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Study on ionic liquid $[bmim]PF_6$ and $[hmim]PF_6$ as plasticizer for PVC paste resin

Lin Xi Hou · Sui Wang

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Abstract Two kinds of room temperature ionic liquids, $[bmim]PF_6$ (1-butyl-3-methylimidazolium hexafluorophosphate) and $[hmim]PF_6$ (1-hexyl-3-methylimidazolium hexafluorophosphate), were respectively used as plasticizer for PVC paste resin. The mechanical properties, thermal and ultraviolet ray stabilities, and migration characteristics of the PVC paste resin samples were determined by universal testing machine, TG/DTA, and HPLC. The results showed that the tensile strength and elastic modulus decreased, the elongation at break and thermal stability of PVC paste resin membranes were improved with the increasing of $[bmim]PF_6$ or $[hmim]PF_6$ dosages. The immersed time and temperature could accelerate leaching and migration of plasticizers in plasticized PVC paste resin films. Moreover, the effect of solvent environment on migration amount was also studied.

Keywords PVC paste resin · $[bmim]PF_6$ · $[hmim]PF_6$ · Plasticizer · Ionic liquid

Introduction

A number of relatively small molecular weight compounds were used as plasticizers to make flexible products. Poly(vinyl chloride) is the most widely plasticized polymer material, due to good chemical stability, easy processing, cheap equipment, and good biocompatibility [1]. PVC paste resin is an important kind of PVC and applied for artificial leather, film applicator coating, and medical catheters' production [2]. In all of the plasticizing agents, dioctyl phthalate (DOP) is nowadays primary plasticizer in PVC paste resin's production [3]. However, recent reports

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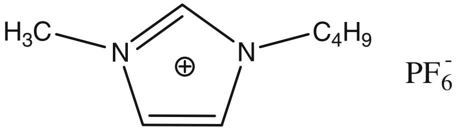
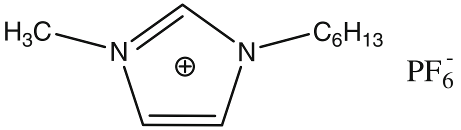
L. X. Hou · S. Wang (✉)
Faculty of Materials Science and Chemical Engineering, The State Key Laboratory Base of Novel Functional Materials and Preparation Science, Ningbo University, Ningbo 315211, China
e-mail: chemwangsui@163.com; wangsui@nbu.edu.cn



1-butyl-3-methylimidazolium hexafluorophosphate, [bmim]PF_6



1-hexyl-3-methylimidazolium hexafluorophosphate, [hmim]PF_6

Scheme 1 Chemical structures of plasticizing agents investigated

have debated the health and environmental aspects of the use of DOP. Especially, the leaching and migration of DOP could interfuse to medical liquid and blood, and it is unhealthy because of its carcinogenesis. Hence, to guarantee the safety of medical material, a number of alternatives to phthalates have been considered, including soy bean oil, poly(ethylene terephthalate), and ionic liquids [4, 5].

Room temperature ionic liquids consist of a cation and anion mixture, and have been increasingly investigated because of their unique solvating properties as well as low melting points. They have been used as solvents for liquid–liquid extraction, organic synthesis, electrochemical research, polymerization reaction, chromatography, and catalysis [6–8]. Also, a few articles have reported that ionic liquids were used as plasticizers in polymer materials including PMMA, PLA, polyamides, and suspension-polymerized PVC [3, 9–14], except for PVC paste resin. One common type of ionic liquids is based on alkyl imidazoliums as a cation, paired with a counterion, such as chlorine, bromine, hexafluorophosphate, or other anions.

In this study, two kinds of ionic liquids, [bmim]PF_6 and [hmim]PF_6 (Scheme 1), were investigated as potential replacements for traditional plasticizers of PVC paste resin, to achieve better material characteristics and reduce volatility and leaching of plasticizers.

