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Thermal degradation studies of alkyl-imidazolium salts and their application in nanocomposites

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Abstract

Increasing the thermal stability of organically-modified layered silicates is one of the key points in the successful technical application of polymer-layered silicate nanocomposites on the industrial scale. To circumvent the detrimental effect of the lower thermal stability of alkyl ammonium-treated montmorillonite, a series of alkyl-imidazolium molten salts were prepared and characterized by elemental analysis, thermogravimetry (TGA) and thermal desorption mass spectroscopy (TDMS). The effect of counter ion, alkyl chain length and structural isomerism on the thermal stability of the imidazolium salts was investigated. Alkyl-imidazolium-treated montmorillonite clays were prepared by ion exchange of the imidazolium salts with Na-montmorillonite. These organically-modified clays were characterized by X-ray diffraction (XRD), TDMS and thermogravimetry coupled with Fourier transform infrared spectroscopy (TGA-FTIR), and compared to the conventional quaternary alkyl ammonium montmorillonite. Results indicate that the counter ion has an effect on the thermal stability of the imidazolium salts, and that imidazolium salts with PF_6^-, $N(SO_2CF_3)_2^-$ and BF_4^- anions are thermally more stable than the halide salts. A relationship was observed between the chain length of the alkyl group and the thermo-oxidative stability; as the chain length increased from propyl, butyl, decyl, hexadecyl, octadecyl to eicosyl, the stability decreased. The results also show that the imidazolium-treated montmorillonite has greater thermal stability compared to the imidazolium halide. Analysis of the decomposition products by FTIR provides an insight about the decomposition products which are water, carbon dioxide and hydrocarbons.

Keywords: Imidazolium salts; Montmorillonite; Nanocomposite; Thermal stability; Degradation

1. Introduction

In recent years, polymer-layered silicate nanocomposites (PLSNs) have attracted a great deal of interest [1,2], since they exhibit dramatic improvements in mechanical [3], thermal [4], barrier [5], and flame-retardant [6–8] properties compared to the neat or traditionally-filled resins. In addition, because of the length scale involved that minimizes scattering, nanocomposites may be transparent. These property improvements result from only a 2–5% addition of the dispersed nanophase.

The layered silicates used for this purpose are mica, fluoromica, montmorillonite (MMT), vermiculite, hectorite, fluorohectorite, saponite, etc. which belong to the structural family known as the 2:1 phyllosilicates [9,10]. Their crystal structure consists of layers made up of two silica tetrahedral sheets fused to an edge-shared octahedral sheet of either aluminum or magnesium hydroxide. Stacking of the layers leads to a regular van der Waals gap between the layers called the interlayer or gallery. Isomorphic substitution within the layers generates charge deficiency (i.e. Fe^{2+} or Mg^{2+} replacing Al^{3+} in montmorillonite and Li^+ replacing Mg^{2+} in hectorite). The deficit charges are compensated by cations (usually Na^+ or K^+) sorbed between the three-layer clay mineral sandwiches. These are held relatively loosely and give rise to the significant cation-exchange properties.

The most commonly used layered silicate is montmorillonite. MMT owes this attention to its ability to show

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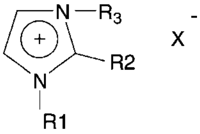
Table 1
Alkyl-imidazolium molten salts with different alkyl groups and counter ions



Salt	R1	R2	R3	X^-
DMPIM·Cl	Methyl	Methyl	Propyl	Cl^-
BDMIM·Cl	Butyl	Methyl	Methyl	Cl^-
BMIM·Cl	Butyl	H	Methyl	Cl^-
DDMIM·Cl	Decyl	Methyl	Methyl	Cl^-
HDMIM·Cl	Hexadecyl	H	Methyl	Cl^-
DMHDIM·Cl	Methyl	Methyl	Hexadecyl	Cl^-
DMHDIM·Br	Methyl	Methyl	Hexadecyl	Br^-
DMEiIM·Br	Methyl	Methyl	Eicosyl	Br^-
DMEtBIM·Br	Methyl	Methyl	Ethylbenzene	Br^-
EtMIM·BF_4	Ethyl	H	Methyl	BF_4^-
DMPIM·BF_4	Methyl	Methyl	Propyl	BF_4^-
BDMIM·BF_4	Butyl	Methyl	Methyl	BF_4^-
DMiBIM·BF_4	Methyl	Methyl	Isobutyl	BF_4^-
DDMIM·BF_4	Decyl	Methyl	Methyl	BF_4^-
DMHDIM·BF_4	Methyl	Methyl	Hexadecyl	BF_4^-
AlDMIM·BF_4	Allyl	Methyl	Methyl	BF_4^-
DMEiIM·BF_4	Methyl	Methyl	Eicosyl	BF_4^-
DMiBIM·PF_6	Methyl	Methyl	Isobutyl	PF_6^-
BDMIM·PF_6	Butyl	Methyl	Methyl	PF_6^-
DDMIM·PF_6	Decyl	Methyl	Methyl	PF_6^-
DMHDIM·PF_6	Methyl	Methyl	Hexadecyl	PF_6^-
DMEtBIM·PF_6	Methyl	Methyl	Ethylbenzene	PF_6^-
EtMIM·$N(SO_2CF_3)_2$	Ethyl	H	Methyl	$N(SO_2CF_3)_2^-$

