The Effects of Magnetite Particles and Lithium Triflate on the Thermal Behavior and Degradation of Epoxidized Natural Rubber (ENR-50)

W.L. Tan and M. Abu Bakar

ABSTRACT

The thermal behavior and non-thermal degradation of magnetite (Fe$_2$O$_3$)/Epoxidized Natural Rubber (ENR-50) composites, lithium triflate (LiCF$_3$SO$_3$)-ENR-50 polymer electrolytes (PEs) and LiCF$_3$SO$_3$-Fe$_2$O$_3$/ENR-50 composite polymer electrolytes (CPEs) were investigated using differential scanning calorimetry (DSC) and thermogravimetric (TG) analysis. The glass transition temperature ($T_g$) of the studied materials generally follow the order of increasing values: ENR-Composite<CPE-PE. This is due to the nature of interaction between the Fe$_2$O$_3$ and ENR and between LiCF$_3$SO$_3$ with Fe$_2$O$_3$ and/or ENR. The degradation activation energy ($E_d$) was determined using the Kissinger and Flynn-Wall-Ozawa (FWO) methods. Both methods revealed that the Ed of the composites was lower compared to pristine ENR suggesting that the Fe$_2$O$_3$ particles catalyzed the decomposition of ENR. The PEs however, exhibited higher $E_d$ as compared to pristine ENR due to the salt-polymer interactions that resulted in thermally stable PEs. In the case of CPEs, the $E_d$ values were relatively higher than the composites but lower than the ENR and the PEs. This was attributed to the LiCF$_3$SO$_3$ that inevitably suppressed the catalytic effect of Fe$_2$O$_3$ particles on the degradation of ENR in the CPEs.

Keywords: Epoxidized Natural Rubbers; Magnetite; Polymer Electrolytes; Degradation; Composite

INTRODUCTION

Epoxidized natural rubber (ENR) is a modified natural rubber (NR) that possesses unique properties [1]. Efforts to further improve and diversify its properties are ongoing. Thus ENR has been incorporated with inorganic fillers like clay [2], silica [3], carbon black [3,4] and calcium carbonate [3] to produce composites with enhanced mechanical properties. Lithium salts such as lithium triflate (LiCF$_3$SO$_3$) [5], lithium perchlorate (LiClO$_4$) [6] and lithium imide (LiN(CF$_3$SO$_2$)$_2$) [6] have also been added into ENR to produce polymer electrolytes (polyelectrolytes, PEs) with moderate ionic conduction. ENR has also been blended with other polymers such as poly(3-hydroxybutyrate) (PHB) [7], polyvinyl chloride (PVC) [8] and chloroprene rubber (CR) [9] to tailor the processing conditions and properties of the resultant materials. For the many types and applications of ENR-based materials, their thermal properties are significant from technical and commercial point of view. For instance, the thermal information would be useful in process design and understanding the material reliability or limitations.

The magnetite, Fe$_2$O$_3$ exhibits interesting optical, magnetic, electrical and catalytic properties. Nano-size Fe$_2$O$_3$ particles are nowadays becoming a common filler in polymer matrix such as polyvinyl alcohol (PVA) [10], polyimide [11], polypyrrole [12,13], L-lysine [14], poly(3,4-ethylenedioxythiophene) (PEDOT) [15] and the likes. The polymer exerts control on the growth of Fe$_2$O$_3$ particles and the particles affect the properties of the resultant composite [16]. Therefore, a superior composite with characteristics of both the filler and polymer may be envisaged. The Fe$_2$O$_3$/polymer composites have shown potential in applications such as medical (MRI contrast agent or drug delivery) [17,18], absorbents (waste water treatment) [19], capacitors [20], membrane for sensors [21] and many more. Nonetheless, the Fe$_2$O$_3$ particles may affect the
thermal degradation of a polymer through improvement [22-26] or reduction [10,13,14,27,28] in thermal stability. The thermal stability of a polymer may be improved via strong interactions between the particles and polymer chains [22]. The thermal destabilization of a polymer however, may arise from several aspects such as effective heat transfer via particles to polymer chains [29], perturbation in the three-dimensional (3-D) structure of the polymer by particles [10] or direct participation (reaction) of particles in the degradation mechanism [30]. Thus far there is no literature report available on the kinetic or thermal stability study of the Fe$_3$O$_4$/ENR composites.

Lithium triflate, LiCF$_3$SO$_3$ has been incorporated into polymers like polyethylene oxide (PEO) [31], poly(vinylchloride) (PVC) [32], diurethanesil hybrid (d-Ut) [33] and polyether urethane acrylate (PEUA) [34] and even in ENR [5, 35]. The ionic conduction arising from the dissolved Li salt coupled with the superior chemical mechanical properties of the polymer make Li$^+$/polymer composites an ideal PE for use in electrochemical devices. However from literature, there is inconsistency in defining the role of LiCF$_3$SO$_3$ on the thermal degradation of a polymer in the PE. For example; Ramesh and Arof [32] have reported that LiCF$_3$SO$_3$-PVC is thermally more stable than pristine PVC whereas Noor and co-workers [36] suggested that LiCF$_3$SO$_3$ decreases the thermal stability of PEO-ENR blends with respect to each polymer constituent. Gonçalves et al. [33] on the other hand, demonstrated that the presence of LiCF$_3$SO$_3$ barely exerts any effect on the degradation of d-Ut. For LiCF$_3$SO$_3$-ENR PEAs, there is scarcely any report on the kinetic studies. Therefore it is worthy of investigation as well as for comparison purposes.