Experimental

Materials and instruments

PVC paste resin (P440, Shanghai Chlor-Alkali Chemical Co., Ltd.); [bmim]PF_6 and [hmim]PF_6 (Hangzhou Chemer Chemical Co. Ltd.); HPLC grade tetrahydrofuran (THF, Fisher Scientific); other reagents were analytical pure grade without further purification.

Pyris Diamond TG/DTA (American Perkin-Elmer Co.); Instron5567 universal testing machine (American Instron Co.); HPLC (LC-10AT, Shimadzu Corporation, equipped with UV detector); pHs-3C meter (Hangzhou DongXing Co., P.R. China);

UV irradiation chamber (BR-UVT, Shanghai BoRui Science Instruments Co., P.R. China); super constant temperature water bath; microfiltration membrane filter, 0.45 μm water filtering membrane.

Preparation of PVC paste resin membranes

All plasticized samples of PVC paste resin were prepared by a solvent casting method. PVC paste resin and ionic liquid were mixed in THF as a solvent, and then they were placed in glass plates by direct scratch coating method. THF was first evaporated at atmospheric pressure and then in a vacuum chamber until their weights were invariable. The prepared films were peeled and tested [9]. The films were about 50 μm thickness.

All samples were formulated using 0, 10, 20, 30, and 40 wt% [bmim]PF_6 or [bmim]PF_6. Other samples were made by the same procedure.

Mechanical properties

The tensile strength, elastic modulus, and elongation at break of plasticized PVC paste resin membranes were obtained from omnipotence test machine. The samples were cut out to be rectangle (approximately 10 × 150 mm), and the situation of tests is 2.5 mm/min.

High temperature stability

Thermal stability was obtained from TG/DTA instruments. About 10 mg of sample was subjected to a temperature ramp of 10 °C/min starting from room temperature up to 250 °C. The N_2 flux was 20 mL/min.

UV stability

Photostability of plasticized PVC samples was tested in the far UV region, and the wavelength was 254 nm. 20 wt% plasticized and un-plasticized PVC samples were exposed to UV ray at 200 wpi for 5 min in an UV irradiation chamber. Elongation at break was measured by universal testing machine and compared before and after irradiation.

Migration

As raw materials of medical catheter, the migration properties of plasticized PVC paste resin production is a key [15, 16]. 20 wt% plasticizer–PVC samples were cut out to be rectangle (about 0.25 g), and then they were taken into 100 mL 15% alcohol–water solution or deionized water in the beaker. After controlling immersed time and temperature and pH, the solutions were filtered by 0.45 μm water filtering membrane, and then 20 μL samples were taken for analysis. HPLC condition: ODS C_{18} column; mobile phase: methyl alcohol–buffer solution (volume ratio: 50:50, the composition of buffer: 25 mmol/L potassium phosphate monobasic solution, 0.5%

triethylamine, pH = 3.0); flow speed: 0.8 mL/min, room temperature; detection wavelength: 215 nm.

Results and discussions

Glass transition temperature

Glass transition temperature (T_g) of un-plasticized and 20 wt% plasticized PVC film samples were obtained by DSC analysis. DSC curves (Fig. 1) showed that the room temperature ionic liquid plasticizer was effective in decreasing T_g of PVC samples. T_g values were about 58, 38, and 25 °C for un-plasticized, [bmim]PF_6 and [hmim]PF_6 plasticized PVC film samples, respectively. The relatively small plasticizer molecules could increase the terminal base ratio and make the free volume increases. Meanwhile, ionic liquids in PVC paste resin could promote the molecular relative motion, and overcome the sliding friction rough caused by uneven surfaces and the adhesion forces generated by van der Waals forces, London forces, hydrogen bond, crystal or master bond. T_g of [hmim]PF_6 plasticized PVC sample was lower than that of [bmim]PF_6 plasticized PVC sample. It showed that the longer side-chain of ionic liquid plasticizer could decrease the steric hindrance and the molecule force, and increase the more free volume. Moreover, the transparency of two plasticized PVC films also presented the good compatibility [9].

