

Ionic liquids: New generation stable plasticizers for poly(vinyl chloride)

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Received 20 January 2006; received in revised form 19 May 2006; accepted 28 May 2006

Available online 20 July 2006

Abstract

Room temperature ionic liquids (ILs), based on ammonium, imidazolium and phosphonium cations, were studied as novel plasticizers for poly(vinyl chloride), PVC. All the ILs tested were able to produce flexible PVC. Upon 20 wt% plasticization, some of the ILs lowered the glass transition temperature (T_g) of PVC more than that done by several traditional plasticizers. They showed good thermodynamic compatibility as well. Several ILs showed better leaching and migration resistance than the traditional plasticizers. This was, in particular, a significant observation considering the ongoing controversy regarding the leaching and migration issues of the commonly-used phthalate plasticizers. High temperature and ultraviolet (UV) ray stability of IL-plasticized PVC samples were also studied.

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Keywords: Ionic liquid; Plasticizer; Poly(vinyl chloride); Leaching; High temperature stability; UV stability

1. Introduction

For decades, plasticizers have been extensively used with polymers for producing flexible plastics to be used in commodity, engineering and medical applications. According to the council of International Union of Pure and Applied Chemistry (IUPAC), as stated in 1951, “a plasticizer is a substance or material incorporated in a material (usually a plastic or an elastomer) to increase its flexibility, workability or extensibility. A plasticizer may reduce the melt viscosity, lower the temperature of a second order transition, or lower the elastic modulus of the product” [1]. The first time application of a plasticizer for producing flexible plastics dates back to as early as 1862 [2]. Since then, plasticizers have come a long way to become an inherent part of current plastic industry. In 2003, worldwide plasticizer market was worth more than 10 billion pounds, with approximately 90% consumed by PVC [3]. In North America, the consumption was 2.2 billion pounds. Adipates, azelates, benzoates, phthalates, trimellitates and phosphates are some of the most frequently used

plasticizers. Phthalates are the most dominant class of plasticizers, composing about 87% of the entire plasticizer industry [4], while di(2-ethylhexyl) phthalate, DEHP, accounts for almost 50% of total plasticizer consumption [5].

Inside the polymer matrix, plasticizers act by breaking up the primary bonds holding the polymer chains together and forming secondary polymer–plasticizer bonds, and thus rendering mobility to polymer chains or chain segments. Since polymer–plasticizer interactions are weak, there exists a dynamic process where a plasticizer molecule attached to one site in the polymer network may be dislodged and be readily replaced by another [3]. Plasticizing efficiency of different plasticizers is thought to be a function of organic/inorganic moiety and functional groups present in the plasticizer molecule, structure, chain length, molecular weight (MW), etc. [6]. Different plasticizers, therefore, yield different plasticization effects because of differences in strength in plasticizer–polymer and plasticizer–plasticizer interactions. Commercially available plasticizers offer a wide range of end-use properties to different polymers. But applications of many of these plasticizers are often associated with a number of potential problems. Limited compatibility, poor stability at high temperatures or when exposed to UV rays, diminished lubricity at low temperatures, and flammability are some of the common technical challenges in the

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plasticizer industry [7]. However, for the past couple of decades, the most debated issue regarding plasticizers has been the leaching and migration of plasticizers, especially of the phthalates, from medical and commodity plastics. The shortcomings of phthalates in outdoor environment as part of engineering plastics have been well documented [7]. The European Union has already banned a number of phthalates from certain applications [8,9] and the US Food and Drug Administration has suggested that the manufacturers of plastic products consider the feasibility of replacing DEHP with safer alternatives [10].

Several alternative plasticizers are currently under investigation. ILs are one of these few novel alternatives which have shown promising results in the early stages of investigation [7]. ILs are actually molten salts that melt below at about 100 °C and typically consist of a bulky inorganic cation and an anion [11]. They have attracted much attention and gained recognition as potential environmentally benign solvents due to some of their unique properties. These properties of ILs result from the composite properties of the wide variety of cations and anions. Most of the ILs are liquid at room temperature and usually exhibit negligible vapor pressure, which reduces the possibility of air pollution and loss of materials at ambient conditions [12]. Many of the ILs are liquid over a wide temperature range (often more than 300 °C). They have low melting points (as low as –96 °C has been reported), which can be attributed to the large asymmetric cations having low lattice energies [13]. As a class of materials, ILs are highly solvating for both organic and inorganic materials. Many of them are nonflammable, non-explosive [14] and have high thermal stability. ILs usually have high electric conductivity (10^{-1} – 10^{-2} S m $^{-1}$) and possess a wide electrochemical window (commonly larger than 3.0 V) [15]. They are also recyclable, which can be helpful in reducing landfill waste.

