Unprecedented exploration of ionic liquids as additives which astonishes the thermal stability of PVC formulations

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Abstract. The use of ionic liquids as additives and an economic and environmentally benign alternative to conventional inorganic and organic additives in poly(vinyl chloride) (PVC) formulation is investigated by using thermogravimetric analysis. The present study deals with an elegant exploration of the resulting thermal profiles to disclose the pattern of thermal degradation for *N*-butylpyridinium hexafluorophosphate and PVC formulation as well. Furthermore, non-isothermal kinetic investigations providing sound information about kinetic parameters, such as activation energy and frequency factor by using the Coats–Redfern equation in the temperature range of 593–663 K for *N*-butylpyridinium hexafluorophosphate and 423–473 K for the resulting PVC formulation were performed.

Keywords. Ionic liquids; PVC formulation; Coats–Redfern model; TGA.

1. Introduction

Poly(vinyl chloride) (PVC) has been extensively used as a thermoplastic material in the preparation of valuable materials, such as in packaging, health care devices, toys, construction materials, clothes, pipes, etc. Utilization of PVC for such widespread applications is because of its versatile nature, low cost, transparency, flexibility and compatibility with a variety of additives, which can improve its mechanical, physical and chemical properties [1]. Its versatile nature and other favourable properties have made PVC the third largest commodity polymer.

It is well known that PVC has a strong tendency to degrade when exposed to heat, shear or radiation (such as ultraviolet (UV) light) during melt-processing and practical applications [2,3]. The process of degradation initiates with a dehydrochlorination reaction and is subsequently accelerated by the release of hydrogen chloride (HCl). Quite a large number of investigations have also been made to increase the stability of PVC by introducing stabilizers during the formulation of PVC. Although the thermal degradation mechanism of PVC is well established, it is assumed that the process of dehydrochlorination is to be auto-catalysed by HCl. Notably, the stabilizing mechanism for PVC accentuates for an irreversible bonding between the stabilizing material and the eliminated HCl; such interactions are responsible for the delayed degradation of the formulations. At present, lead salts, metal soaps and organotin compounds as well as organic heterocyclic motifs are highly exploited for this purpose [4,5], but certain limitations have been advocated to define the

scope of these organic and inorganic materials, such as their toxicity, environmental issues related to these metallic pollutants, their efficiency and, of course, their expensiveness. Additionally, the lead salts are found to be toxic and pose severe environmental issues, whereas organotin compounds are very expensive. As a consequence, PVC formulations with optimized thermal stability and efficiency, as well as sustainable stabilizing materials, are strongly desired to fulfil the needs for a healthy and clean society. Considering the overall properties viz. non-volatility, environmental friendliness, high thermal stability and comparatively cheaper ionic liquids (ILs) can be potential candidates for prohibition of thermal degradation of PVC or extending the scope of ILs in the industrial scale up processes of polymer formulations.

The unique set of properties of ILs is the key reason for their utilization in every field of present-day science. ILs are supposed to be considered as supramolecular materials and provide a broad spectrum of applications, such as green medium for organic reactions, electrolytes for solar and fuel cells, heat transfer fluids in nuclear reactors, in dissolution of cellulose, etc. [6–8]. The versatility of these molecules is attributed to their exceptional structural behaviour in vapour and solution phases [9–11]. Pursuing alternative applicative paradigms for the ILs that go away from this omnipresent attitude has the potential to uncover corresponding materialistic regimes. To date, a tremendous literature exists on the applications of ILs in the synthesis and processing of polymerization, where ILs played vital roles in polymerization, depolymerization and plasticization [12–15]. In this context, Mustafizur and Christopher [12] elegantly explored room

temperature imidazolium and phosphonium-based ILs as plasticizer materials for PVC. In accordance with their results, it has been cleared that imidazolium and phosphonium ILs were found to be excellent plasticizing materials for PVC. In 2011, Sui and Lin [13] utilized room temperature ILs, [bmim]PF₆(1-butyl-3-methylimidazolium hexafluorophosphate) and [hmim]PF₆(1-hexyl-3-methylimidazolium hexafluorophosphate), as plasticizers for PVC paste resin. The results of the study revealed that the thermal properties of the PVC resin were improved notably. Independently, Lin and Sui [14] demonstrated the use of room temperature ILs, such as [omim]PF₆, [bupy]PF₆, [C₁₄mim]Br and [C₁₆mim]Br as plasticizers for PVC paste resin. To our delight, we [15], very recently initiated the use of ILs in the field of sealants and thiakols. It has been noted that ILs exhibit exceptional solvating properties and enhance the solubility of the thiakol material in ILs *via* the possible breakdown of the structural framework of the thiakol material very elegantly.