The incorporation of a filler or salt into the respective polymer electrolyte or polymer composite may alter the thermal characteristics of the polymer matrix. The lack of information on the role of this second component in a PE or polymer composite is obvious. This role is believed to be dependent on the various factors and differs from case to case. These include the type of polymer, presence of additive and feature of the particles such as size and particle distribution. For example, Leszczynska et al. [37] reported the relationship between the thermal stability of polymer/montmorillonite (MMT) composites with respect to surface modifiers. Kim et al. [30] studied the effect of a range of metal chlorides (metal = Na, Ca, Al, Zn and Sn) on the thermal degradation of poly(3-hydroxybutyric) acid (P(3HB)), poly(4-hydroxybutyric) acid (P(4HB)) and poly(ε-caprolactone) (PCL). They found that these metal chlorides accelerate the degradation of P(4HB), while NaCl and CaCl$_2$ affect the P(3HB) and only ZnCl$_2$, SnCl$_2$ and AlCl$_3$ affect PCL.

The literature on the kinetic study of thermal degradation of ENR-based materials is justifiably scarce. To best of our knowledge, only the work by Yu and co-workers [38,39] and Mohanthy et al. [40] have been reported thus far. Yu and co-workers [38,39] applied Coats and Redfern (CR) method to determine the degradation activation energy (E$_d$) of the ENR in both oxidative and inert environments. Their results inferred that the degradation of ENR followed first-order reaction. On the other hand, Mohanthy et al. [40] applied the Flynn-Wall (FW) method on the blends of poly(ethylene-co-acrylic) acid (PEA)/ENR. They found that the E$_d$ of the blend is higher than the respective polymer components and attributed this to the formation of ester linkages between the polymer chains. The persistent thermal and kinetic issues described above need to be addressed.

2. Objectives:

In this work, we employed ENR as the matrix while magnetite (Fe$_3$O$_4$) particles and LiCF$_3$SO$_3$ were added as the filler and additive respectively. Thus various Fe$_3$O$_4$/ENR composites [16], LiCF$_3$SO$_3$/ENR PEAs [35] and LiCF$_3$SO$_3$-Fe$_3$O$_4$/ENR CPEs were prepared. The thermal properties as well as the kinetic analyses of non-isothermal degradation of the Fe$_3$O$_4$/ENR composites and LiCF$_3$SO$_3$-Fe$_3$O$_4$/ENR CPEs were evaluated and compared with the LiCF$_3$SO$_3$-ENR PEAs. The Kissinger and Flynn-Wall-Ozawa (FWO) methods were used. These model-free methods have been extensively applied on polymer-based materials where the values of E$_d$ and A (pre-exponential factor) are found to be reliable [41].

Materials and Methods

All chemicals were obtained commercially and used without further purification unless otherwise stated. Lithium trifluoromethane sulfonate (lithium triflate), LiCF$_3$SO$_3$ (Aldrich, USA), tetrahydrofuran, THF (Merck, Germany), iron (II) sulphate, FeSO$_4$.7H$_2$O, potassium hydroxide, KOH and toluene (all from R&M Chemicals, UK) were employed. Epoxidized natural rubber with 50% epoxidation, ENR-50 was supplied by Guthrie Polymer (Malaysia) Sdn. Bhd. and was purified according to the literature before used [7].

3.1. Preparation of Samples:

Typical preparation of Fe$_3$O$_4$/ENR composite is as follows; an aqueous solution containing a certain amount of Fe$_3$O$_4$.7H$_2$O was mixed with a solution of 0.25 g ENR in 5 mL toluene while stirring. This was followed by the addition of 1 mL ethanol. The mixture was further stirred for 1 h. Then, 0.5 mL of 2.5M KOH was added slowly and the mixture was heated to 70°C while stirring. The stirring and reaction temperature was maintained for another 2 h. The resultant black colloid of Fe$_3$O$_4$/ENR was stripped off solvent using a rotary evaporator and the
residue was rinsed repeatedly with distilled water and air dried to obtain the composite. The various samples of Fe$_2$O$_3$/ENR composite were prepared accordingly (see Table 1).

For the preparation of LiCF$_3$SO$_3$-Fe$_2$O$_3$/ENR CPE, the Fe$_2$O$_3$/ENR base composite with Fe$_2$O$_3$ content of 3.9 wt% was chosen. The base composite was redispersed in 10 mL THF containing 5, 10, 15, 20, 25, 40 or 50 wt% of LiCF$_3$SO$_3$ (w.r.t. ENR) to obtain the various samples of CPEs as shown in Table 1. The sample solution was then cast onto a Teflon mould and air dried to obtain a solid thin film. The thin film was further dried in a vacuum oven at 50°C overnight.

For comparison purposes, LiCF$_3$SO$_3$-ENR PEs containing 5, 10, 15, 20 or 25 wt% LiCF$_3$SO$_3$ (w.r.t. ENR) were also prepared. The preparation was as described in literature [5,35]. Typically, an appropriate amount of LiCF$_3$SO$_3$ was weighed and added into a stirring solution comprising of 0.25 g ENR in 10 mL THF. The various samples of the PEs prepared are also shown in Table 1. The sample solution was then cast onto a Teflon mould and air dried to obtain a solid thin film. The thin film was further dried in a vacuum oven at 50°C overnight.

