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An appraisal of the thermal decomposition mechanisms of ILs as potential lubricants.Waleed Al-Sallami^{1,*}, Pourya Parsaeian¹, Anne Neville¹¹School of Mechanical Engineering, University of Leeds, UK**Abstract**

Ionic Liquid (IL) lubricants are rapidly seeing increased use as either base lubricants or additives for a wide range of functionalities. This study considers the thermal stability of the ILs with the emphasis being their use as potential lubricants. The effect of IL chemistry, including anion chain length, cation chain length, anion type and cation type, on their thermal stability is studied. The decomposition mechanism as a function of time and temperature is considered. Five ILs are studied by utilizing both ThermoGravimetric Analysis (TGA) for the dynamic thermal decomposition and Fourier Transform IR spectroscopy (FTIR) for the static thermal decomposition. For static thermal decomposition both time and temperature are varied. The results show that the variation of IL chemistry directly influences their thermal stability. The increase of either cation or anion chain length decreases their thermal stability. Both anion and cation type have a significant influence on the thermal stability.

Keywords: ILs lubricants, FTIR, TGA, cation chain length, anion chain length, cation type, anion type, static thermal decomposition and dynamic thermal decomposition.

1. Introduction

The main aim of lubricants is to enhance the tribological performance of interacting surfaces in terms of reducing both wear and friction whilst managing energy dissipation and the translation of energy into heat. Further, many other crucial properties are desirable in lubricants such as their thermal stability, fluidity range and thermal conductivity (1). ILs have been proposed as lubricants due to their ability to provide excellent tribological behaviour for various tribopairs. In addition, they exhibit highly desirable properties that are matching the required properties in lubricants (2-5). ILs can be simply defined as molten salts that are available in the liquid state over a wide range of temperatures. ILs' properties can be controlled easily by varying their chemistry, i.e., anion/cation chain length and/or anion/cation type. They basically consist of an organic cation and either an organic or inorganic anion when both ions contain a controllable alkyl chain length (6).

In the last two decades, ILs have been widely used as either base lubricants or additives. ILs have shown excellent tribological performance when lubricating various tribopairs in various

conditions (2-5). Ye et al (7) suggested ILs as versatile base lubricants since imidazolium based ILs showed excellent tribological performance when lubricating steel, aluminium, copper and ceramics. A few studies suggested the use of ILs as base lubricants in vacuum environments (8-13). The results implied that ILs can provide better tribological performance than Polyether Ether Fluorine (PFPE) which is one of the most conventional lubricants in vacuum conditions. Besides, the use of ILs as additives started when Phillips et al (14) added various ILs into water to lubricate ceramic tribopairs. The results demonstrated that ILs can be used as effective anti-wear additives. However, the majority of ILs are insoluble in non-polar lubricants due to their high polarity (2-5). Nevertheless, fully oil-miscible ILs have been proposed by Qu et al (15) and their results suggested that oil-miscible ILs can provide a significant protection against wear.

The thermal stability of lubricants is also crucial since it determines the maximum limit of the working temperature. The thermal stability of ILs can be affected by the operating environment, their chemistry and the heating process methodology (16). Villanueva et al (17) reported that ILs are more stable in a nitrogen environment than air. The effect of anion type, cation type and cation chain length were investigated by Maaiké et al (18). They found that all parameters influence the thermal stability. Later studies revealed that the anion is more significant than the cation (19, 20). The effect of the heating process methodology was examined. The results implied that the use of TGA to assess the dynamic thermal stability provides an overestimation for the thermal stability of ILs (16, 19, 21-24). Other methodologies were applied to examine the static thermal stability of ILs in order to find the real maximum working temperature by using various periods at constant temperature and then calculating the weight loss (25, 26).

IR spectroscopy can be used to study the thermal decomposition of ILs by comparing between IR spectra at room temperature and after heating process. Chowdhury and Thynell (27) used FTIR to analyse the decomposition products that are obtained from TGA of various imidazolium based ILs. The results implied that the decomposition occurred only in the anion and the highest decomposition was obtained in the nitride anion. Feng et al (28) also used TGA to study the thermal decomposition of ILs. The FTIR spectra of the decomposed species were utilized to assess the thermal decomposition mechanism of imidazolium tetrafluoroborate. Their results showed that the decomposition started by the decomposition of the anion.

Very recently, Wheeler et al (24) investigated the thermal decomposition of ethyl methyl imidazolium ethyl sulfate using FTIR. The results demonstrated that, as expected, the increase of either time or temperature increases the concentration of the decomposed species.

There is a lack of data for IR spectra of ILs at room temperature (29-32). To the best of the authors' knowledge, this study is the first one that presents the FTIR spectra for both phosphonium sulfate and imidazolium phosphate ILs. In addition, as mentioned above only one study has investigated the thermal decomposition mechanism of IL (imidazolium sulfate) using FTIR (24). The aim of this paper is to assess the effect of ILs' chemistry including; anion chain length, cation chain length, anion type and cation type on their dynamic and static thermal decomposition. Also, the effect of ILs' chemistry on their IR spectra at room temperature is reported.

2. Experimental methods

2.1 Ionic Liquids

Five ILs are used in this study as presented in Table 1 including their structures, impurities and vendors. The selection of these ILs aims to cover the influence of ILs' chemistry including effect of anion chain length, cation chain length, anion type and cation type. From the top of the table, the first two are utilized to investigate the effect of anion chain length. The second and third are utilized to investigate the effect of cation chain length. The fourth and fifth are compared with the first one to investigate the effect of anion type and cation type respectively.