extensive interlayer expansion or swelling which, in turn, is related to its peculiar structure. The efficiency of the MMT in improving the properties of the polymeric materials is primarily determined by the degree of its dispersion in the polymer matrix. However, the hydrophilic nature of the MMT surface impedes homogenous dispersion in the organic polymer phase. To overcome this problem, it is often necessary to make the surface organophilic, prior to its use, by ion-exchange reactions involving the exchange of organic cationic surfactants for the interlayer cations. This necessarily results in an increase in the interlayer separations. The number of surfactant molecules that reside in the galleries is determined by the cation-exchange capacity (CEC) of the silicate, and is measured in meq./g. The role of organic cation is to reduce the surface energy of the MMT surface, improving the wetting characteristics with the organic polymer. Successful formation of a hybrid is, to a great extent, determined by the miscibility of individual components of the system.

Although the organo-clay complexes have been recognized for a long time [11,12], the interest in studying these layered silicate materials as nanoscale reinforcing agents for polymeric materials has been developed recently. Elevated temperatures are necessary for nanocomposite processing [13–15], and most polymeric materials require prolonged service in air at higher temperatures. Thus, the onset of the thermal decomposition of the organic modifier sets the ceiling temperature for polymer processing. Therefore, it is of prime importance to study the thermal stability of the organic modifier and its implications on the nanocomposite processing and properties.

The objective of this study stems from our observation of poor nanocomposite processing stability. Therefore, in the pursuit of achieving higher thermostability for the PLSNs, and to avoid the deleterious degradation of organo-layered silicates, a series of montmorillonite clays were treated with several imidazolium molten salt surfactants. In order to assess the potential of using the imidazolium molten salts as a substitute for the conventional alkyl ammonium surfactant, a detailed study was carried out using thermogravimetry (TGA), Fourier transform infrared spectroscopy (FTIR) and thermal desorption mass spectroscopy (TDMS) techniques. The effect of counter ions, alkyl chain length and structural isomerism on the decomposition of the imidazolium salts was investigated.

2. Experimental[2]

2.1. Preparation and characterization of alkyl-imidazolium salts

Imidazolium salts were typically prepared as follows: 1,2-dimethyl-imidazole (distilled, 0.95 mol) was added to

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[2] The identification of any commercial product or trade name does not imply endorsement or recommendation by the National Institute of Standards and Technology or the Air Force Office of Scientific Research.