Heating of a sample at a specified rate, under optimized conditions, leads to quite a large number of structural transformations, such as melting, sublimation, polymorphic transformation or degradation. These solid-state reactions are highly appreciated in material sciences, especially polymorphic transformations, glass transition and degradation [16–18]. Thermal analytical methods, which deal with the weight or enthalpy change of the system, are of high interest, because the data can be further explored to investigate the kinetics of the studied system. Many solid-state kinetic models have been developed in the past century. Coats–Redfern is one of the widely used models based on the use of the integral form of the non-isothermal rate law and provides the best linear fit. Basically, the Coats–Redfern equation was derived by assuming a first-order model, but it has also been explored like any other reaction model [19,20].

In continuation with our previous work [21] to clarify the chemistry of processes which inhibits the thermal degradation of PVC by ILs and to explain the synergistic effect in the presence of such salts, herein, the attempts have been made to study the thermal stability of the PVC sheet formulated in ILs

Scheme 1. Synthesis of *N*-butylpyridinium bromide.

(*N*-butylpyridinium bromide [bpy]Br and *N*-butylpyridinium hexafluorophosphate [bpy]PF₆). For the first time, [bpy]Br and [bpy]PF₆ are used as processing aid ingredients in the PVC formulation. The details of thermogravimetric analysis (TGA) profiles and the energy of activation by applying the Coats–Redfern model are presented and discussed in the following sections.

2. Experimental

2.1 Materials

The materials used in the experiments, viz. Advastabase and PE-wax, were of commercial grade and used as received. Pyridine, tetrabutylammonium bromide and *n*-butylbromide were purchased from S.D. Fine Chemicals Ltd., Mumbai, India. Potassium hexafluorophosphate was procured from Sigma, Aldrich and used as received. PVC resin was received as a gift sample from Reliance Industries, Mumbai, India.

The details regarding the synthesis and the instrumentation involved for the tuning and characterization of ILs and PVC formulation are given below.

2.2 Procedure for synthesis of *N*-butylpyridinium bromide

Our earlier communication suggested an effective, inexpensive and rapid method for the synthesis of imidazolium and pyridinium-based ILs [6]. The typical procedure for the synthesis of IL [bpy]Br (scheme 1) and a process of an anion metathesis for the preparation of [bpy]PF₆ (scheme 2) are described below.

An equimolar stirred solution of pyridine (30 mmol) and butyl bromide (30 mmol) was slowly added to molten tetrabutylammonium bromide. After the complete addition, the reaction mixture was cooled to room temperature forming a white solid. The resulting white solid was then washed with an excess of tetrahydrofuran to collect an oily white solid of [bpy]Br and was immediately transferred to a vacuum oven for drying.

2.3 Procedure for synthesis of *N*-butylpyridinium hexafluorophosphate

Saturated solutions of potassium hexafluorophosphate [KPF₆] and [bpy]Br in quartz doubly distilled water were prepared

Scheme 2. Synthesis of *N*-butylpyridinium hexafluorophosphate *via* anion metathesis.

Table 1. Formulations of PVC using ILs.

Entry	PVC resin (g)	IL (g)		Commercial stabilizer (g)	PE-wax (g)
		[bpy][Br]	[bpy][PF ₆]		
A	10	—	0.05	0.15	0.05
B	10	—	0.10	0.10	0.05
C	10	—	0.15	0.05	0.05
D	10	—	0.20	0.00	0.05
E	10	0.05	—	0.15	0.05
F	10	0.10	—	0.10	0.05
G	10	0.15	—	0.05	0.05
H	10	0.20	—	0.00	0.05
I	10	—	—	—	0.05

separately. Then, an aqueous solution of [KPF₆] was slowly added to an aqueous solution of [bpy]Br with constant stirring. During addition, a white solid of *N*-butylpyridinium hexafluorophosphate [bpy]PF₆ was precipitated and the product was separated and collected over a suction pump. Finally, the resulting white solid was washed with excess of distilled water to remove water soluble impurities.