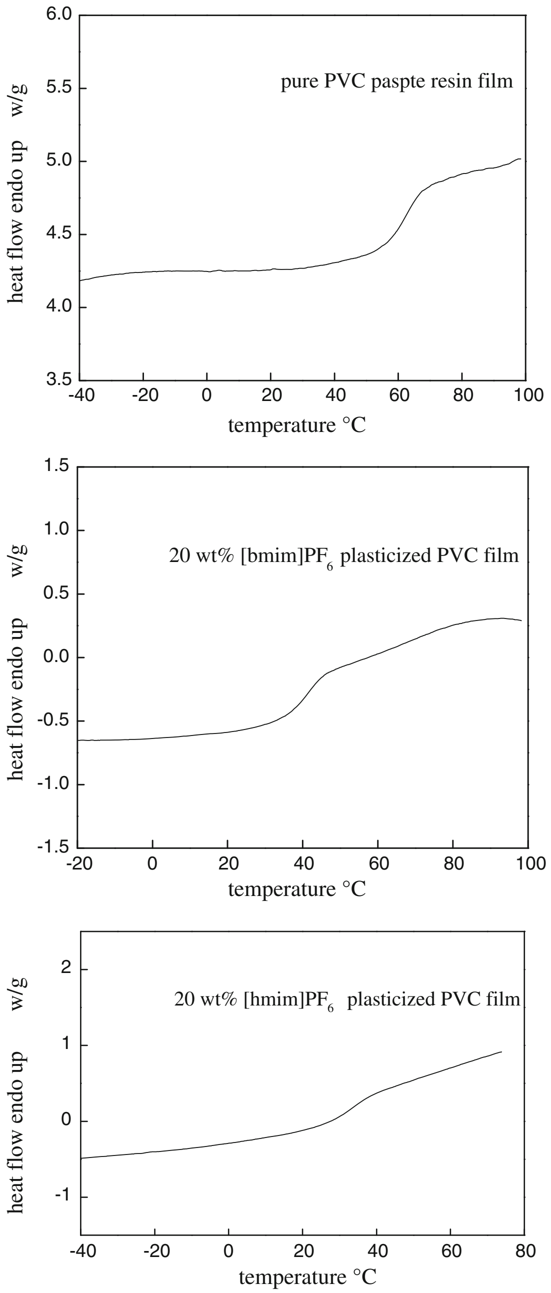
Mechanical properties

Table 1 provided the tensile strength, elastic modulus, and elongation at break of [bmim]PF_6 and [hmim]PF_6 plasticized PVC membranes. The data showed that two plasticizers could affect intensively samples' mechanical properties. With the plasticizer content increasing, the elastic modulus and tensile strength of samples decreased and elongation at break increased gradually. The elastic modulus of un-plasticized PVC paste resin membrane was about 2 times than the 40 wt% [bmim]PF_6 plasticized sample, the tensile strength 5 times, and the elongation at break 13 times. The effects of two plasticizers on mechanical properties were similar, only elastic modulus of [hmim]PF_6 plasticized sample was slightly lower than that of [bmim]PF_6 plasticized sample. Comparing the structures of [bmim]PF_6 with [hmim]PF_6, the side-chain length was different. More length flexible side-chain means more soft characteristics, which leads to more elastic modulus decrease. The low-molecular weight ionic liquid could diffuse into PVC macromolecules to form flexibility material, and the plasticized PVC paste resin showed rubber's characteristic. Besides, the lubrication of ionic liquid could weaken interface energy between PVC paste resin and plasticizer and increase material plasticity.