Even though the use of ILs in an industrial process for organic synthesis dates back to 1990 [16], most IL-research has been

confined to academic laboratories. They have been studied as novel solvents for organic synthesis, polymerization, and liquid–liquid extraction [17,18], in electrochemical studies [19,20], gas chromatography [21,22], for catalysis [23] and biocatalysis [24–26], as plasticizers [27–33], storage and transportation media for highly toxic and flammable gases [16] and mass spectrometry [34]. One of the unique applications of ILs is as novel plasticizers, as has been shown in a number of earlier publications [27–33]. Considering the diverse challenges associated with different traditional plasticizers [7], ILs hold prospects as alternative plasticizers in the rapidly growing plastic industry.

As plasticizers, ILs were initially found to have better compatibility with poly(methyl methacrylate), PMMA than DEHP [27]. It was also found that they were capable of lowering the T_g of PMMA much more than DEHP does, while improving the high temperature stability of PMMA and also providing a wide temperature range for flexible PMMA-based plastics [27–30]. With the breadth of the PVC-plasticizer market in mind, the effectiveness of ILs as plasticizers for PVC was studied. Here we focus on the use of ILs as plasticizers for diverse applications in flexible PVC.

2. Experimental

2.1. Materials

Suspension polymerized PVC ($M_n = 22,000$) was obtained from Aldrich Chemical Company Inc., Milwaukee, WI, and HPLC grade tetrahydrofuran (THF) was obtained from Fisher Scientific, Fairlawn, NJ. ILs and traditional plasticizers studied are shown in Table 1 along with their abbreviated names and the names of the suppliers. Fig. 1 shows the chemical structures of these ILs and the traditional plasticizers.

The effectiveness of these ILs and traditional plasticizers were studied in terms of flexibility, mechanical properties,

Table 1
List of different ILs and traditional plasticizers, their abbreviated names, and suppliers

Plasticizer	Abbreviated name	Supplier
<i>Traditional plasticizer</i>		
Di(2-ethylhexyl) phthalate	DEHP	Sigma Chemical co., St. Louis, MO
Diisodecyl phthalate	DIDP	Fluka chemie GmbH, Switzerland
Trioctyl trimellitate	TOTM	Aldrich Chemical Co., Milwaukee, WI
Acetyl tri- <i>n</i> -hexyl citrate (Citroflex [®] A6)	Citroflex A6	Aldrich Chemical Co., Milwaukee, WI
<i>N</i> -Butyryl tri- <i>n</i> -hexyl citrate (Citroflex [®] B6)	Citroflex B6	Aldrich Chemical Co., Milwaukee, WI
<i>IL</i>		
1-Butyl-3-methylimidazolium hexafluorophosphate	[bmim ⁺][PF ₆ ⁻]	Dr. William M. Reichert, The Univ. of Alabama
1-Hexyl-3-methylimidazolium dioctylsulfosuccinate	[hmim ⁺][doss ⁻]	Dr. Jim Davis Jr., Univ. of South Alabama
1-Hexyl-3-methylimidazolium hexafluoroborate	[hmim ⁺][BF ₄ ⁻]	Dr. William M. Reichert, The Univ. of Alabama
1-Hexyl-3-methylimidazolium hexafluorophosphate	[hmim ⁺][PF ₆ ⁻]	Dr. William M. Reichert, The Univ. of Alabama
Tetrabutyl ammonium dioctylsulfosuccinate	[tbam ⁺][doss ⁻]	Dr. Jim Davis Jr. Univ. of South Alabama
Tetrabutyl phosphonium dioctylsulfosuccinate	[tbPh ⁺][doss ⁻]	Sachem, Inc., Austin, TX
Tributyl (tetradecyl) phosphonium dodecylbenzenesulfonate	[tbtdPh ⁺][dbs ⁻]	Dr. Rex Ren, IL-Tech Inc.
Tributyl (tetradecyl) phosphonium methanesulfonate	[tbtdPh ⁺][mes ⁻]	Dr. Rex Ren, IL-Tech Inc.
Trihexyl (tetradecyl) phosphonium bis(trifluoromethane) sulfonylimide	[thtdPh ⁺][Tf ₂ N ⁻]	Cytec Canada, Inc., Ontario, Canada
Trihexyl (tetradecyl) phosphonium chloride	[thtdPh ⁺][Cl ⁻]	Cytec Canada, Inc., Ontario, Canada
Trihexyl (tetradecyl) phosphonium decanoate	[thtdPh ⁺][deca ⁻]	Cytec Canada, Inc., Ontario, Canada
Trihexyl (tetradecyl) phosphonium dodecylbenzenesulfonate	[thtdPh ⁺][dbs ⁻]	Dr. Rex Ren, IL-Tech Inc.
Trihexyl (tetradecyl) phosphonium methanesulfonate	[thtdPh ⁺][mes ⁻]	Dr. Rex Ren, IL-Tech Inc.

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