For TG analyses, ~10 mg of the sample was sealed in an aluminium pan and heated from room temperature to 120°C at a heating rate of 20 °C min$^{-1}$. The attained temperature was held for 3 min. This was followed by quenching to ~50°C at a rate of 100 °C min$^{-1}$ and the quench temperature was held for 3 mins. The sample was then reheated to 150°C at a heating rate of 20 °C min$^{-1}$. For DSC analyses, ~10 mg of the sample was heated from 30 to 600°C under nitrogen atmosphere at various heating rates. The TG analysis of the pristine LiCF$_3$SO$_3$ at a heating rate of 10 °C min$^{-1}$ was also performed. A Perkin-Elmer Analyst 200 atomic absorption spectroscopy (AAS) was utilized to determine the actual iron content in the composites. Typically, 20 mg of each sample was acid digested prior to AAS analyses. In this work, the amount of Fe is expressed as wt% Fe$_2$O$_3$.

3.2. Characterizations:
The thermal behavior of the entire samples was studied using differential scanning calorimetry (DSC) and thermogravimetric (TG) analysis. The former were performed using a Perkin Elmer Pyris calorimeter and the later using a Perkin-Elmer TGA-7. For DSC analyses, ~10 mg of the sample was sealed in an aluminium pan and heated from room temperature to 120°C at a heating rate of 20 °C min$^{-1}$. The attained temperature was held for 3 min. This was followed by quenching to ~50°C at a rate of 100 °C min$^{-1}$ and the quench temperature was held for 3 mins. The sample was then reheated to 150°C at a heating rate of 20 °C min$^{-1}$. For TG analyses, ~10 mg of the sample was heated from 30 to 600°C under nitrogen atmosphere at various heating rates. The TG analysis of the pristine LiCF$_3$SO$_3$ at a heating rate of 10 °C min$^{-1}$ was also performed. A Perkin-Elmer Analyst 200 atomic absorption spectroscopy (AAS) was utilized to determine the actual iron content in the composites. Typically, 20 mg of each sample was acid digested prior to AAS analyses. In this work, the amount of Fe is expressed as wt% Fe$_2$O$_3$.

### Table 1: The $T_d$ (°C) and the apparent activation energy, $E_a$ (kJ mol$^{-1}$) according to Kissinger method of various ENR-based composites, polymer electrolytes and composite polymer electrolytes (linear regression value, $R$ in parentheses).

<table>
<thead>
<tr>
<th>Sample</th>
<th>Base</th>
<th>Filler/Additive</th>
<th>Loading</th>
<th>$T_d$</th>
<th>$E_a$ for ENR</th>
</tr>
</thead>
<tbody>
<tr>
<td>Composite</td>
<td>ENR</td>
<td>Fe$_2$O$_3$</td>
<td>0</td>
<td>-19.0</td>
<td>234 (0.9978)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>2.8</td>
<td>-16.8</td>
<td>132 (0.993), 224 (0.9748)</td>
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<tr>
<td></td>
<td></td>
<td></td>
<td>3.9</td>
<td>-18.4</td>
<td>151 (0.9934), 231 (0.9759)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>5.1</td>
<td>-17.6</td>
<td>155 (0.9942)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>9.4</td>
<td>-17.3</td>
<td>163 (0.9914)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>16.3</td>
<td>-17.3</td>
<td>190 (0.9941)</td>
</tr>
<tr>
<td>Polymer electrolyte</td>
<td>ENR RS</td>
<td>LiCF$_3$SO$_3$</td>
<td>0</td>
<td>-19.0</td>
<td>234 (0.9978)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>5</td>
<td>-15.2</td>
<td>219 (0.9936)</td>
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<td></td>
<td></td>
<td></td>
<td>10</td>
<td>-12.4</td>
<td>257 (0.9858)</td>
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<td></td>
<td></td>
<td></td>
<td>15</td>
<td>-7.6</td>
<td>270 (0.9861)</td>
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<td></td>
<td></td>
<td></td>
<td>20</td>
<td>-5.7</td>
<td>293 (0.9945)</td>
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<td></td>
<td></td>
<td></td>
<td>25</td>
<td>-12.2</td>
<td>333 (0.9851)</td>
</tr>
<tr>
<td>Composite Polymer electrolyte</td>
<td>magnetite/ENR RS</td>
<td>LiCF$_3$SO$_3$</td>
<td>0</td>
<td>-18.4</td>
<td>151 (0.9934), 231 (0.9759)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>5</td>
<td>-18.2</td>
<td>141 (0.9919), 328 (0.9611)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>10</td>
<td>-17.2</td>
<td>279 (0.9815)</td>
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<tr>
<td></td>
<td></td>
<td></td>
<td>15</td>
<td>-18.2</td>
<td>300 (0.9957)</td>
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<td></td>
<td>20</td>
<td>-14.2</td>
<td>268 (0.9988)</td>
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<tr>
<td></td>
<td></td>
<td></td>
<td>25</td>
<td>-14.0</td>
<td>215 (0.9965)</td>
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<tr>
<td></td>
<td></td>
<td></td>
<td>40</td>
<td>-</td>
<td>191 (0.9934)</td>
</tr>
</tbody>
</table>