2.2 Dynamic thermal decomposition

TGA (Mettler Toledo, University of Leeds, UK) is utilized in this study to detect the decomposition temperature. In the current study, the temperature is increased at a rate of 10 °C/min (non-isothermal mode) as utilized for ILs in (19, 33, 34). The starting temperature is 55 °C. Air atmosphere is utilized to maintain the same environment in both static and dynamic experiments. Further, alumina oxide 70 µL crucibles, from Mettler Toledo, are utilized. A comparable amount of IL (8 mg) is utilized in all experiments. The first derivative of weight loss against surface temperature is evaluated to find the decomposition temperature.

2.3 Static thermal decomposition

2.3.1 Experiments procedure

The temperature is kept constant for a certain period (iso-thermal mode) and FTIR is used to assess thermal stability by comparing between the spectra of ILs before and after each test.

Two temperatures are utilized (80 °C and 100 °C) at three periods (2 hours and 5 hours), see Table 2. The same amount of IL is used in all experiments (2 ml). ILs are placed in glass beakers (see Fig. 3-4). A hot plate is utilized for the heating process when the pre-set temperature is maintained by using a feedback signal. The error is $\pm 2^{\circ}\text{C}$. The hot plate is placed in a well ventilated place to exhaust the produced fumes directly.

2.3.2 IR spectroscopy

The PerkinElmer spectra 100 FTIR-ATR is utilized to investigate the effect of ILs' chemistry on IR spectra before and after the heating process. The background signal is collected firstly. The incorporated software spectra spectroscopy software is utilized to subtract the background signal and process the obtained signal of lubricants. The signal is collected within the range of 650 to 4000 cm^{-1} . An average of 25 scans is utilized when the resolution is 2 cm^{-1} . The obtained spectra are analysed using the handbook for IR spectra for both organic and inorganic compounds (35) in addition to the available data in the literature (24, 29-32)

3. Results

3.1 Dynamic thermal decomposition

The results of the dynamic thermal decomposition of the examined ILs are depicted in Fig. 3-1. The effect of anion chain length is evaluated by comparing between EMIM ESU (both chains are ethyl) and EMIM OSU (cation chain is ethyl and anion chain is octyl). The effect of cation

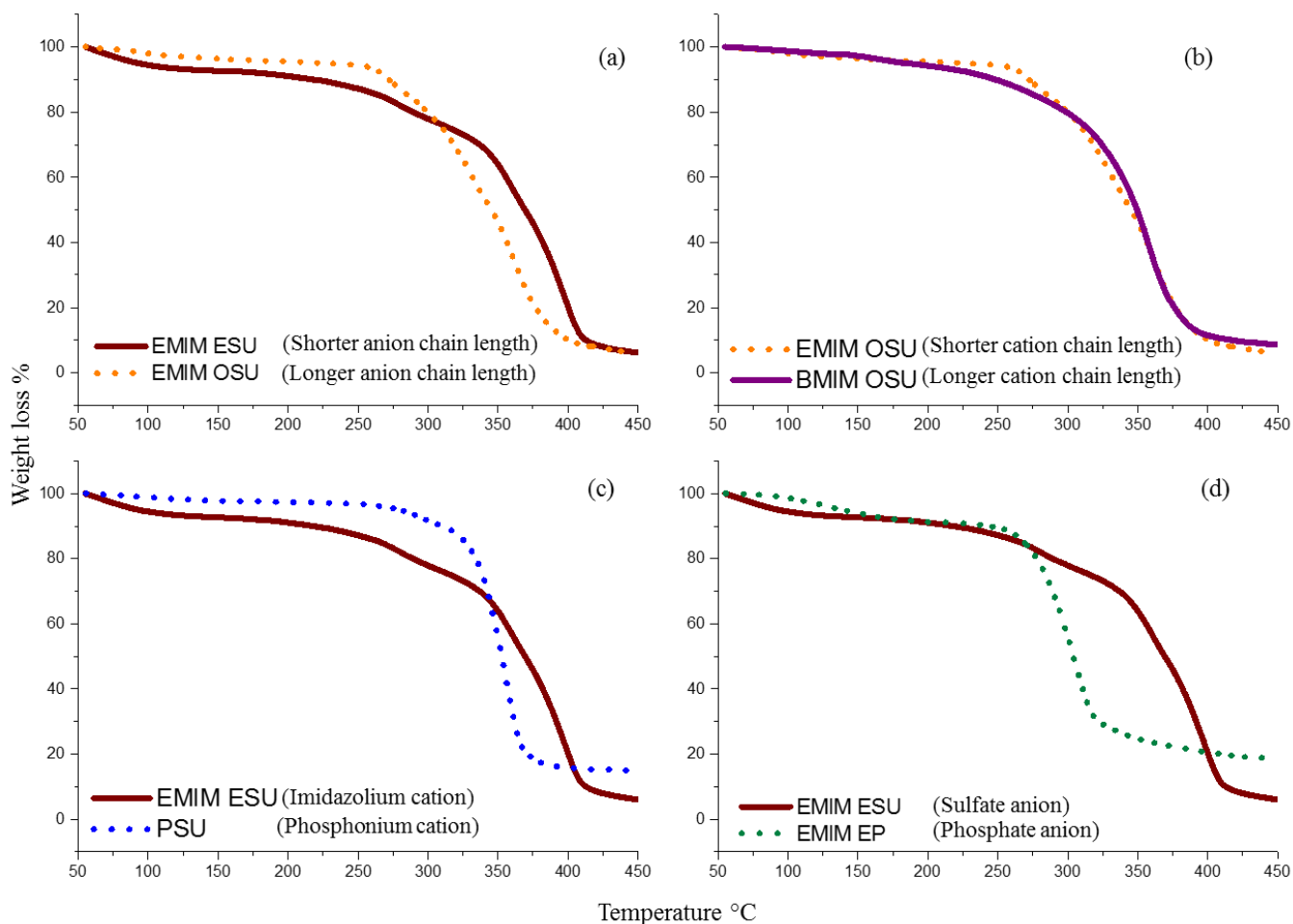


Fig. 3-1: Dynamic thermal decomposition of the examined ILs to reveal the effect of: (a) anion chain length, (b) cation chain length, (c) cation type and (d) anion type.