Table 2
Elemental analysis data of alkyl-imidazolium molten salts

Compound	Molecular formula	Molecular weight	C (%)	H (%)	N (%)	Cl (%)	Br (%)	B (%)	P (%)	F (%)	S (%)	O (%)
DMPIM·Cl	$C_8H_{15}N_2Cl$	174.67	54.08 (55.01)	9.03 (8.67)	15.53 (16.04)	20.59 (20.29)	NA	NA	NA	NA	NA	NA
BDMIM·Cl	$C_9H_{17}N_2Cl$	188.73	57.30 (57.27)	9.19 (9.10)	14.93 (14.85)	19.30 (18.78)	NA	NA	NA	NA	NA	NA
BMIM·Cl	$C_8H_{15}N_2Cl$	174.70	53.60 (55.0)	8.71 (8.67)	15.04 (16.04)	21.41 (20.29)	NA	NA	NA	NA	NA	NA
DDMIM·Cl	$C_{15}H_{29}N_2Cl$	272.91	65.66 (66.01)	10.85 (10.73)	10.12 (10.27)	13.37 (13.00)	NA	NA	NA	NA	NA	NA
HDMIM·Cl	$C_{20}H_{39}N_2Cl$	343.06	69.65 (70.02)	11.37 (11.48)	8.11 (8.17)	10.87 (10.33)	NA	NA	NA	NA	NA	NA
DMHDIM·Cl	$C_{21}H_{41}N_2Cl$	357.09	69.79 (70.63)	11.81 (11.60)	8.08 (7.85)	10.32 (9.93)	NA	NA	NA	NA	NA	NA
DMHDIM·Br	$C_{21}H_{41}N_2Br$	401.48	62.57 (62.83)	10.59 (10.29)	6.92 (6.98)	NA	19.92 (19.90)	NA	NA	NA	NA	NA
DMEiIM·Br	$C_{25}H_{49}N_2Br$	457.66	63.12 (65.61)	10.77 (10.81)	5.40 (6.12)	NA	17.27 (17.46)	NA	NA	NA	NA	NA
DMEtBIM·Br	$C_{13}H_{17}N_2Br$	269.19	55.21 (55.52)	6.37 (6.11)	9.98 (9.96)	NA	28.44 (28.41)	NA	NA	NA	NA	NA
EtMIM·BF_4	$C_6H_{11}N_2BF_4$	197.96	36.52 (36.40)	5.65 (5.61)	14.46 (14.15)	NA	NA	4.78 (5.46)	NA	38.59 (38.37)	NA	NA
DMPIM·BF_4	$C_8H_{15}N_2BF_4$	226.03	42.21 (42.52)	6.70 (6.69)	12.17 (12.39)	NA	NA	4.67 (4.69)	NA	31.98 (33.62)	NA	NA
BDMIM·BF_4	$C_9H_{17}N_2BF_4$	240.05	44.58 (45.03)	7.28 (7.15)	11.53 (11.67)	NA	NA	4.44 (4.50)	NA	32.17 (31.66)	NA	NA
DMiBIM·BF_4	$C_9H_{17}N_2BF_4$	240.05	44.64 (45.03)	7.39 (7.15)	11.42 (11.67)	NA	NA	4.50 (4.50)	NA	32.05 (31.66)	NA	NA
DDMIM·BF_4	$C_{15}H_{29}N_2BF_4$	324.23	55.65 (55.56)	8.97 (9.03)	8.77 (8.64)	NA	NA	3.33 (3.33)	NA	23.28 (23.43)	NA	NA
DMHDIM·BF_4	$C_{21}H_{41}N_2BF_4$	408.41	61.72 (61.75)	10.07 (10.14)	6.94 (6.86)	NA	NA	2.75 (2.65)	NA	18.52 (18.60)	NA	NA
AlDMIM·BF_4	$C_8H_{13}N_2BF_4$	224.00	43.04 (42.89)	5.90 (5.86)	12.73 (12.51)	NA	NA	4.81 (4.83)	NA	33.52 (33.91)	NA	NA
DMEiIM·BF_4	$C_{25}H_{49}N_2BF_4$	464.53	64.73 (64.64)	10.60 (10.65)	6.02 (6.03)	NA	NA	2.43 (2.33)	NA	16.22 (16.35)	NA	NA
DMiBIM·PF_6	$C_9H_{17}N_2PF_6$	298.19	36.40 (36.25)	5.74 (5.76)	9.50 (9.40)	NA	NA	NA	10.4 (10.4)	37.96 (38.21)	NA	NA
BDMIM·PF_6	$C_9H_{17}N_2PF_6$	298.21	35.90 (36.25)	5.94 (5.75)	9.35 (9.39)	NA	NA	NA	10.46 (10.4)	38.35 (38.22)	NA	NA
DDMIM·PF_6	$C_{15}H_{29}N_2PF_6$	382.37	47.19 (47.11)	7.81 (7.66)	7.32 (7.33)	NA	NA	NA	8.1 (8.1)	29.58 (29.79)	NA	NA
DMHDIM·PF_6	$C_{21}H_{41}N_2PF_6$	466.54	53.0 (54.06)	8.89 (8.86)	6.05 (6.00)	NA	NA	NA	6.64 (6.64)	23.87 (24.43)	NA	NA
DMEtBIM·PF_6	$C_{13}H_{17}N_2PF_6$	346.23	44.88 (45.09)	5.18 (4.96)	7.96 (8.09)	NA	NA	NA	9.11 (8.9)	32.87 (32.91)	NA	NA
EtMIM·$N(SO_2CF_3)_2$	$C_8H_{11}N_3F_6S_2O_4$	391.26	24.67 (24.56)	2.83 (2.84)	10.88 (10.74)	NA	NA	NA	NA	29.04 (29.12)	16.59 (16.39)	15.99 (16.4)

Data in parentheses are calculated.

an excess of the alkyl bromide or chloride (1 mol) in 50 ml acetonitrile in a thick-walled, single-neck 2 l round-bottom flask equipped with a reflux condenser. The solution was degassed several times with dry nitrogen, gradually heated to 60 °C, and allowed to react for 1 day under nitrogen pressure. Then the temperature was increased to 90 °C and the reaction refluxed for an additional 6 days under nitrogen. After the reaction was complete, a large excess of ethyl acetate was added to precipitate the imidazolium salt. This solid was filtered and washed several times with ethyl acetate to remove all of the unreacted imidazole and alkyl halide. Residual solvent was removed from the resulting 1-alkyl-2,3-dimethyl-imidazolium salt under vacuum, at 80 °C, for 12 h. The solid was re-dissolved in a minimum of acetonitrile and precipitated with ethyl acetate. The white solid was filtered and washed with ethyl acetate, and solvent removed under vacuum at 80 °C. Salts with different anions (BF_4^-, $PF_6^-$and $N(CF_3SO_2)_2^-$) can be attained by exchanging the halide ion for the desired anion. For a typical reaction, in a 1 l reaction flask 1 mol of the substituted imidazolium salt was added to 5% molar excess of the NH_4BF_4 or NH_4 PF_6 in 500 ml acetonitrile. The flask was then sealed and allowed to stir at room temperature for 7 days under nitrogen. After which, the flask was removed for the last purification steps. A complete list of the imidazolium molten salts used during the course of this study is recorded in Table 1. The products were characterized using elemental analysis, the chemical analyses performed in duplicate at Galbraith Laboratories. The results are shown in Table 2.