3.3. Kinetic Analyses:

Kissinger and Flynn-Wall-Ozawa (FWO) methods were employed in the kinetic analyses of the non-isothermal degradation of ENR-based composites, PEs and CPEs. Both methods were applied without the precise knowledge of the kinetic model. These two methods were derived from the common fundamental kinetic equations using differential (Kissinger, Equation 1) [42] or integral (FWO, Equation 2) [43] approaches.

$$\frac{-\ln \left( \frac{q}{T^d} \right)}{T^d} = \frac{E_a}{R T^d} - \frac{\ln AR}{E_a}$$

(1)
Here, \( q \) is the heating rate, \( T_p \) is the temperature at maximum degradation rate, \( E_g \) is the degradation activation energy, \( A \) is the pre-exponential factor, \( R \) is the gas constant, \( T \) is the absolute temperature and \( g(\alpha) \) is the integral form of \( f(\alpha) \) where \( \alpha \) is the degree of conversion. The respective \( E_g \) values were obtained from the slope and the \( y \)-intercept of the respective plots of \( -\ln q/T_p^2 \) against \( 1/T_p \) or \( \log q \) against \( 1/T \).

As a note, the Kissinger method is based on \( T_g \) which is the maximum peak for ENR degradation in DTG curve. In this study, those samples that exhibit two distinct DTG peaks at all heating rates, give two \( E_g \) values. As for the rest, only a single \( E_g \) is presented.

**Result and Discussion**

**4.1. Thermal Properties:**

Addition of inorganic fillers into a polymer matrix reduced the free volume of the polymer [44]. The existence of filler-polymer interaction restricts the flexibility or movement of the polymer segments and resulted in an increase in the glass transition temperature (\( T_g \)) [44]. Table 1 shows the \( T_g \) values of the various ENR-based composites, PEs and CPEs.

The \( T_g \) of purified ENR is \(-19^\circ C\). Upon incorporation of \( \text{Fe}_2\text{O}_3 \) particles into ENR, the \( T_g \) of the composites was marginally shifted to higher temperature (\( i.e. < 2^\circ C \)) compared to purified ENR. The FTIR spectra (not shown) of the polymer and the composites also suggest that the interaction (if any) between the \( \text{Fe}_2\text{O}_3 \) particles and ENR in the composites is negligible [16]. Thus the \( \text{Fe}_2\text{O}_3 \) particles do not significantly affect the ENR chain mobility in the composite.

The \( T_g \) for \( \text{LiCF}_2\text{SO}_3 \)-ENR PEs increases with the increase in \( \text{LiCF}_2\text{SO}_3 \) content up to a certain value beyond which this starts to decrease. For instance, the \( T_g \) for PE with 5 wt% \( \text{LiCF}_2\text{SO}_3 \) loading was \(-15.2^\circ C\). This increases to \(-12.4 \) to \(-7.6 \) to \(-5.7^\circ C\) upon every 5 wt% increase in the salt loading up to 20 wt%. Further increase in loading to 25 wt% of \( \text{LiCF}_2\text{SO}_3 \) caused the \( T_g \) to decline to \(-12.7^\circ C\). This trend in \( T_g \) for the various \( \text{LiCF}_2\text{SO}_3 \)-ENR PEs is consistent with the previous reported work [5]. The increment in \( T_g \) in this case is related to the salt-polymer interactions [5,6,35]. This creates pseudo-crosslinking between the ENR chains via \( \text{Li}^+ \) ions and thus restricts the mobility of the ENR chains and consequently raised the \( T_g \). The decrement in \( T_g \) at higher wt% content of \( \text{LiCF}_2\text{SO}_3 \) is however, attributed to the inevitable salt aggregations that reduce the pseudo-crosslinking in the PE.

In the case of \( \text{LiCF}_2\text{SO}_3 \)-\( \text{Fe}_2\text{O}_3 \)/ENR CPEs, the \( T_g \) increases \( i.e. \) from \(-18.4^\circ C\) for the base composite to \(-14^\circ C\) upon gradual addition of up to 25 wt% of \( \text{LiCF}_2\text{SO}_3 \) in the CPE. It is also noted that the \( T_g \) values for the CPEs are lower compared to the respective PEs. This may be due to the competing interactions between \( \text{LiCF}_2\text{SO}_3 \) with \( \text{Fe}_2\text{O}_3 \) or with the ENR chains. It has previously been reported that the \( \text{Li}^+ \) also has an affinity to interact with the oxygen of metal oxide [45] as well as of the epoxide of ENR [6,35]. The former reduce the pseudo-crosslinking between the ENR chains.