High temperature stability

Table 1 simultaneously provided the thermal stabilities of plasticized PVC samples, including mass loss ratio and decomposition temperature. Thermal stabilities of two

Fig. 1 DSC curves of three samples



plasticizers were nearly same. The mass loss ratio at 250 °C decreased with plasticizer content increasing, it reduced to about 17% till 40 wt% plasticizers. Especially, when the plasticizer contents increased to 30 and 40 wt%, the mass loss ratio decreased distinctly. Along with the increase of plasticizer content, the

Table 1 Mechanical properties and high-temperature stabilities of plasticized samples

Plasticizer	Content/wt%	Elastic modulus/MPa	Tensile strength/MPa	Elongation at break/%	Mass loss/%	Decomposition temperature/°C
	0	3755	43.4	13.1	34.44	226
[bmim]PF_6	10	3024	37.5	37.4	31.95	227
	20	2657	26.0	58.3	30.81	229
	30	2122	15.7	127.6	17.76	232
	40	1826	7.4	169.8	16.04	237
[hmim]PF_6	10	2654	37.0	37.9	32.30	228
	20	2234	28.5	60.2	30.26	230
	30	1837	15.3	128.2	24.67	234
	40	1543	7.9	171.3	17.74	236

decomposition temperature increased gradually. Based on the above facts, it is valid to enhance the thermal stability of PVC paste resin membranes by adding to ionic liquid [bmim]PF_6 or [hmim]PF_6.

UV stability

The PVC paste resin materials are prone to aging, and the stability of plasticized PVC resin is important to usage life. The physical and chemical durability of plasticizer is affected by structure, content, and external environment condition. Under most end-use conditions, the combination of plasticizer PVC paste resin can be maintained for a long period of time, but eventually phase separation occurs. Decomposition of PVC by UV light is dependent on additives present in PVC. Hence, this experiment adopted UV irradiation for testing the UV stability of plasticized PVC paste resin films.

The results showed that there was no weight loss and plasticizer exudation of samples before and after UV irradiation, except for elongation at break increasing. Table 2 provided the information on elongation at break of un-plasticized and plasticized PVC samples. Before and after exposure to UV ray, un-plasticized PVC sample had about four times increasement, while the ionic liquid plasticized samples had only about 10% change. The increasement of elongation at break was mainly due to polymer chain cleavage. UV light can make the polymer chain

Table 2 Elongation at break of samples before and after UV irradiation

Plasticizer content	Elongation at break before exposure (%)	Elongation at break after exposure (%)	Ratio (after/before)
None	13.1	53.2	4.06
20% [bmim]PF_6	58.3	62.5	1.07
20% [hmim]PF_6	60.2	65.8	1.09

generating free radicals and lead to cleavage finally. These radicals form aggregates or cross-connects and the crosslinking density increase. Because the ionic liquids consist of a cation and anion mixture, the interaction would lead to the free radical disappearing when the single electron of active free radical encounters the positive charge or negative charge of the ionic liquids. Hence, the plasticizer molecules can hinder the crosslinking of polymer chains by scavenging free radicals at the open ends [17–20].

Migration

Effect of the immersed time and environment media on migration

20 wt% [bmim]PF_6 or [hmim]PF_6 plasticized PVC samples were immersed in 100 mL 15% ethyl alcohol–water solution or deionized water, respectively. Every certain time interval, 20 µL sample from solution was analyzed by HPLC according to experimental procedure [21]. The results (Fig. 2) showed that two plasticizers could be detected after 1 day in water environment, due to the relatively weaker interaction between plasticizers and PVC paste resin. With time increasing, the migration sped up gradually, which was probably attributed to diffusion process. After the plasticizer molecules on the surface of PVC membrane were partly diffused into environment media, the produced empty holes increased contact area of solvent molecules and membrane samples, and the exchange rate was finally accelerated. The other possible factor resulted from solvent swelling. Compared