2.2. Preparation and characterization of alkyl-imidazolium montmorillonite

Montmorillonite clay (Southern Clay Products) was treated with seven alkyl-imidazolium salts according to the standard ion-exchange procedure [16]. This method consists of a cation-exchange reaction between the montmorillonite-layered silicate and excess of alkyl-imidazolium salt (twice the exchange capacity of the host). The alkyl-imidazolium salt was first dissolved in 50:50 mixture of ethanol and deionized water at 60 °C. Aqueous suspension of montmorillonite (1 wt.%) was added to the alkyl-imidazolium solution and the mixture was stirred for 5 h at 60 °C. The imidazolium exchanged montmorillonite was collected by filtration and washed with a mixture of hot ethanol and deionized water to remove all the residual anions. The final product was dried at room temperature and then under vacuum at 100 °C for 5 h. The prepared complexes are: 1,2-dimethyl-3-propyl-imidazolium montmorillonite, 1-butyl-2,3-dimethyl-imidazolium montmorillonite, 1-decyl-2,3-dimethyl-imidazolium montmorillonite, 1,2-dimethyl-3-hexadecyl-imidazolium montmorillonite, 1,2-dimethyl-3-eicosyl-imidazolium montmorillonite, 1,2-dimethyl-3-ethylbenzene-imidazolium montmorillonite and 1-ethyl-3-methyl-imidazolium montmorillonite. The imidazolium-treated layered silicate samples were characterized using X-ray diffraction (XRD), thermogravimetry, FTIR and thermal desorption mass spectroscopy.

Thermogravimetric data were collected from 30 to 800 °C at 10 °C/min under N_2 and air atmosphere using a TA Instruments SDT 2960. Each sample was run in triplicate and the mean value was taken. The results are reported in terms of the onset decomposition temperature (5% mass fraction loss) and the peak decomposition temperature, both of which have uncertainty of 1.2 °C (2σ).

Thermogravimetry coupled with Fourier transform infrared spectroscopy (TGA-FTIR) experiments were carried out using TA Instrument SDT 2960 TGA interfaced with MIDAC FTIR spectrometer with 10 cm internal cell (ZnSe optics). The N_2 purge gas carried the decomposition products through stainless steel line to the gas cell for infrared detection. Using heating tape, the transfer line and the gas cell were kept at 150 °C to prevent gas condensation.

Thermal desorption mass spectrometry was performed on a Finnigan TSQ-70 triple quadrupole mass spectrometer. Samples were prepared as a slurry in water and applied to the tip of a direct exposure probe, which consists of a small tungsten filament. The probe was then positioned in the ion source of the mass spectrometer. Samples were desorbed from the probe by passing a current through the wire and increasing the temperature of the probe tip. The desorption profile was generated by holding the current constant at 50 mA for 6 s, increasing the current (linearly) from 50 to 1000 mA over 45 s, and holding the current constant at 1000 mA for 6 s. Molecules desorbed from the probe were ionized with 70 eV electrons. Mass spectra were obtained at 0.5 s per scan.

3. Results and discussion

3.1. Imidazolium molten salts

Thermogravimetric measurements were carried out on a series of imidazolium molten salts (Table 1) as well as dimethyl dioctadecyl ammonium bromide salt. The results (see Table 3) are reported in terms of onset decomposition temperature and peak decomposition temperature. The measurements were conducted under N_2 or air.

Some important observations can be drawn from these results:

(1) The imidazolium cation is more thermally stable than the alkyl ammonium cation. This observation has been reported by Ngo et al. [17]. Begg et al. [18] pointed out that the imidazole is resistant to ring fission during thermal rearrangements of 1-alkyl- and 1-aryl-imidazoles at temperatures above 600 °C.

(2) The type of the anion has an effect on the thermal stability of the imidazolium salts. The hexafluorophosphate, tetrafluoroborate and bis(trifluoromethylsulfonyl)imide salts show more than 100 °C increase in the onset

Table 3
Decomposition temperatures of alkyl-imidazolium and quaternary ammonium salts under N_2 and air atmosphere

Sample	TGA under N_2 (°C)		TGA under air (°C)	
	T_{onset}	T_{peak}	T_{onset}	T_{peak}
DMDODA·Br	225	236	185	228
DMPIM·Cl	260	297	259	299
BDMIM·Cl	257	294	255	294
BMIM·Cl	234	285	232	284
DDMIM·Cl	239	287	237	284
HDMIM·Cl	230	292	229	287
DMHDIM·Cl	239	292	239	286
DMHDIM·Br	253	301	250	304
DMEiIM·Br	259	308	260	315
DMEtBIM·Br	275	339	275	330
DMPIM·BF_4	390	461	360	434
BDMIM·BF_4	405	475	347	428
DMiBIM·BF_4	350	429	347	404
DDMIM·BF_4	400	469	342	425
DMHDIM·BF_4	400	464	278	391
AlDMIM·BF_4	332	410	323	392
DMEiIM·BF_4	390	454	271	406
BDMIM·PF_6	425	499	358	396
DMiBIM·PF_6	382	439	357	424
DDMIM·PF_6	420	469	327	376
DMHDIM·PF_6	400	478	308	370
DMEtBIM·PF_6	386	464	334	397
EtMIM·$N(SO_2CF_3)_2$	410	479	401	477

Standard uncertainty ±1.2 °C (2σ).