chain length is evaluated by comparing between EMIM ESU and BMIM OSU (cation chain is butyl and anion chain is octyl). The results demonstrate that decreasing of either cation or anion chain length increases the dynamic thermal stability of IL. This can be resulted due to the decrease of the stability of carbocation (36). The effect of anion chain length is significantly higher than cation chain length (see Figs. 3-1a and 3-1b). This finding is expected since the increase of anion chain length (from ethyl to octyl) is higher than that applied for cation chain length (from ethyl to butyl).

The effects of both anion type and cation type are considered by comparing EMIM ESU with PSU and EMIM EP. Previous findings showed that the correlation between either anion type

or cation type and the thermal stability cannot be determined precisely. Some ions (anion/cation) demonstrated a significant influence while other ions did not demonstrate any influence (19, 20). However, in this study, both anion and cation demonstrate a considerable effect on the thermal stability. It is observed that the presence of phosphorus as either a cation (phosphonium cation) or anion (phosphate anion) instead of imidazolium or sulfate respectively, decreases the dynamic decomposition temperature (see Fig. 3-1). This finding is in agreement with the previous study that compared phosphonium with imidazolium when both were combined with a halogenic anion (20).

Both the onset temperature and the decomposition temperature are considered. The former is obtained when only a slight reduction in mass is detected which suggests that the decomposition is just started (see Fig. 3-2). The highest reduction in the mass was defined as the decomposition temperature (37) as presented in Fig. 3-2.

It is clear that the ILs' chemistry has a considerable effect not only on the decomposition temperature but also on the onset temperature (see Fig. 3-2). Longer cation or anion chain length appears to lead to a decrease in the decomposition temperature while there is no significant effect on the onset temperature. In addition, sulfate anion and imidazolium cation show a lower onset temperature in comparison with phosphate anion and phosphonium cation respectively (see Fig. 3-2).

Previous studies reported that the use of TGA to study the dynamic thermal decomposition of ILs can provide an overestimation for their thermal stability (16, 24). In other words, the thermal decomposition can be started in a temperature by far lower than that estimated by TGA. Thus, the static thermal decomposition experiments are utilized in this study to obtain complementary information.