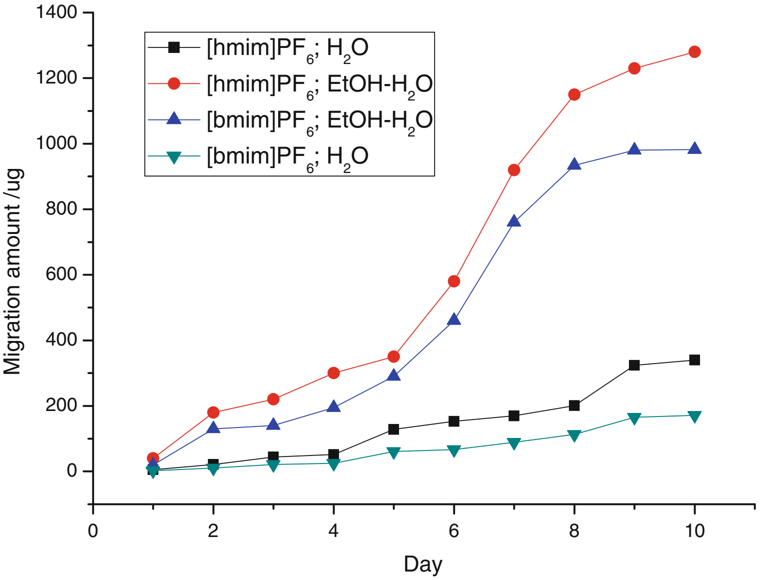


Fig. 2 Effect of the immersed time and environment media on migration

with the environment of deionized water, the migration of plasticizer in 15% ethyl alcohol–water solution was evidently greater.

Influence of temperature on migration

20 wt% plasticized samples were tested by immersing in 100 mL deionized water for 30 min, under constant temperature from 10 to 90 °C, respectively. Figure 3 showed the effect of temperature on migration amount. It could be seen that the plasticized PVC samples were relatively stable at room temperature. And the migration amount would increase rapidly with temperature increasing, especially, when the temperature exceeded 40 °C. Heating could promote the thermal motion of molecules and the swelling, and effectively promote the migration of plasticizers to the water.

Impact of pH on migration

The tested samples were immersed in 100 mL pH 2–10 water solution for 4 days at room temperature. pH was adjusted by adding diluted HCl or $NH_3 \cdot H_2O$ into deionized water. The results (Fig. 4) showed that the migration of plasticizers in PVC samples was greatly influenced by pH. Migration amount was smaller under near neutral condition than acidic or alkaline condition. It indicated that strong acidic or alkaline condition could promote the hydrolysis and water solubility of ionic liquids, and the migration was accelerated.