2.4 Formulation of PVC resin

Formulation of PVC resin was achieved *via* the solution cast method and by varying the concentration of the stabilizer with synthesized ILs. In a round bottomed flask, PVC (100 phr) was stabilized by 1 phr of advastabase (OBS) and a combination of the synthesized ILs ([bpy]Br or [bpy]PF₆) in variable weight ratios in tetrahydrofuran as a solvent as per the formulation shown in table 1. The mixture was further kept for 12 h to swell.

Thereafter, the swelled material was heated at 343 K to obtain a clear solution, in which a solution of polyethylene wax in xylene was added. Finally, the resulting mixture was poured on a square-shaped mould to obtain a PVC sheet by evaporation of the solvent. The resulting sheet was dried by evaporation of the solvent in open air and considered for further testing.

2.5 Analytical methods

2.5a UV-visible spectrophotometric analysis of [bpy]Br:

A Shimadzu UV-visible spectrophotometer with UV-Probe 3.5 software was used for the analysis of [bpy]Br. For the authenticity of the results, the instrument was calibrated using 0.1 M KNO₃ (which shows absorption at 302 nm) and other UV absorbing standards such as benzene, ethanol, etc.

2.5b FTIR analysis of [bpy]Br and [bpy]PF₆: Fourier transform infrared (FTIR) analysis of the synthesized ILs was performed on the FTIR affinity model, Shimadzu; dry KBr is used to set the background; thereafter, a KBr pellet was

Figure 1. UV-visible spectrum of pure *N*-butylpyridinium bromide.

developed and analysed. Prior to the analysis, the instrument was calibrated by performing an IR scan of a polystyrene film.

2.5c Oven test: The compressed PVC sheets were cut into 1 cm × 1 cm strips. A total of seven samples from each formulation were placed in an oven at 453 K and subjected to a static thermal test for comparison of discolouration. At a time, one strip was removed after every 10 min from each formulation for visual examination.

2.5d Details of TGA: To examine an effect of [bpy]Br and [bpy]PF₆ on the thermal stability of the PVC, samples were subjected to TGA. In this case, a solution cast method was used for formulating and preparing PVC samples. A Perkin-Elmer TGA-4000 thermogravimetric analyser was used to study the thermal stability of the synthesized ILs and a PVC sheet under a N₂ atmosphere, which was kept in an air-conditioned lab with a humidity of 5–10%. Samples having weights in the range of 4 to 6 mg were used for the measurements. The sample volumes of the alumina pans were

10 mm³ with a cell volume of 3.4 ml and were subjected to nitrogen purging with a flow rate of 20 ml min⁻¹. The heating rate of the sample was always kept at 5 K min⁻¹.

2.5e Coats–Redfern model: Amongst the thermal methods of analysis, TGA is an important method which subtly provides information about the processes like nucleation,

change in geometry and kinetics [22]. The Coats–Redfern method was used to determine the energy of activation (equations 1 and 2) [23].

$$\ln \frac{g(\alpha)}{T^2} = \ln \left[\frac{AR}{\beta E_a} \left(1 - \frac{2RT}{E_a} \right) \right] - \frac{E_a}{RT}, \quad (1)$$

and assuming $2RT/E < 1$, leads to

$$\ln \frac{g(\alpha)}{T^2} = \ln \left[\frac{AR}{\beta E} \right] - \frac{E_a}{RT}. \quad (2)$$

The slope of the plots of $\ln(g(\alpha)/T^2)$ vs. $1/T$ allows the calculation of activation energy (E_a).

3. Results and discussion

3.1 Tuning of an IL [bpy]Br

When [bpy]Br was subjected to anion metathesis with potassium hexafluorophosphate yields [bpy]PF₆. Before implementation of the strategy, i.e., the use of ILs in PVC formulation, the purity of ILs is much more important. Therefore,

Figure 2. FTIR spectrum of *N*-butylpyridinium bromide.

Figure 3. Thermogram of *N*-butylpyridinium bromide.

Figure 4. FTIR spectrum of *N*-butylpyridinium hexafluorophosphate.

the purity of [bpy]Br was checked by performing UV–visible and FTIR analyses.

3.2 UV–visible spectrophotometric analysis of [bpy]Br

Spectrophotometry and spectrometric methods provide a broad spectrum of applications in present-day science. In the case of ILs, an impurity due to oxidation is very difficult to analyse either by using infrared or NMR spectrophotometry or even by mass spectrometry. Thus, UV–visible spectrophotometry [24] is the most suitable method to predict an impurity related to the oxidations of ILs. To our delight, the absorption spectrum (figure 1) of pure [bpy]Br showed appreciable absorption in the UV region, while there is no such absorption found in the visible region. This spectral response can be attributed to π electronic transitions of the pyridinium ring moieties.