TG and DTG curves of purified ENR and the ENR-based composites containing various wt% \( \text{Fe}_2\text{O}_3 \) obtained at a heating rate of 10 °C min\(^{-1}\) are shown in Figure 1. From Figure 1(a)(i), the purified ENR exhibits a weight loss in the range of 360–460°C. However, the respective DTG curves (Figure 1(b)(i)) show peak maximum (ca. 390°C) carrying a shoulder (ca. 410°C). During the thermal treatment, the chemical bonds in the polymer break into smaller fragments. The weakest bonds are expected to severe the earliest. Thus, in the case of ENR, the C-O bonds of epoxide with low bond dissociation energy [46] are the potential sites for facile bond rupture. Mohanty et al. [40] has previously postulated the degradation mechanism for ENR. The ENR degradation was initiated with the decomposition of epoxide to form \( \gamma \)-lactones, aldehyde, furan as well as \( \alpha_3\beta \)-unsaturated compounds. This was followed by the complete breakdowns of the ENR main chains at temperature ~ 375°C whereby all the ENR characteristics were lost. These sequence of degradation phenomena/modes are significant in the present work as the first DTG peak (maximum) may represents the decomposition of the epoxide while the second peak (shoulder) represents the breakdown of ENR main chains.

Incorporating a small amount of \( \text{Fe}_2\text{O}_3 \) (\( i.e. \leq 3.9 \) wt%) into the ENR has caused the TG and DTG curves of the composites (Figure 1(a-b)(ii-iv)) to shift to lower temperatures as compared to purified ENR. Besides, there are two distinct weight losses with respect to the ENR degradation modes as observed in the DTG curve of Figure 1(b)(ii-iv). The first loss occurs in the region of 330-380°C; while the second loss occurs in the region of 380–460°C. The former is attributed to the decomposition of epoxide while the latter is due to the breakdown of the ENR main chains as discussed earlier. Thus, low \( \text{Fe}_2\text{O}_3 \) particle loadings (\( i.e. \leq 3.9 \) wt%) in the composite promote an early degradation of ENR as compared to purified ENR. However, at high \( \text{Fe}_2\text{O}_3 \) loadings (\( i.e. >5.1 \) wt%) in the composite, an unsymmetrical DTG peak was observed as shown in Figure 1(b)(v-vi). This is probably due to the progressive merging of the two ENR degradation peaks. Thus the first degradation is obviously slower and gradually overlaps with the second degradation as the particle loading in the composite gets higher. Also from Figure 1, the intensity of the DTG peak sequentially decreased from 5.1 to 9.4 to 16.3 wt% of \( \text{Fe}_2\text{O}_3 \) loading in the composite. This suggests that
Fe₃O₄ particles eventually lost their catalytic effectiveness in the composite upon increase in filler loading. At high filler loading, the particles tend to aggregate during heating [47]. Particle aggregations reduce the effective surface area and so reduce the particle’s catalytic effectiveness. The higher residue as compared to purified ENR observed for all the Fe₃O₄/ENR composites are due to the Fe₃O₄ particles in the composites.

![Figure 1: The (a) TG and (b) DTG curves of (i) purified ENR (green) and ENR compositied with (ii) 2.8 wt% (red), (iii) 3.9 wt% (brown), (iv) 5.1 wt% (purple), (v) 9.4 wt% (blue) and (vi) 16.3 wt% (orange) of Fe₃O₄ (heating rate of 10 °C min⁻¹).](image)

The TG and DTG curves for LiCF₃SO₃-ENR PEs exhibit multiple weight loss stages as shown in Figure 2. The first weight loss was at <200°C and is attributed to the removal of moisture associated with the LiCF₃SO₃ salt or solvent residues. Within this temperature range, the % of wt loss increases with the increase in LiCF₃SO₃ loading in the PE. The LiCF₃SO₃ is hygroscopic. Therefore more salt loading means more of the associated moisture. The second weight loss occurred within the range 340–450°C and constitutes more than 85% of the total weight loss. This weight loss is due to the two modes of degradation of ENR described above [35,40]. At lower salt content (viz. <15 wt%), two modes of ENR degradation are merged as shown by the broad DTG peaks in Figure 2(b)(ii-iv). Nevertheless, these are gradually separated into a maximum with a shoulder for PEs with higher salt content, i.e. ≥15 wt% (Figure 2(b)(v-vi)). The presence of the salt has also caused broader DTG peak for the PEs compared to purified ENR or even the composite. This signifies that a longer time is required for ENR to degrade in the presence of LiCF₃SO₃ as compared to purified ENR or ENR in the presence of Fe₃O₄ particles. As mentioned previously, the pseudo-crosslinking caused by the interaction between the Li salt and the epoxide group of ENR chains in the PEs has resulted in a macrostructure which cause the PE to be thermally more stable. Hence, extra energy and longer time-lapse is needed to degrade the ENR in the PE. Furthermore, due to the involvement of epoxide group in the pseudo-crosslinking reaction, the decomposition of epoxide (first mode of degradation) in PE is delayed and overlapped with the second mode of degradation which gave a broad DTG feature. However, salt-salt interaction is favorable in the PEs with higher wt% of LiCF₃SO₃ where the two modes of ENR degradation are detectable. The salt-salt interaction has caused salt aggregations. This reduces the crosslinking between the Li salt and ENR chains. The third weight loss occurs within the range of 450-560°C and is due to the decomposition of the LiCF₃SO₃ salt [35,48]. As a note, the decomposition of pristine LiCF₃SO₃ crystals shows a DTG peak at 462°C. The DTG peak with respect to the third weight loss is more intense upon increase in the salt content. In addition, a shoulder appeared at 450-490°C besides a sharp peak.
at 530°C for PE with 25 wt% LiCF₃SO₃. As the shoulder only appeared at higher wt% content of LiCF₃SO₃, it is believed that this shoulder is attributed to the destruction of the salt aggregates. On the other hand, the sharp peak may be due to the char-coated LiCF₃SO₃ that experience decomposition at higher temperatures of ~500°C.

