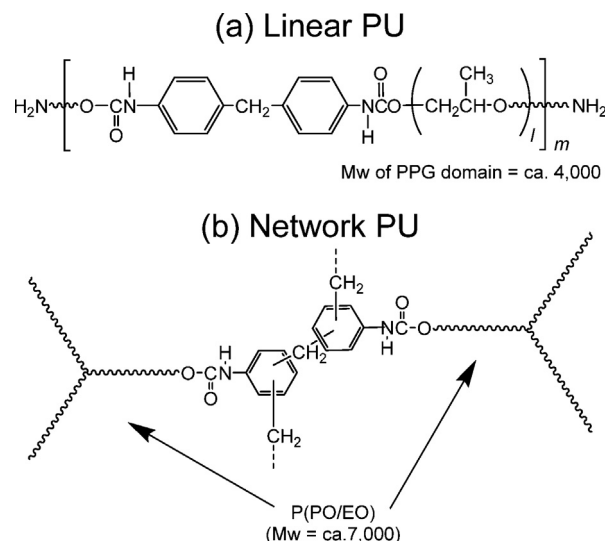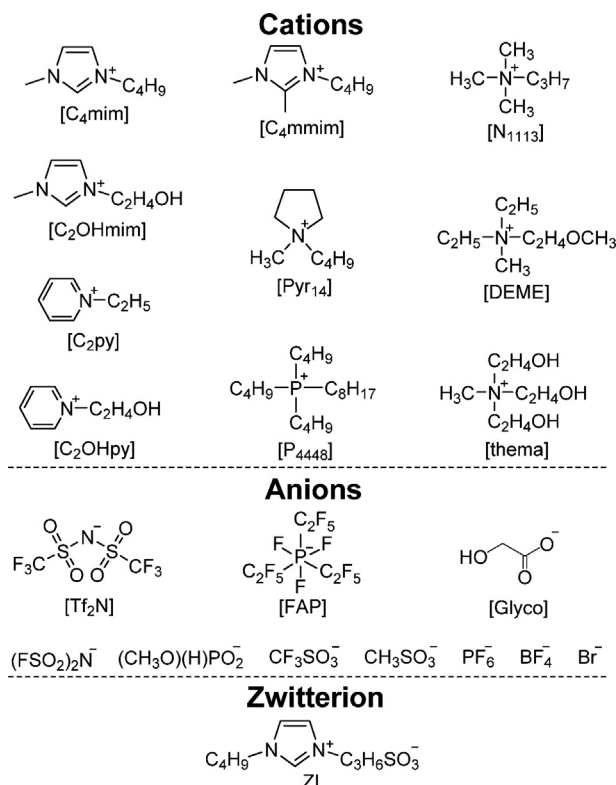

Fig. 1. Structure of ions for ILs and ZI used in this study.

Fig. 2. Structure of (a) a linear and (b) a network PUs used in this study.