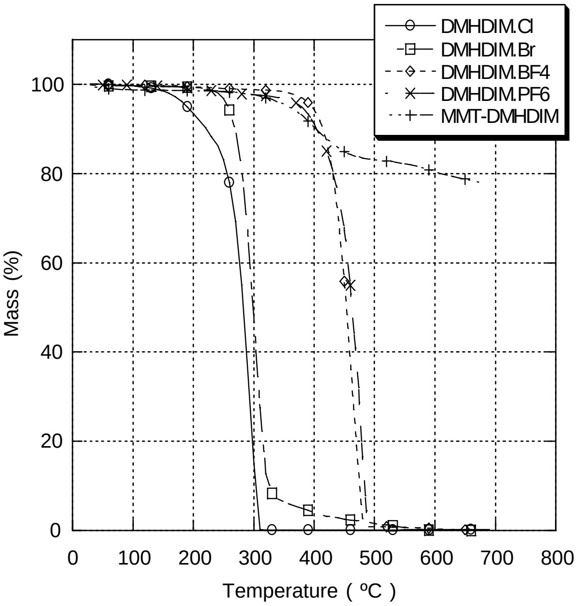


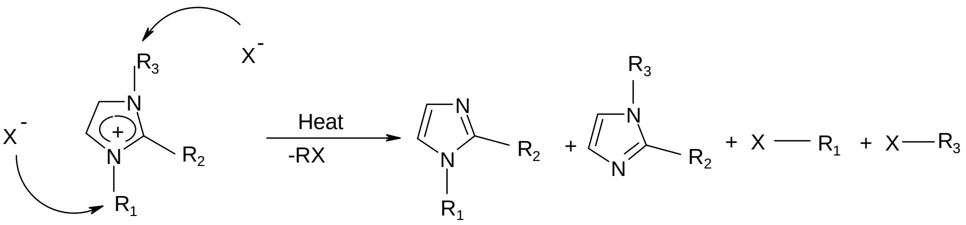
Fig. 1. TGA of dimethyl hexadecyl-imidazolium salts with different anions (Cl^-, Br^-, $BF_4{}^-$, $PF_6{}^-$) and montmorillonite clay treated with dimethyl hexadecyl-imidazolium salt.

decomposition temperature compared to the halide salts (see Fig. 1). The thermal stability increases in the order: $PF_6 > N(SO_2CF_3)_2 > BF_4 >$ Cl, Br. It would be instructive at this point to indicate that previous authorities [19,20] indicated that the facility with which various groups are cleaved from quaternary salts involves S_N1 or S_N2 mechanism. The pyrolysis of the imidazolium quaternary salt most likely proceeds via S_N2 process (see Scheme 1) and the present results seem to support this understanding since the order of nucleophilicity is: $Br^- > Cl^- > F^-$.

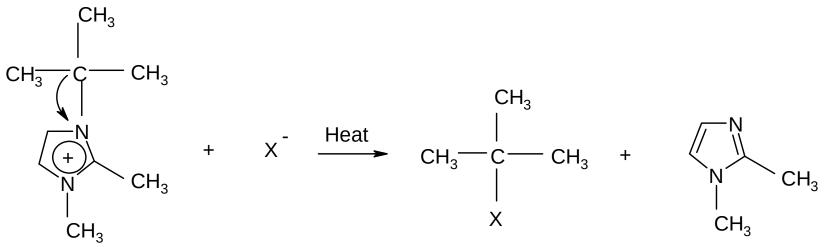
(3) The imidazolium thermal stability is affected by the type of isomeric structure of the alkyl side group. This is evidenced by the observation that both 1-butyl-2, 3-dimethyl-imidazolium tetrafluoroborate and hexafluorophosphate salts have higher onset decomposition temperature than 1,2-dimethyl-3-isobutyl-imidazolium tetrafluoroborate and hexafluorophosphate salts, respectively, this reaction presumably proceeds via S_N1 reaction since the cleavage of the tertiary carbon atom will most readily occur (see Scheme 2).

(4) Methyl substitution in the 2-position (i.e. between the two N atoms) enhances the thermal stability. This is evident from the increase in the onset decomposition temperature of both 1-butyl-2,3-dimethyl-imidazolium chloride and 1,2-dimethyl-3-hexadecyl-imidazolium chloride compared to 1-butyl-3-methyl-imidazolium chloride and 1-hexadecyl-3-methyl-imidazolium chloride, respectively. This may be due to the high acidic character of the C-2 proton [21].

(5) The atmosphere has an effect on the thermal stability of certain imidazolium salts, namely the tetrafluoroborate and hexafluorophosphate (see Table 3). Both the onset decomposition temperature and the peak decomposition temperature were markedly decreased if the sample was run under air atmosphere compared to that under N_2 atmosphere. In addition, a relationship was observed between the chain length of the alkyl group attached to the nitrogen atom and the oxidative decomposition of the imidazolium salts, indicating that the thermal stability decreases as the organic content of the molecule increases. On the other hand, it was noticed that the



Scheme 1.