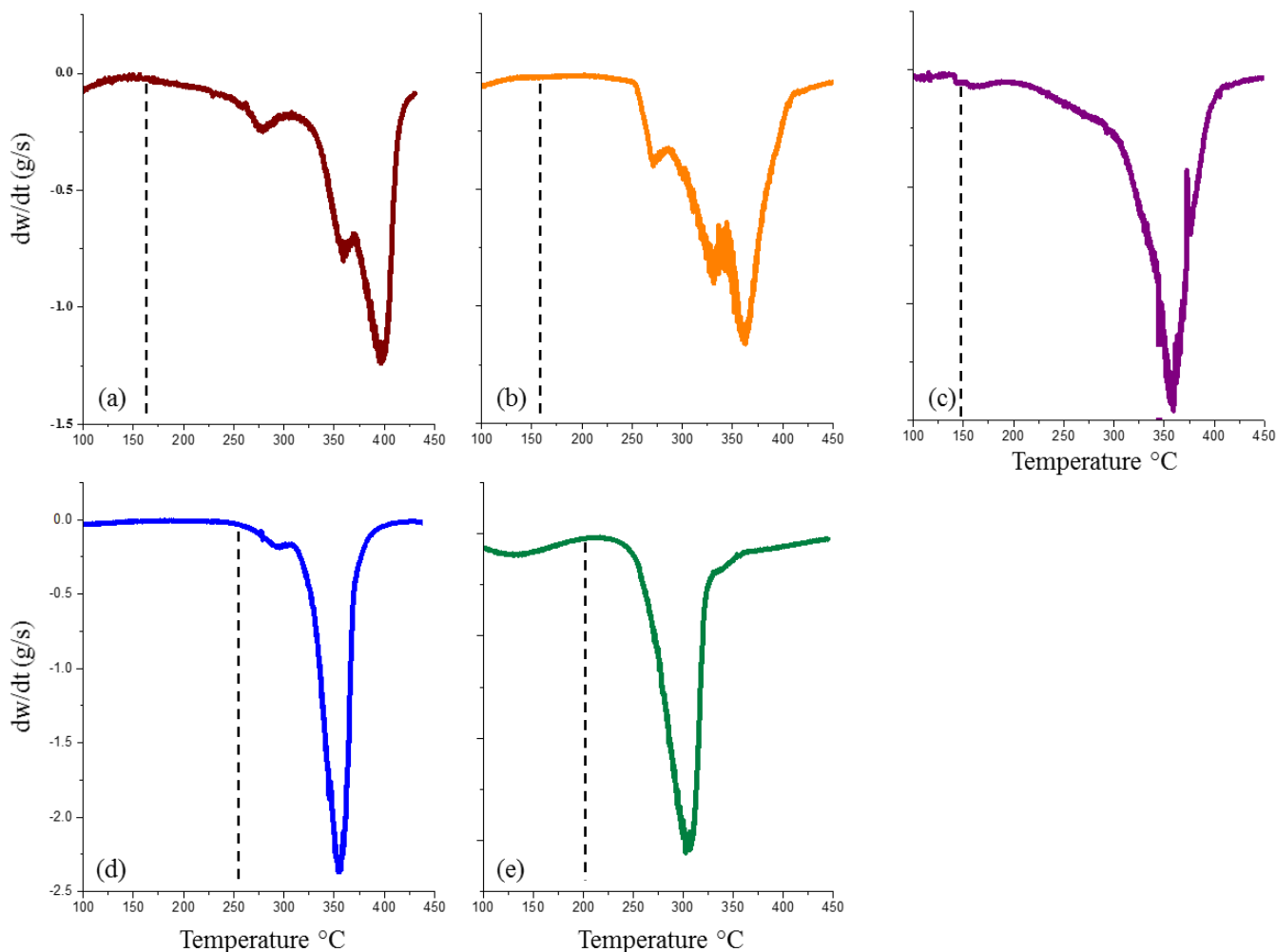


Fig. 3-2: First derivative of the weight loss against surface temperature curve for: (a) EMIM ESU, (b) EMIM OSU, (c) BMIM OSU, (d) PSU and (e) EMIM EP.

3.2 Static thermal decomposition

FTIR is utilized to examine the static thermal decomposition by comparing IR spectra of the utilized ILs at room temperature and then after each heating process.

3.2.1 FTIR results at room temperature

IR spectra for the examined ILs are depicted in Fig. 3-3. The analysis starts with EMIM ESU, because it is the only IL in this study that is widely analysed in the literature (24). Table 3 demonstrates the assigned peaks for EMIM ESU, and all peaks are in agreement with (24, 29). It can be clearly seen in Fig. 3-3 that the variation of anion chain length plays a more significant role than cation chain length. The intensities of peaks related to the hydrocarbons are increased with the increase of either anion or cation chain length (see Fig. 3-3).

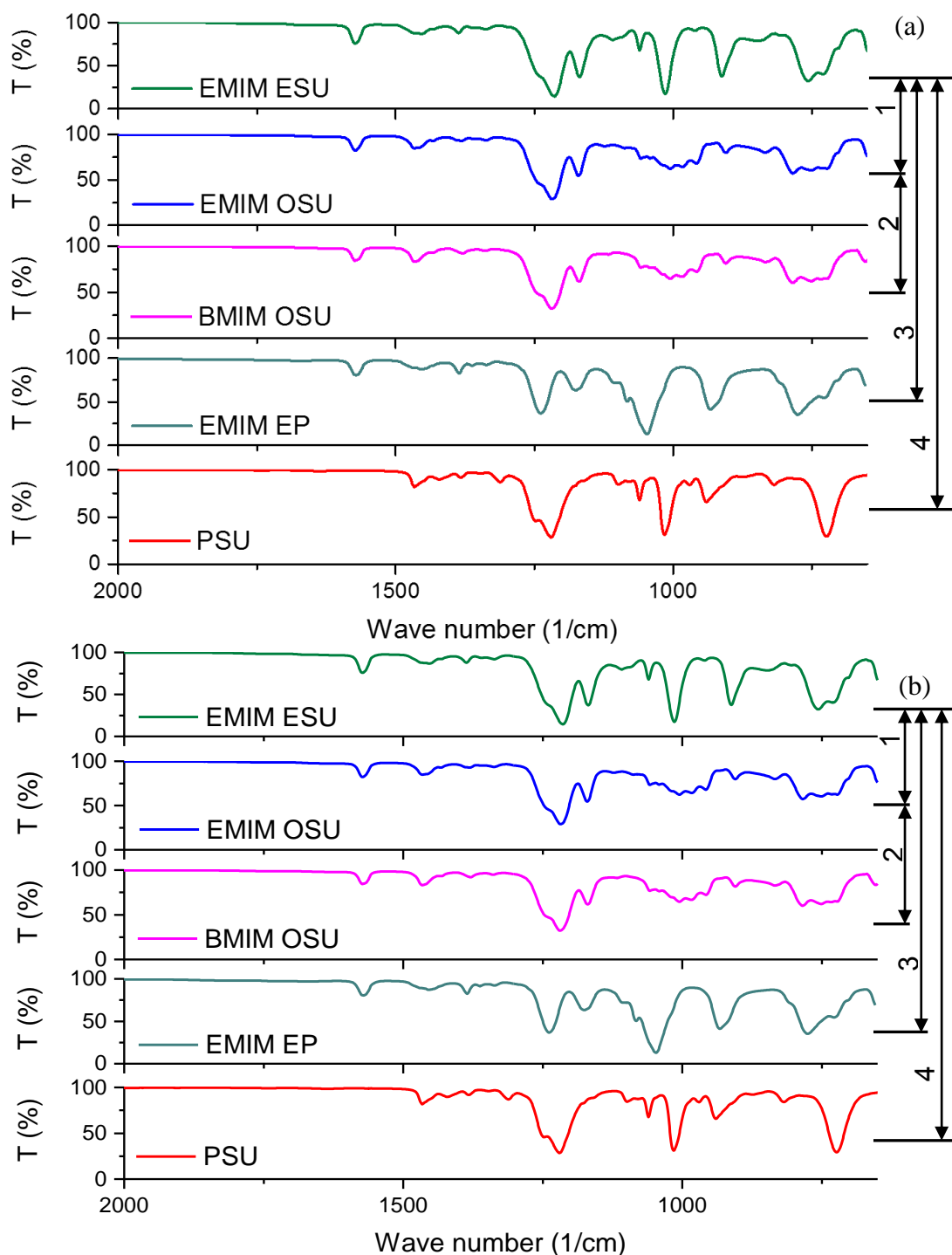


Fig. 3-3: IR spectra of five ILs at room temperature; (a) spectra between 4000 cm^{-1} and 2000 cm^{-1} and (b) spectra between 2000 cm^{-1} and 650 cm^{-1} . 1: increase anion chain length, 2: increase cation chain length, 3: change anion from sulfate to phosphate and 4: change cation type from imidazolium to phosphonium.