3.3 FTIR studies of [bpy]Br

The appearance of a broad spectrum over 3500 cm^{-1} in the FTIR of [bpy]Br confirmed the presence of water molecules and the hydrophilic nature of the salt (figure 2). The C–H stretching vibrations were observed between 3035 and

2933 cm^{-1} . On the other hand, the C=C and C=N vibrations appeared in a region between 1630 and 1525 cm^{-1} and our FTIR spectrum showed absorption at 1633 cm^{-1} . The absorptions due to ring vibrations appeared near 1168, 970, 833 and 777 cm^{-1} as shown in figure 2.

3.4 TGA-differential thermal analysis (DTA) of [bpy]Br

The thermal profile (figure 3) of the synthesized IL [bpy]Br indicated that a continuous weight loss started from 373 to 533 K cleared the removal of associated water molecules with the IL [bpy]Br.

3.5 Tuning of [bpy]PF₆

After successful synthesis of highly pure [bpy]Br, an anion metathesis was performed to obtain [bpy]PF₆. Thereafter, the product of anion metathesis was characterized *via* FTIR and the thermal method of analysis. Finally, both of these synthesized salts as additives in the PVC formulations have been investigated thoroughly.

3.6 FTIR studies of [bpy]PF₆

FTIR analysis (figure 4) of the resulting [bpy]PF₆ showed the absence of a broad peak in the range of 3600 – 3300 cm^{-1} ,

Figure 5. Thermogram of *N*-butylpyridinium hexafluorophosphate.

Figure 6. Thermogram of the pure PVC material.

Table 2. Oven test of the synthesized PVC resin with and without ILs.

Time/min	Commercial Stabilizer + [bpy][PF ₆]				Without ILs
	A	B	C	D	I
10
20
30
40
50
60
70
80
Time/min	Commercial Stabilizer + [bpy][Br]				
	E	F	G	H	
10
20

Table 2. (continued)

Time/min	Commercial Stabilizer + [bpy][Br]			
	E	F	G	H
30
40
50
60
70
80

which revealed that the compound was free from moisture. Hence, it can be stated that [bpy]PF₆ is not hygroscopic like [bpy]Br. The C–H stretching vibrations were observed in the region of 3100–3000 cm^{−1}. Sharp peaks observed over 1650 and 1550 cm^{−1} were attributed to C=C and C=N vibrations, respectively.

The rotational–vibrational spectra of [bpy]Br and [bpy]PF₆ exhibited moderate to weak absorption bands between 1150 and 1080 cm^{−1}, which are attributed to exocyclic N–C stretching vibrations present in *N*-alkylated pyridinium salts. The accumulation of a positive charge on the nitrogen atom in the synthesized pyridinium salts ([bpy]Br and [bpy]PF₆) is evident that the quaternization of pyridine introduces changes in the structure of the pyridine molecule. Generally, the absorptions for pyridine in the IR region found that 3070–3020 cm^{−1} (C–H stretch), 1660–1590 and 1500 cm^{−1} (C=C and C=N) and ring vibrations are found near 1200, 1100–1000, 900–650 and 710 cm^{−1} [25] by altering the absorption in the regions of aromatic C–H vibrations and in the region of C=C and C=N vibrations.

3.7 TGA-DTA of [bpy]PF₆

The thermogram (figure 5) of [bpy]PF₆ showed that the IL was quite stable up to 593 K. The thermal degradation step observed in the TGA curve was single and sharp. It was also found that the weight loss was about 90.78% in the temperature range of 593 to 653 K, while the rest of TGA was free from any weight loss during the starting temperature to 373 K, which indicated that the IL was free from water molecules and having high moisture stability. After completion of single step degradation, the TGA curve further showed sluggish degradation due to the thermal breakdown of the residual part.

3.8 TGA of pure PVC

The thermogravimetric profile (figure 6) of the pure PVC material cleared that PVC degrades in three steps, which is in good agreement with the literature [26]. Further, the TGA curve cleared that the first step of thermal degradation was

Figure 7. Thermogram of PVC formulation (entry A, table 1).

Scheme 3. A probable mechanism of the zipper elimination reaction of pure PVC.