Scheme 2.

presence of oxygen does not appear to have any effect on the breakdown of the halide salts. This may reflect that the activation energy required for the thermal decomposition of the halide salts is lower than that for their oxidative decomposition.

3.2. Imidazolium-treated layered silicates

In an attempt to understand the thermal degradation of the imidazolium-treated montmorillonite, the decomposition of pristine Na-montmorillonite will be considered first. Previous reports recognized two regions in its differential thermal analysis curve:

(a) The temperature range 100–300 °C that corresponds to the loss of adsorbed water.
(b) The dehydroxylation of structural hydroxyl groups occurs in the temperature range 500–1000 °C [22].

The amounts of both molecular H_2O and structural OH^- thus can be determined for use in calculating the structural formula of the layered silicates. It is interesting to indicate that a relationship was observed between the exchangeable cation and the amount of water lost before dehydroxylation. It was pointed out that in TGA results it is usually difficult to recognize a break separating the loss of interlayer water from the dehydroxylation process is due to the defect in the crystalline structure of montmorillonite [23].

The exchangeable cations present in montmorillonite can be replaced by alkyl-imidazolium salts via ion-exchange reactions according to the standard procedure [16]. The most obvious manifestation of the introduction of organic molecules into the interlayer space of the layered silicates is a modification of the basal spacing of the mineral; therefore, formation of a complex can be ascertained from XRD measurement. Information on the probable packing and orientation arrangement of the molecules can be obtained by combining spacing measurements and consideration of molecular geometry. The resulting imidazolium modified montmorillonite has lower surface energy than Na-montmorillonite, and hence has the important property of being able to swell and disperse in organic polymers. These imidazolium-treated montmorillonites have been subjected to thermogravimetric analysis under N_2 and air atmosphere; the results are shown in Table 4.

One of the most interesting findings of this work is the enhancement in the thermal stability of imidazolium compounds after being intercalated into montmorillonite (see Table 4 and Fig. 1). Fig. 1 shows the dramatic increase in the thermal stability of dimethyl hexadecyl-imidazolium-intercalated montmorillonite as compared to the dimethyl hexadecyl-imidazolium chloride and bromide salts. This may be due to the removal of the halide effect. This reflects the importance of getting rid of all the halide residue that may contaminate the intercalated product after the ion exchange. On the other hand, it seems that there is no significant improvement in the thermal stability of the intercalated tetrafluoroborate and hexafluorophosphate salts, this may be due to the weak nucleophilicity of BF_4^- and PF_6^- anions. The results also indicated that the thermal stability of imidazolium-treated montmorillonite decreases as the chain

Table 4
Thermal characteristic data of alkyl-imidazolium and quaternary ammonium-treated montmorillonite

Sample	TGA under N_2 (°C)		TGA under air (°C)		Imidazolium content			Change in *d*-spacing vs. Na-montmorillonite (nm)
	T_{onset}	T_{peak}	T_{onset}	T_{peak}	Theoretical	Under air	Under N_2	
DMDODA/MMT	280	308	226	299	34.11	34.43	31.15	1.49
EtMIM/MMT	325	492	290	482	9.39	8.65	8.10	0.12
DMPIM/MMT	340	445	305	422	11.57	10.30	8.77	0.2
BDMIM/MMT	340	448	303	381	12.59	11.60	9.17	0.16
DDMIM/MMT	320	432	234	312	18.26	17.14	13.63	0.49
DMHDIM/MMT	343	406	250	298	23.21	23.50	20.53	0.72
DMEiIM/MMT	308	409	250	317	26.20	27.10	26.09	0.94
DMEtBIM/MMT	262	418	235	384	14.95	13.88	13.30	0.35

Standard uncertainty ±1.2 °C (2σ).

length of the alkyl group attached to the nitrogen atom increases (see Fig. 2).

Studies of the thermal reactions of imidazolium-treated montmorillonite taking place both in the presence and absence of oxygen atmosphere are useful since they provide information about the thermal stability of imidazolium-treated montmorillonite under different processing conditions, which is crucial for industrial applications. Table 4 shows the influence of oxygen on the thermal decomposition of imidazolium-treated montmorillonite. The oxygen atmosphere significantly diminishes the thermal stability of the imidazolium-treated clay as evidenced by the decrease in both the onset decomposition temperature and the peak decomposition temperature; the thermal stability is still higher than that of quaternary ammonium-treated montmorillonite under the same conditions.

Table 4 shows the calculated and experimental organic fraction contents. The total organic content was lost in the temperature range 200–500 °C and was determined by taking into account the mass loss corresponding to the dehydroxylation process of montmorillonite. Satisfactory agreement was observed between the theoretical values and those determined by oxidative decomposition. However, the results also indicated that imidazolium and quaternary ammonium cations may be taken up in amounts exceeding cation-exchange capacity. This is evident from the higher values for montmorillonite clay treated with dimethyl dioctadecyl ammonium, dimethyl hexadecyl-imidazolium and dimethyl eicosyl-imidazolium cations (see also Fig. 2). A possible explanation is that for the polar cations (small R group), the excess salt accumulated in interlayer space may be easily desorbed by washing with water or alcohol–water mixtures, which is the typical purification following the ion-exchange reaction. For less polar cations (long chain R group), the excess will resist washing [24,25].