Referring to the Beer-Lambert law (38); the increase of intensity (decrease the transmissivity) has a linear relationship with molar concentration. This means that the reduction of peaks' intensity suggests a reduction of the concentration of their related chemicals.

The increase of anion chain length lead to a decrease in the intensity (concentration) of both sulfate and imidazolium related peaks, as expected. In contrast, the intensities of the peaks related to chain lengths; such as C-C, C-H and CH-CH are increased. This finding is expected since the chain length is increased and the concentration of these bonds is increased. The same behaviour is obtained as a result of the increase of cation chain length (see Fig. 3-3).

Changing cation type from imidazolium to phosphonium lead to a full diminishing of imidazolium related peaks, as expected. Five new peaks are detected and assigned to the phosphonium cation. Three peaks are assigned to P-CH₃ at 1421 cm⁻¹ asymmetric vibration, 1313 cm⁻¹ symmetric vibration and 939 cm⁻¹ rocking vibration. For the last two peaks, the one at 729 cm⁻¹ is assigned to P-C stretching vibration and the second one at 1090 cm⁻¹ is assigned to the asymmetric stretching of P-C. Besides, the rest peaks that are assigned to either sulfate anion or hydrocarbons are still existed. However, a new peak at 2825 cm⁻¹ is appeared and assigned to the stretching of OCH₃ that exists in methyl sulfate. The assignmensts of all these peaks are made based on the available data in (35).

Changing anion type from sulfate to phosphate leads a full diminishing of sulfate related peaks, as expected. Five new peaks are appeared when four of them are related to phsphate anion. The assignments of the phosphate related peaks are as follows: P-O stretching at 776 cm⁻¹, P-O-C symmetric stretching at 933 cm⁻¹, P-O-C assymetric stretching at 1050 cm⁻¹, P=O at 1240 cm⁻¹. Furhter, the last peak is assigned to OH since it is a broad peak between 3190 to 3580 cm⁻¹. The OH related peak can be resulted from the water content. Again, the assignments of all these peaks are made based on the available data in (35).

3.2.2 FTIR results after heating process

ILs are heated up to 80 °C for 2 and 5 hours. The IL colour was changed to black after 30 minutes of heating (see Fig. 3-4). The change of colour from transparent to black is a reported feature of the oxidation of lubricants (39). In addition, a partial decomposition is observed when the intensity of anion and/or cation related peaks are decreased. The increase of time from 2 hours to 5 hours lead to a further decrease of anion and/or cation related peaks. The temperature is also increased to 100 °C for 2 and 5. The results show that the increase of temperature also lead to decrease of anion and/or cation related peaks. This finding suggests the increase of either time or temperature increases the amount of the decomposed species.

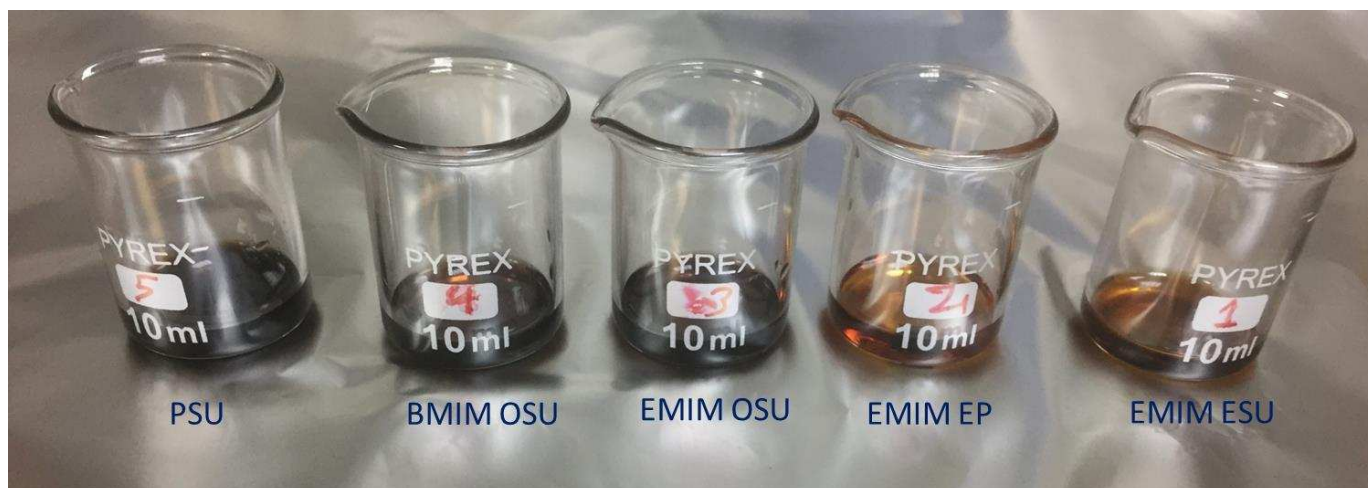


Fig. 3-4: ILs after heating them into 80 °C and for 2 hours.

Fig. 3-5 presents the IR spectra of ILs after heating them to 100 °C for five hours. Starting from BMIM OSU, a broad weak peak was obtained between 3400 and 3600 cm^{-1} . This peak is assigned to OH (16). This can be resulted from the decomposition of IL as pointed out in (24). Subsequently, the intensities of peaks related to imidazolium and hydrocarbon peaks, $\text{CH}_3\text{-CH}_2$ and $\text{CH}_3\text{-HCH}$, are increased which means that their molar concentrations are increased. In contrast, three peaks related to the sulfate anion are diminished which are SO_4 at 1110 cm^{-1} and at 912 cm^{-1} , C-O-S-O and S=O at 757 cm^{-1} . This means that the decomposition process starts in the sulfate anion. This finding is in agreement with the previous studies (24, 28)

Decreasing cation chain length is expected to increase thermal stability of IL, based on TGA results (see Fig. 3-1b). As expected, only one peak related to sulfate anion is diminished while the rest sulfate related peaks still exist with a considerable reduction in their intensities (see Fig. 3-5). In contrast, cation and hydrocarbon related peaks are increased. Similarly, the decrease of anion chain length leads to increase the thermal stability (see Fig. 3-5). This finding is again in agreement with TGA results (see Fig. 3-1a).