![Fig. 2: (a) TG and (b) DTG curves of (i) purified ENR (blue) and the various LiCF₃SO₃-ENR polymer electrolytes containing (ii) 5 (red), (iii) 10 (green), (iv) 15 (purple), (v) 20 (orange) and (vi) 25 wt% LiCF₃SO₃ (light blue) (heating rate of 10 °C min⁻¹).](image)

The TG profiles of LiCF₃SO₃-Fe₃O₄/ENR CPEs, shown in Figure 3, also exhibit multiple weight loss stages. The first weight loss is at <200°C and is <8 % of the total weight loss. The DTG peak of the first weight loss also intensifies with the increase in LiCF₃SO₃ content in the CPE. This is due to the removal of moisture associated with the hygroscopic LiCF₃SO₃ salt or solvent residue described previously. The second weight loss stage is at 320-450°C and is attributed to the two modes of ENR degradation. The DTG feature for ENR degradation in CPE with lowest LiCF₃SO₃ content (viz. 5 wt%) is similar to base composite where the two distinct peaks represent the two modes of degradation of ENR as discussed earlier. Therefore, in a CPE with low LiCF₃SO₃ content, the Fe₃O₄ particles catalyze the decomposition of epoxide in the ENR chains. The CPEs with a loading of 10 to 20 wt% LiCF₃SO₃ gave a broad DTG peak. For CPEs with >20 wt% LiCF₃SO₃, the peak splits giving a maximum carrying a shoulder. The DTG peak attributed to the ENR in the CPEs is wider than those of purified ENR. Thus the degradation of ENR is slower in CPEs compared to the degradation in purified ENR but is relatively faster than the respective PEs. This may be due to the LiCF₃SO₃ salt that competitively interacts with either Fe₃O₄ or ENR in the CPE. In the CPE with low wt% of LiCF₃SO₃, the degradation of epoxide in ENR is faster due to lesser pseudo-crosslinking reaction as well as the catalytic effect of Fe₃O₄ towards the ENR matrix. Therefore, two distinct DTG peaks which represent the two modes of degradation are observed. For CPEs with 10-20 wt% LiCF₃SO₃ (moderate LiCF₃SO₃ content), the catalytic effect of Fe₃O₄ particles is suppressed via salt-Fe₃O₄ interactions. At the same time, the salt-ENR interactions are more dominant which produce greater amount of pseudo-crosslinking in the CPEs. This delays the decomposition of epoxide and caused the degradation peaks to merge. In the case of CPEs with high LiCF₃SO₃ content (i.e. >20 wt%), the Li salt tends to form aggregates. This reduced the crosslinking reaction and therefore two modes of degradation are again separated. The third weight loss is within 420–520°C and is due to the decomposition of LiCF₃SO₃ salt. Interestingly, the DTG profiles within this temperature range (420–520°C) revealed only one peak at lower salt content...
(≤ 15 wt%) but two peaks at higher salt content. As discussed earlier, the peak at lower temperature arises from the destruction of salt aggregates while the decomposition of the char-coated LiCF$_3$SO$_3$ is located at higher temperature.

Fig. 3: (a) TG and (b) DTG curves of Fe$_3$O$_4$/ENR base composite incorporated with (i) 5 (red), (ii) 10 (blue), (iii) 15 (light blue), (iv) 20 (orange), (v) 25 (brown), (vi) 40 (purple) and (vii) 50 wt% LiCF$_3$SO$_3$ (green) (heating rate of 10 °C min$^{-1}$).

4.2. Non-isothermal Degradation:

In order to understand the effect of LiCF$_3$SO$_3$ salt and or Fe$_3$O$_4$ particles on the degradation of ENR in the composites, PEs and CPEs, the ENR degradation in these materials was evaluated. The Kissinger and Flynn-Wall-Ozawa (FWO) methods were adopted to obtain the $E_d$ and the relevant kinetic parameters.

The Kissinger plots for the composites, PEs and CPEs are shown in Figure 4 and the extracted data are tabulated in Table 1. The $E_d$ of pristine ENR is 234 kJ mol$^{-1}$. The incorporation of Fe$_3$O$_4$ into the ENR has caused the $E_d$ to decrease as compared to pristine ENR. The composites containing 2.8 and 3.9 wt% of Fe$_3$O$_4$ show two DTG peaks attributed to the two degradation modes of ENR as discussed earlier. The respective $E_d$ values of 132 kJ mol$^{-1}$ and 151 kJ mol$^{-1}$ are due to the decomposition of the epoxide in the ENR while the respective $E_d$ values of 224 and 231 kJ mol$^{-1}$ are due to the breakdown of the ENR main chain. Further increase in Fe$_3$O$_4$ loading in the composite to 5.1, 9.4 and 16.3 wt% of Fe$_3$O$_4$ show two DTG peaks attributed to the two degradation modes of ENR as discussed earlier. The presence of LiCF$_3$SO$_3$ enhances the thermal stability of ENR in the PE and the effect is more pronounced at high loading of LiCF$_3$SO$_3$ in the PE. As mentioned in the previous section, this may be due to the pseudo-crosslink between the ENR chains via Li+
ions that enhances the thermal stability of ENR in the PE [35].