3.3. Degradation products

TGA-FTIR measurements were carried out on 1,2-dimethyl-3-hexadecyl-imidazolium tetrafluoroborate and the montmorillonite clay after being modified by this salt. Very close resemblance between the infrared spectra of these two compounds was observed. This observation suggests that the end products of the degradation reactions for both compounds are similar, although the reaction pathways may be different due to the limitations that the interlayer space imposes on the orientation and packing arrangement of the molecules. This point will need further investigation to see the effect of other factors, such as the type of counter ion on the degradation mechanism.

The results (figure not shown) show that the ν(N–H) of the imidazole N–H bond exhibits typical broad hydrogen-bonding N–H stretching absorptions in the 3100–3300 cm^{-1} region. The $\nu_{as}(CH_2)$ and $\nu_{s}(CH_2)$ spectral feature of hydrocarbon chain was observed in the 2851–2970 cm^{-1} region. A peak at 2368 cm^{-1} was identified to correspond to the undissociated molecular CO_2. Water vapor has an infrared spectrum which covers large parts of the FTIR wavenumber window as given by the broad band characteristic of hydrogen bonded OH stretching vibration in the 3500–3700 cm^{-1} region, and the usual H–O–H bending vibration band in the 1400–1600 cm^{-1} region.

3.4. Thermal desorption mass spectroscopy

TDMS results provide additional support for the observed enhancement in the thermal stability of imidazolium-treated montmorillonite. TDMS spectra provides a total ion current (TIC) as well as selected ion monitoring as a function of both temperature and time. The temperature at which the intensity maximum occurs is considered to be the desorption

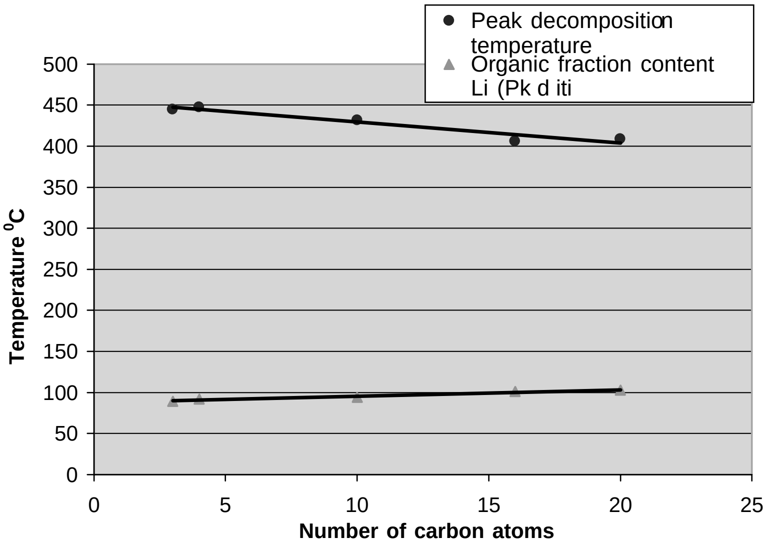


Fig. 2. Effect of chain length on the thermal stability (T_{peak} under N_2) and organic fraction content of imidazolium-treated montmorillonite.

temperature. TDMS measurements were carried out on 1-decyl-2,3-dimethyl-imidazolium tetrafluoroborate, 1,2-dimethyl-3-eicosyl-imidazolium tetrafluoroborate and montmorillonite clay intercalated with these two salts.

The thermal desorption spectrum of 1-decyl-2,3-dimethyl-imidazolium tetrafluoroborate (see Fig. 3) consists of two desorption maximums (A and B) at 2.6 and 3.35 min. The desorption occurs in the temperature range 400–550 °C. The components of the two desorption maximums are basically the same (A = B) and consist of degradation products of the parent cation (*m*/*z* 237.3) due to loss of methyl group at lower temperature and loss of H at higher temperature. The peak corresponding to the intact parent cation (decyl dimethyl-imidazolium, *m*/*z* 237.3) appears only at higher temperature region (C), but it is not a predominant peak. By contrast, intercalating 1-decyl-2,3-dimethyl-imidazolium into montmorillonite clay shifts the desorption maximum to higher temperature (800 °C at 5.04 min) and leads to an