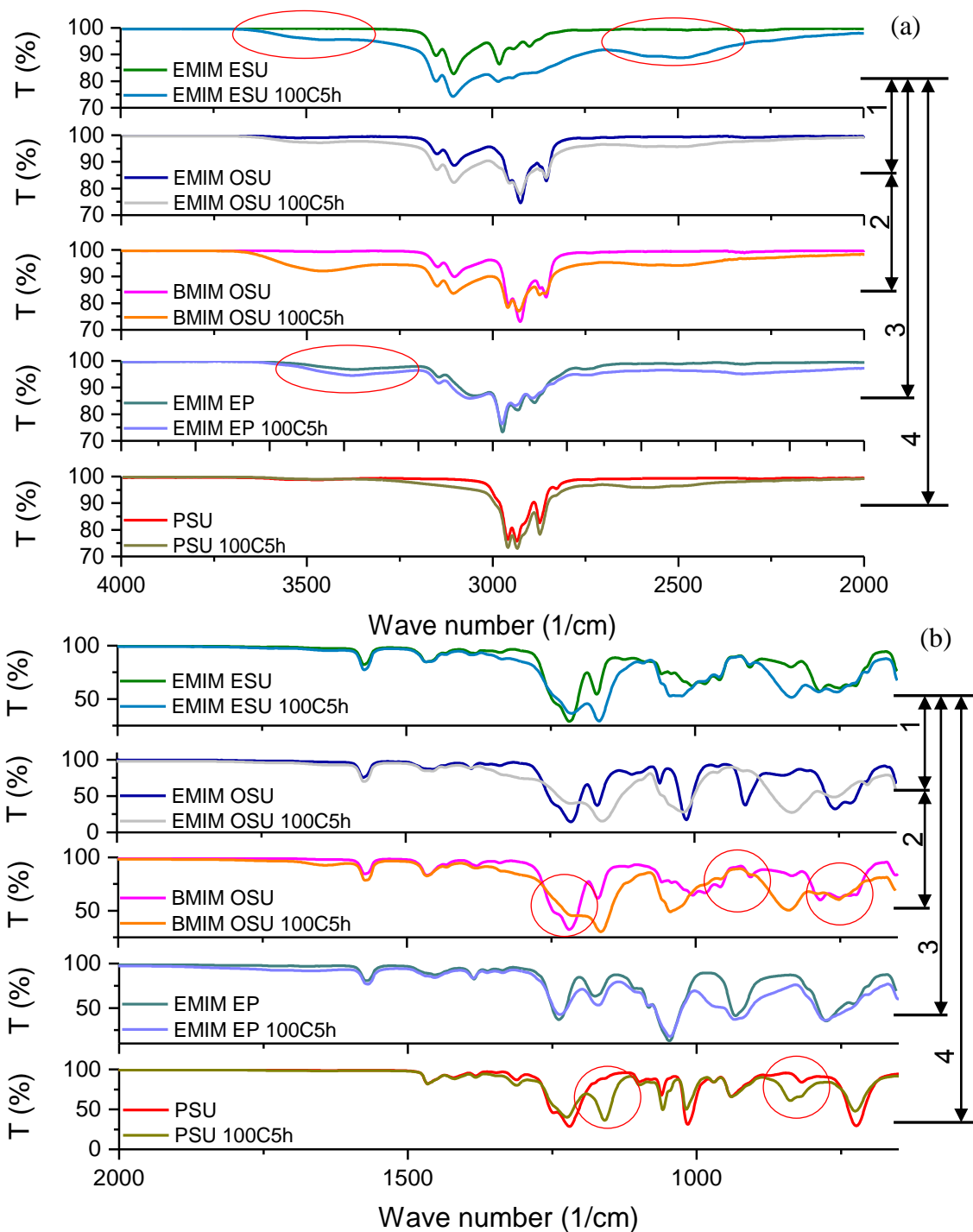


Fig. 3-5: : IR spectra of five ILs after heating into 100 °C for five hours; (a) spectra between 4000 cm⁻¹ and 2000 cm⁻¹ and (b) spectra between 2000 cm⁻¹ and 650 cm⁻¹. 1: increase anion chain length, 2: increase cation chain length, 3: change anion from sulfate to phosphate and 4: change cation type from imidazolium to phosphonium.

Changing anion type from sulfate to phosphate lead to increase the stability of IL. Thus, in EMIM EP no peaks are neither diminished nor produced due to the heating process (see Fig. 3-5). This outcome is in agreement with TGA results since the onset temperature of EMIM ESU is lower than EMIM EP (see Fig. 3-1d). However, a slight reduction in the intensities of the hydrocarbon related peaks occurs. In addition, a noticeable increase of the intensity of OH related peak is observed. This finding suggests that a partial decomposition occurs in the anion/cation chain.

Changing cation type shows a slight influence on the static thermal stability. Again, only sulfate peak intensities are decreased (see Fig. 3-5). Further, a new peak appears at 1160 cm^{-1} which is assigned to methyl sulphoxides (35). This suggests that the change of cation from imidazolium to phosphonium leads to higher oxidation as a result of heating. The phosphonium cation related peaks are almost same before and after the heating process (see Fig. 3-5). These findings suggest that the anion has a more significant role in the thermal decomposition process than cation.