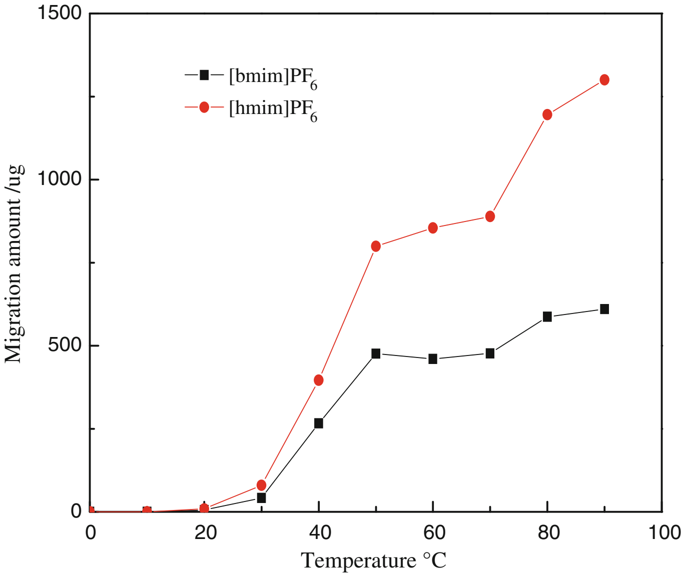


Fig. 3 Effect of temperature on migration

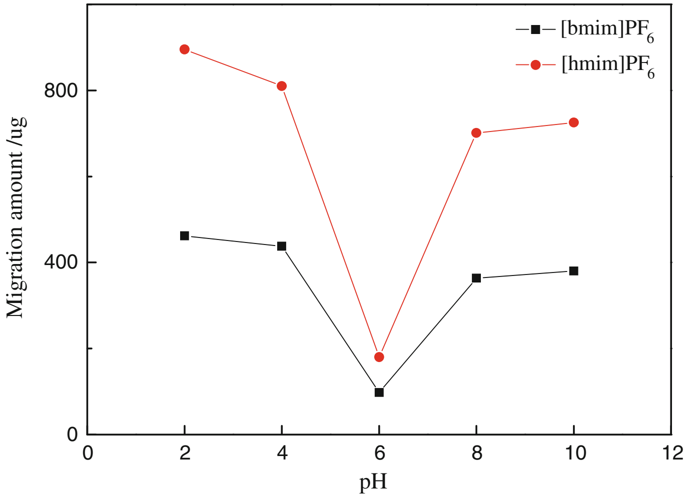


Fig. 4 Effect of pH on migration

Table 3 Properties of [bmim]PF$_6$ and DOP-plasticized PVC film samples

Plasticizer	30 wt% [bmim]PF$_6$	30 wt% DOP
Elongation at break %	128	119
Ratio (after/before) %/elongation at break after/before UV exposure	1.02	12.13
Mass loss of plasticizer %/migration in water for 10 days	5.1	10.6

Comparison of [bmim]PF$_6$ and DOP-plasticized PVC paste resins

Different from general purpose PVC resin, PVC paste resins often have quite different nature because of different manufacturers and their compositions. Hence, the reported data come from different sources are not comparable directly. For comparison of ILs and well-known plasticizers plasticized PVC paste resins, [bmim]PF$_6$ and DOP-plasticized PVC film samples were tested referring to the above experiments. The results (Table 3) showed that [bmim]PF$_6$ plasticized PVC sample had better stability and plasticizing ability than DOP-plasticized PVC sample.

Conclusions

The PVC paste resin is widely applied for artificial leather, film applicator coating, and medical catheters' production. These soft materials are usually improved by adding traditional plasticizers and other auxiliary agents. Though the current plasticizers are enough to offer numerous applications, different plasticizers have their shortcomings which often make their use inappropriate for certain applications. For example, phthalate plasticizers have been banned for medical and commodity applications. Hence, the replaceable plasticizers are considered in recent years.

For this purpose, we employed two kinds of room temperature ionic liquids, [bmim]PF_6 (1-butyl-3-methylimidazolium hexafluorophosphate) and [hmim]PF_6 (1-hexyl-3-methylimidazolium hexafluorophosphate), as plasticizer for PVC paste resin. The mechanical properties, thermal and ultraviolet (UV) ray stabilities, and migration characteristics of the PVC paste resin samples were investigated in details. The results showed that the mechanical properties of samples were improved obviously with the increasing content of plasticizers. The tensile strength and elastic modulus decreased, and the elongation at break of PVC paste resin membranes was distinctly enhanced. Moreover, thermal and UV stabilities of plasticized PVC samples also raised remarkably. The migration of plasticizers from plasticized PVC membranes to solvents was studied by HPLC analysis. The results showed that long time and high temperature could accelerate leaching and migration of plasticizers. Migration amount also increased under strong acidic-alkaline or alcohol conditions significantly.

Although the research results could not be immediately applied in plasticizer industry, it proved us more information on ionic liquids as plasticizers. It could help us to understand thoroughly the thermodynamics of ionic liquid–PVC interactions and design the desired characteristics of ionic liquid plasticizers by different combinations of anions and cations, also including the choice of the particular ILs for biodegradable polymers [22, 23].

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