Figure 4(c) shows the Kissinger plots for the CPEs. The Ed of the CPEs shown in Table 1 was generally higher compared to the base composite. Unlike the other CPEs, the CPE containing 5 wt% LiCF₃SO₃ shows two ENR degradation peaks. The respective Ed values are 141 and 328 kJ mol⁻¹. However, only the CPEs with 10 to 20 wt% of LiCF₃SO₃ show Ed higher than pristine ENR. The Ed for CPE with 10 wt% LiCF₃SO₃ is 279 kJ mol⁻¹. This continues to increase to 300 kJ mol⁻¹ for CPE containing 15 wt% LiCF₃SO₃. Beyond this, the Ed decreases with the respective values of 268, 215, 191 and 216 kJ mol⁻¹ for 20, 25, 40 and 50 wt% LiCF₃SO₃ loading in the CPE. The initial increment in Ed is probably due to the LiCF₃SO₃ salt suppressing the catalytic effect of the Fe₃O₄ particles via LiCF₃SO₃-Fe₃O₄ interactions [35] whereby the salt coats the Fe₃O₄ particles surfaces. This creates a dominance of salt-ENR interactions. The later decrement of Ed however, may be due to the LiCF₃SO₃ salt aggregations whereby it reduces the pseudo-crosslinking between the ENR chains. This leads to the destabilization of the ENR in the CPE.

![Kissinger plots for different CPEs](image)

**Fig. 4**: Kissinger plots of (a) Fe₃O₄/ENR composites containing various wt% of Fe₃O₄ [0(+); 2.8(ð); 3.9(D); 5.1(x); 9.4(*); 16.3(a)] (b) LiCF₃SO₃-ENR polymer electrolytes and (c) LiCF₃SO₃-Fe₃O₄/ENR composite polymer electrolytes with various wt% of LiCF₃SO₃ [0(+)#; 5(ð); 10(D); 15(x); 20(*); 25(α); 40(ã) and 50(-)] [Note: # base composite; 1st degradation (solid line) and 2nd degradation (dash line)].

The respective Ed values at different degrees of conversion, α = 0.1-0.9 using FWO method are tabulated in Table 2. The Ed for pristine ENR was not constant throughout the conversion range. Instead, it increases with the increase in α up to α = 0.7 and thereafter experiencing a slight drop. For instance, the Ed at α = 0.1, 0.3, 0.5 and 0.7 respectively increases from 178 to 224 to 276 and to 295 kJ mol⁻¹ before decreasing to 282 kJ mol⁻¹ at α = 0.9. This trend is similar to those reported by Mohanty et al. [40]. Nevertheless, the values of Ed obtained in this work were slightly higher than that reported. This difference in the Ed value may due to the difference in material processing and instrument employed.
between the previous [40] and the present work. Furthermore, the trend of $E_a$ also signifies the possible occurrence of complex degradation reactions. The non-dependence of $E_a$ on $\alpha$ suggests that the degradation reaction may involve at least two mechanisms [49]. This agrees with the two degradation modes of ENR reported earlier [40].

The $E_a$ of Fe$_3$O$_4$/ENR composites increases at low $\alpha$ ($\alpha < 0.3$) but is almost constant at $\alpha > 0.4$. The value of $E_a$ is lower than pristine ENR at low $\alpha$ but is comparable to pristine ENR at high $\alpha$. The $E_a$ values for ENR incorporated with 2.8, 3.9, 5.1, 9.4 and 16.3 wt% of Fe$_3$O$_4$ are respectively 160, 169, 171, 182 and 170 kJ mol$^{-1}$. The results obtained via the FWO method agree with those obtained via the Kissinger method and reiterates that the Fe$_3$O$_4$ particles catalyzed the decomposition of ENR.

The $E_a$ of LiCF$_3$SO$_3$-ENR PEs increases with the increase in $\alpha$. For instance, the $E_a$ for PE containing 5 wt% LiCF$_3$SO$_3$ was 225, 231, 248, 265 and 270 kJ mol$^{-1}$ as $\alpha$ increases from 0.1 to 0.3 to 0.5 to 0.7 to 0.9. The $E_a$ values for the PEs at low $\alpha$ ($\alpha < 0.3$) are higher compared to pristine ENR but are lower as the content of LiCF$_3$SO$_3$ in the ENR is increased. For example, at $\alpha = 0.1$, the $E_a$ values for ENR incorporated with 0, 5, 10, 20 and 25 wt% LiCF$_3$SO$_3$ are respectively 178, 225, 212, 202 and 202 kJ mol$^{-1}$. These results generally suggest that the LiCF$_3$SO$_3$ enhanced the thermal stability of ENR in the PE especially at low salt loading. At high salt loading, the thermal stability is reduced due to salt aggregation as discussed earlier.

The $E_a$ of LiCF$_3$SO$_3$-Fe$_3$O$_4$/ENR CPEs generally increased with $\alpha$ especially for those with lower LiCF$_3$SO$_3$ content. However, there was some decrement (in $E_a$) at $\alpha > 0.7$ for the sample with higher LiCF$_3$SO$_3$ content (viz. $>15$ wt%). The LiCF$_3$SO$_3$-Fe$_3$O$_4$/ENR showed higher $E_a$ than the base composite at low $\alpha$ range. This means that the presence of LiCF$_3$SO$_3$ suppressed the catalytic effect of Fe$_3$O$_4$ particles with respect to the decomposition of ENR. These results are also in agreement to those obtained by Kissinger method.