To investigate the influence of time and temperature on the decomposition process. The results of BMIM OSU at various conditions are analysed, since it exhibits the lowest static thermal stability. Fig. 3-6 depicts the FTIR spectra for BMIM OSU at room temperature, after heating to $80\text{ }^{\circ}\text{C}$ for 2 and 5 hours and after heating to $100\text{ }^{\circ}\text{C}$ for 5 hours. The variation is mainly observed in sulfate related peaks rather than imidazolium ones. The intensity of OH peak increased with the increase of either time or temperature which confirmed that this peak results from the decomposition process as reported before in (24). The increase of either time or temperature leads to a reduction in the intensity (concentration) of the decomposed species (sulfate). It is obvious that the increase of temperature is more significant than time. This could suggest that the increase of temperature increases the decomposition rate. The slight effect of time can be resulted from the increase of the amount of the decomposed species at constant decomposition rate.

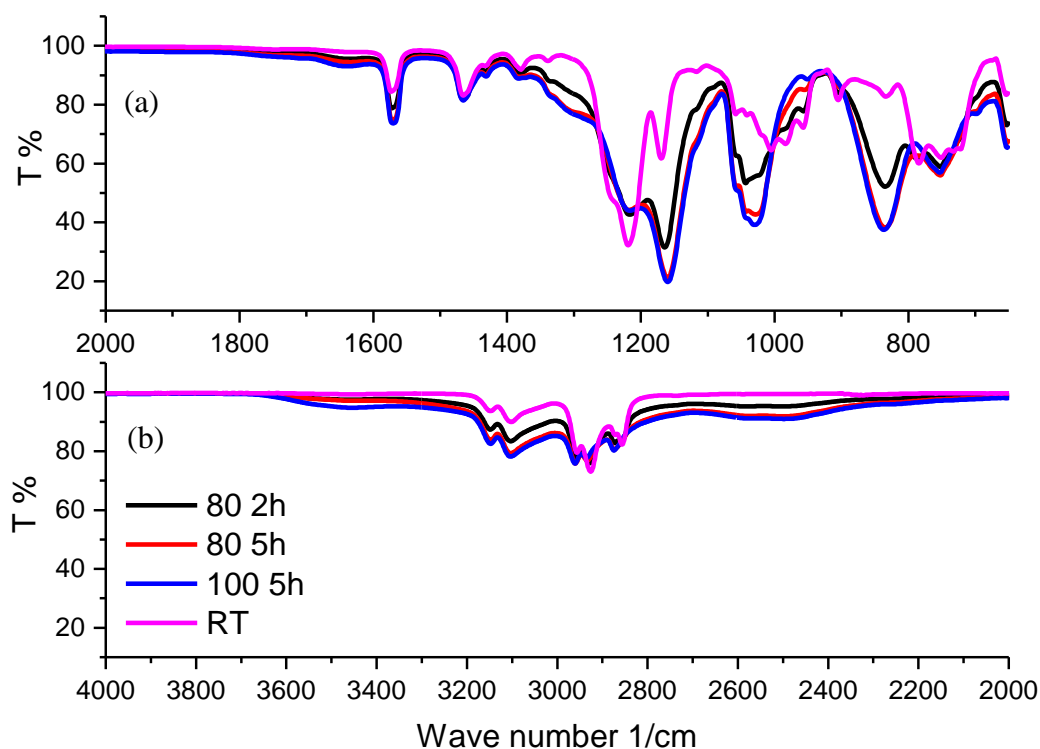


Fig. 3-6: Effect of time and temperature on BMIM OSU IR spectra; (a) spectra between 2000 cm^{-1} and 650 cm^{-1} and (b) spectra between 4000 cm^{-1} and 2000 cm^{-1} .

4. Discussion

4.1 Comparison between dynamic and static thermal decomposition

The use of TGA (in non-isothermal mode) to predict the thermal stability of ILs can result in an overestimation for their stability as also pointed out in (16, 24). However, the initiation of the thermal decomposition can be observed by the slight reduction of mass before the decomposition temperature (see Fig. 3-2). Nevertheless, the use of FTIR to assess the thermal stability of ILs can provide more accurate results. The partial thermal decomposition can be captured by the static thermal decomposition (using FTIR).

However, the results of both techniques show that the thermal decomposition of ILs is strongly effected by IL chemistry. Consequently, the increase of either cation or anion chain length results in a reduction of the thermal stability of ILs in both techniques. In addition, phosphate anion is more stable than sulfate anion. This finding suggests that TGA overestimates the decomposition temperature but it can provide a good prediction when it is utilized for comparison purposes.

4.2 Decomposition mechanism

The decomposition mechanisms are obtained from the static decomposition results. For imidazolium sulfate ILs, decomposition starts from the anion (see Figs. 3-5 and 4-1). The decomposition process starts when the concentrations (intensities) of the sulfate related peaks decrease. The second step is the breaking of anion chain length when SO_4 and C-O-S-O peaks are diminished.