Scheme 4. Probable mechanism of the dehydrochlorination of the PVC sheet.

Table 3. Energy of activation for the decomposition of [bpy]PF₆ and PVC sheets.

Entry	Order of reaction (<i>n</i>)	Temperature (K)		Energy of activation (kJ mol ⁻¹)		Frequency factor		<i>R</i> ²	
		A	B	A	B	A	B	A	B
1	0.1	—	423–473	—	30.77	—	208.42	—	0.99
2	0.5				13.77		0.6863		0.99
3	0.1	593–663	568–623	129.09	1.21	2.6306×10^{10}	1.5458×10^{-2}	0.99	0.99
4	0.5			67.08	—	3.5138×10^4	—	0.99	—

A: *N*-butylpyridinium hexafluorophosphate and B: PVC resin.

due to the dehydrochlorination of PVC resin and it was in the temperature range of 573–693 K with the weight loss of 63.54%. The second and third steps of the thermal decomposition were in the range of 693–803 and 803–973 K, respectively. The second step indicates the possibility of thermal rearrangements in the polyenes (after dehydrochlorination), while the third step represents the scissoring of the carbon skeleton.

3.9 Oven test

The PVC formulations with varying concentrations of [bpy]Br and [bpy]PF₆ were subjected to oven test at 453 K. The results seem to show that sample I (without any stabilizer) was unstable, since it developed colour after 10 min of testing. The formulations (entry A) with [bpy]PF₆ were stable up to 50 min, the colour of the formulation was slightly brownish, but not blackish, while the other formulations B, C and D decomposed after 30 min (turned black). The formulation entries E, F, G and H containing [bpy]Br did not show the stabilization effect on PVC, as they resulted in rapid degradation within 10 min (table 2).

On the basis of oven test carried on samples with [bpy]Br and [bpy]PF₆, it can be concluded that [bpy]PF₆ is a stabilizer, while [bpy]Br does not have any stabilization effect.

3.10 TGA of PVC composites

A thermogram of the PVC formulation enabled the use of [bpy]PF₆ with commercial stabilizers as the stability of the PVC sheet and the formulation was observed to be 790–800 K. A four-step decomposition of a PVC formulation and a possible mechanism involved for such decomposition is shown in figure 7. The weight loss during the first step was 47.238%, which was comparatively low in the case of PVC formulation. The probable reason behind this may be the active involvement of [bpy]PF₆ through an interaction between ILs and PVC. Probably, [bpy]PF₆ performs the role of an HCl scavenger and hindered the process of dehydrochlorination.

The major polymer chain degradation of PVC occurs by the elimination of HCl (dehydrochlorination, zipper elimination reaction) and simultaneous formation of the conjugated double bond along the length of the polymer backbone

(scheme 3), leading to a colour change (progressing with the extent of breakdown from light yellow, through reddish brown, to almost black in severe cases), which causes deterioration in physical, chemical and electrical properties of the PVC end product [27–33].

The stability of PVC formulation is attributed to the thermal reaction between ILs and the PVC backbone as shown in scheme 4. We suggest that during the course of the reaction, an ionic mechanism is involved in trapping liberated HCl along [bpy]PF₆ and HF. Trapping of liberated HCl will stop catalytic activity of HCl, which removes HCl further from the PVC molecule and degrades it [21].

3.11 Coats–Redfern model

The values for calculated energy of activation are summarized in table 3. The results indicated that the energies of activation for the decomposition of [bpy]PF₆ were 129.09 and 67.08 kJ mol⁻¹ (593–663 K) for *n* = 0.1 and 0.5, respectively. The PVC sheet showed 30.77 and 13.77 kJ mol⁻¹ (423–473 K) for *n* = 0.1 and 0.5, respectively. Indeed, it is difficult for us to account for the order of reaction as in the fraction (0.1 and 0.5).

4. Conclusion

During the last few decades, a wide variety of innovative additives, either stabilizers or plasticizers, were developed for polymeric formulations. IL [bpy]PF₆, which was synthesized in the laboratory, worked excellently as a stabilizer for PVC formulations. The work outlined suggested a framework of the use of ILs, which seems comprehensive because it expands the consideration of hazard from the use of toxic inorganic metal precursors, as well as the use of less stable and highly reactive materials to include environmental, physical and global hazards to a certain extent. These findings surely open avenues in front of the chemists to explore ILs elegantly towards sustainable polymeric formulations.

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