Table 2: The apparent activation energy, $E_a$ (kJ mol$^{-1}$) according to Flynn-Wall-Ozawa method of various ENR-based composites, polystyrene composites and polyurethane composites (linear regression value $R$ in parenthesis). The $E_a$ values for ENR $\alpha$ (0.9992) and $E_a$ for the composites.

<table>
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<th>Sample</th>
<th>Base</th>
<th>Piller or additive</th>
<th>Loading (wt%)</th>
<th>0.1</th>
<th>0.2</th>
<th>0.3</th>
<th>0.4</th>
<th>0.5</th>
<th>0.6</th>
<th>0.7</th>
<th>0.9</th>
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<td>Composite ENR Fe$_3$O$_4$</td>
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<td>198 (0.9965)</td>
<td>224</td>
<td>253</td>
<td>276</td>
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<td>295</td>
<td>291</td>
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<td>190 (0.9981)</td>
<td>249</td>
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<tr>
<td></td>
<td>3.9</td>
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<td>191 (0.9995)</td>
<td>240</td>
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<td>285</td>
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<td>285</td>
<td>286</td>
<td>286</td>
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<tr>
<td></td>
<td>5.1</td>
<td>171 (0.9940)</td>
<td>180 (0.9964)</td>
<td>201</td>
<td>264</td>
<td>308</td>
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<td>319</td>
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<td>9.4</td>
<td>182 (0.9941)</td>
<td>189 (0.9957)</td>
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<td>16.3</td>
<td>170 (0.9857)</td>
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<td>230</td>
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<tr>
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<td>198 (0.9965)</td>
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<td>253</td>
<td>276</td>
<td>290</td>
<td>295</td>
<td>291</td>
<td>282</td>
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<tr>
<td></td>
<td>5</td>
<td>225 (0.9981)</td>
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<td>Composite Polymer electrolyte Fe$_3$O$_4$ ENR LiCF$_3$SO$_3$</td>
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Conclusions:

The $T_g$ of Fe$_3$O$_4$/ENR composites, LiCF$_3$SO$_3$-ENR PEs and LiCF$_3$SO$_3$-Fe$_3$O$_4$/ENR CPEs were generally higher than the pristine ENR. For the composites, this was due to the interactions between the Fe$_3$O$_4$ and the ENR. For the PEs and CPEs, these were due to the interactions between LiCF$_3$SO$_3$ with the ENR chains and/or Fe$_3$O$_4$. Nevertheless, the increment was dependent on the extent of the said interactions. The increment in $T_g$ for the composites is small due to the very weak interaction between the Fe$_3$O$_4$ particles and ENR. However, in the PEs and CPEs, the ENR chains were pseudo-crosslinked via Li$^+$ ions which give rise to higher $T_g$. In the CPEs, there exist competing reactions between the salt with Fe$_3$O$_4$ particles and the salt with ENR chains. The TG-DTG profile of pristine ENR showed smooth weight loss in the range of 360-460°C with a DTG.
peak carrying a shoulder. The DTG peak maximum represents the decomposition of epoxide while the peak shoulder represents the breakdown of ENR main chains. In the case of the Fe$_2$O$_3$/ENR composites, at low Fe$_2$O$_3$ loading (i.e. < 5.1 wt%), two distinct DTG peaks in the range of 330-460°C were observed. Therefore, at low loading of Fe$_2$O$_3$ in the composite, the particles promote an earlier degradation of ENR. Nonetheless, the catalytic effectiveness of the Fe$_2$O$_3$ particle at higher loading was reduced due to the agglomerations of the particles. The Li$_2$CF$_3$SO$_4$-ENR PEs and Li$_2$CF$_3$SO$_4$-Fe$_2$O$_3$/ENR CPEs revealed multiple weight losses in the TG-DTG profiles. Besides the weight loss due to the ENR degradation, the additional weight losses in the range of 450-530°C in these materials were attributed to the decomposition of Li$_2$CF$_3$SO$_4$ salt. Data obtained via the Kissinger and Flynn-Wall-Ozawa methods revealed that the Fe$_2$O$_3$ particles catalyzed the decomposition of the ENR in the Fe$_2$O$_3$/ENR composites where the Fe$_2$O$_3$ particles facilitate the heat transfer within the ENR chains thus promoting the ENR degradation process. In contrast, in the Li$_2$CF$_3$SO$_4$-ENR PEs, the degradation of ENR was slower due to the existence of pseudo-crosslinking between the ENR chains. In the Li$_2$CF$_3$SO$_4$-Fe$_2$O$_3$/ENR CPEs, the catalytic effectiveness of Fe$_2$O$_3$ particles was reduced due to competing interactions of Li$_2$CF$_3$SO$_4$ salt with Fe$_2$O$_3$ particles and salt with ENR. The preferable Li$_2$CF$_3$SO$_4$-Fe$_2$O$_3$ interactions create a barrier that prevents a close contact between the polymer and the Fe$_2$O$_3$ particles. This suppresses the heat transfer between the Fe$_2$O$_3$ particles and the ENR and therefore delays the degradation of ENR in the CPEs.

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