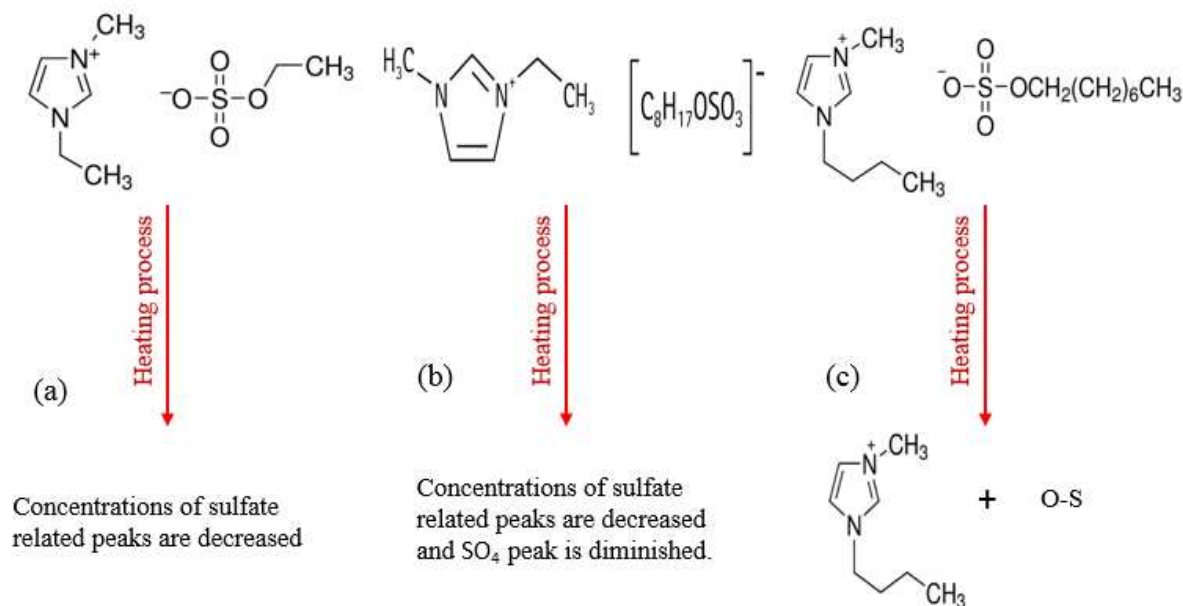


Fig. 4-1: Thermal decomposition mechanism for: (a) EMIM ESU, (b) EMIM OSU and (c) BMIM OSU.

For EMIM EP, the decomposition only occurs in the hydrocarbons since a slight reduction in their intensities was observed. The increase of the intensity of OH peak confirmed that a partial decomposition occurred in the hydrocarbons (See Fig. 3-5). Besides, PSU IL demonstrates a partial decomposition in the sulfate anion results a formation of methyl sulphoxides (See Fig. 3-5). This suggested that the decomposed sulfur is bonded with CH_3 instead of O.

4.3 Effect of time and temperature on the decomposition process

The increase of either time or temperature demonstrates an increase in the concentration of the decomposed species. However, the increase of temperature demonstrates a higher influence than time, see Fig. 3.6. This finding suggests that at particular temperature the decomposition has a particular rate, and the increase of temperature lead to increase the decomposition rate. This finding is in agreement with Arrhenius equation (40) since it states that the rate constant

is increased exponentially temperature. The increase of time lead to increase the concentration of the decomposed bonds due to the increase of their amount at constant decomposition rate.

5. Conclusions

The dynamic and static thermal decompositions of five ILs have been studied. TGA and FTIR are utilized to assess the static and dynamic thermal stabilities respectively. The following conclusions have been obtained:

- TGA provides an overestimation to the thermal stability of ILs. However, it provides an acceptable prediction to the effect of ILs' chemistry on their thermal stability.
- The increase of either cation chain length or anion chain length decreases the thermal stability of IL due to the decrease of the stability of carbocation.
- Both anion type and cation type influence on the thermal decomposition mechanism of IL. However, anion is more crucial in the determination of the thermal stability.
- Phosphate anion is more stable than sulfate anion when both combined with imidazolium cation.
- The decomposition is started from the anion rather than the cation.
- The increase of temperature increases the thermal decomposition rate.

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Table 1: The utilized ILs and their impurities and vendors.

ILs	Purity %	Vender
Ethyl Methyl Imidazolium Ethyl Sulfate (EMIM ESU)	98	Merck
Ethyl Methyl Imidazolium Octyl Sulfate (EMIM OSU)	98	Merck
Butyl Methyl Imidazolium Octyl Sulfate (BMIM OSU)	98	Merck
Ethyl Methyl Imidazolium Ethyl Phosphate (EMIM EP)	98	Sigma Aldrich
Butyl Methyl Phosphonium Methyl Sulfate (PSU)	95	Santa Cruz

1: Anion chain length is increased, 2: cation chain length is increased, 3: Anion type is changed and 4: cation type is changed.

Table 2: The applied conditions for the static decomposition experiments.

Condition number	Temperature (°C)	Time (hours)
1	80	2
2	80	5
3	80	24
4	100	2
5	100	5

Table 3: The assigned peaks for EMIM ESU at room temperature.

Intensity	Wave number cm^{-1}	Assigned to
w	3150	HCCH ring
m	3100	$\text{CH}_3(\text{N})$ HCH
w	2980	H-C-H
w	2940	CH_3 HCH
w	2900	Ring CH_3 HCH sym str
m	1574	$\text{CH}_3\text{-N}$ or $\text{CH}_2\text{-N}$
w	1468	N- CH_3 symmetric vibration
w	1380	C-H stretching, CH_3 (N) bending
w	1360	CH_2 (N) or CH_3 (N) stretching
w	1330	CH_2 (N) stretching
s	1215	S-O stretching
s	1170	(N) with CH_2 or CH_3
w	1110	SO_4 asymmetric vibration
m	1060	O-C
s	1015	C-O- SO_4 stretching, S=O stretching
w	960	C-C stretching, CH bending
s	912	C-O- SO_3
w	847	CCH bending
s	757	C-O-S-O bending
m	729	S-O stretching
w	705	In plane bending resulted from imidazolium ring; $\text{CH}_3(\text{N})$, $\text{CH}_2(\text{N})$.