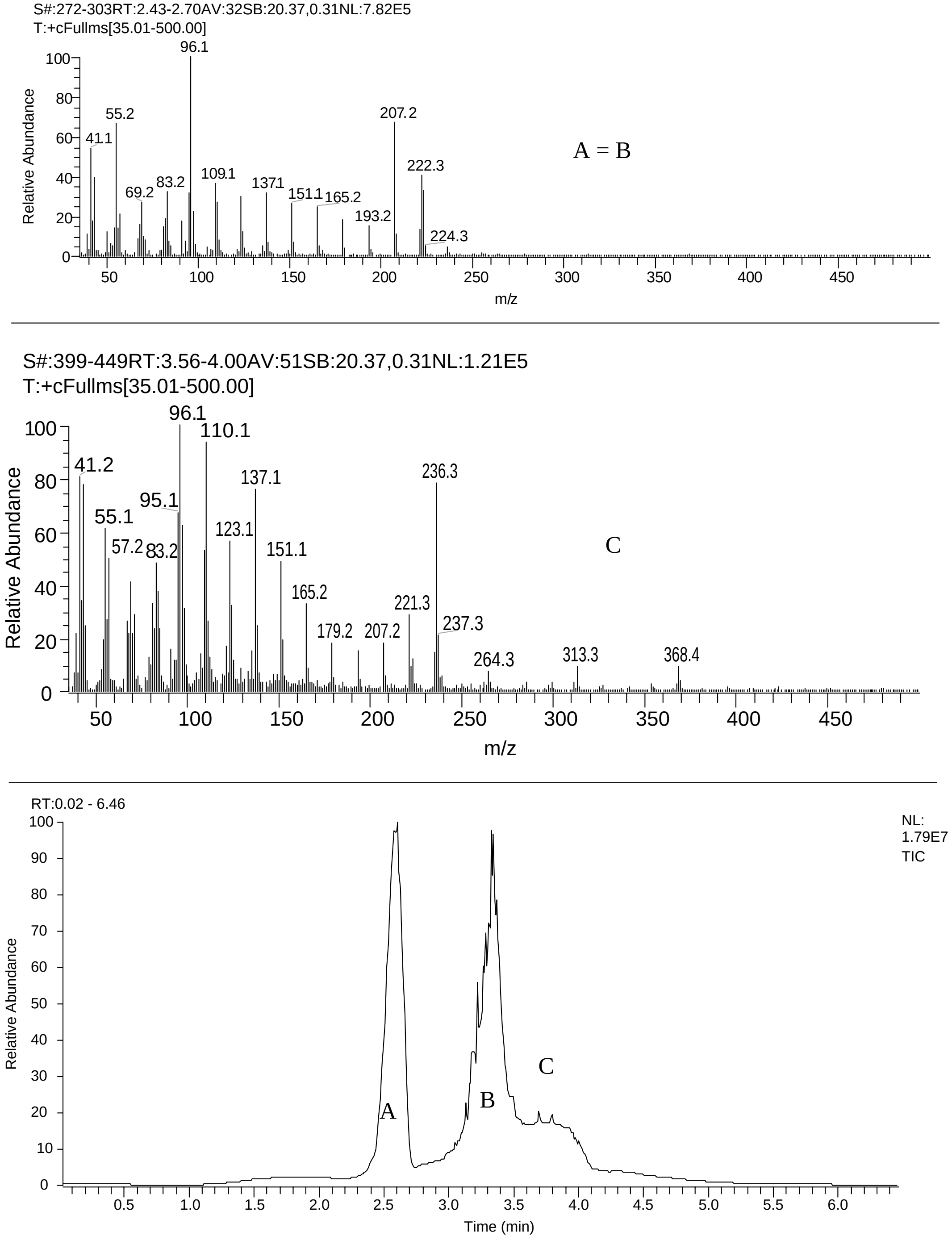


Fig. 3. Thermal desorption mass spectra of 1-decyl-2,3-dimethyl-imidazolium tetrafluoroborate.

enhanced abundance of the intact cation *m*/*z* 237.2 peak (figure not shown).

TDMS spectra of 1,2-dimethyl-3-eicosyl-imidazolium tetrafluoroborate (figure not shown) yielded no intact cation (*m*/*z* 377.4) and only small fragments were observed. On the other hand, the spectra of Montmorillonite salt (figure not shown) revealed the non-degraded cation (*m*/*z* 377.3) at higher temperature (800 °C at 4.95 min). Mass spectra of dimethyl eicosyl-imidazolium tetrafluoroborate displays a peak at *m*/*z* 376.4 corresponding to the loss of H from the intact parent cation. A peak at *m*/*z* 361.4 is apparently due to the loss of CH_3 group, and the remaining series of peaks correspond to the consequent loss of CH_2 groups from the long chain. The peak at *m*/*z* 96.2 tentatively corresponds to dimethyl-imidazole and the imidazole ring displays a peak at *m*/*z* 69.2. These TDMS results strongly support our contention that the montmorillonite-layered silicates stabilize the imidazolium salts.

4. Conclusions

In this contribution, we have discussed the oxidative and non-oxidative thermal stability of several alkyl-imidazolium molten salts and imidazolium-treated montmorillonite-layered silicates. In the presence of oxygen, the thermal stability was markedly decreased compared to the nitrogen atmosphere. The main degradation products as probed by FTIR are water, carbon dioxide and hydrocarbon. The type of the anion proved to play a crucial rule in these degradation reactions and the thermal stability was found to increase in the order: $PF_6 > N(SO_2CF_3)_2 > BF_4 > Cl$, Br. Montmorillonite clay treated with imidazolium salts showed superior thermal properties compared to the quaternary alkyl ammonium montmorillonite, and this conclusion was strongly supported by the thermal desorption mass spectrometric technique. These results seem to be promising in terms of the potential application of these imidazolium molten salts for the preparation of high temperature polymer-layered silicates.

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