Modification of polyetherimide by phenylethynyl terminated agent for improved tribological, macro- and micro-mechanical properties

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The incorporation of 4-phenylethynylphthalic anhydride (4-PEPA) was utilized to synthesize a series of phenylethynyl terminated oligomers, according to different calculated number-average molecular weight (Mn). Modified polyetherimide (PEI) resins were prepared by the thermal curing reaction of phenylethynyl terminated etherimide oligomers. For comparison, unmodified PEI was also prepared. Thermal, macro- and micro-mechanical characterizations showed that the incorporation of phenylethynyl terminated agent resulted in a significant increase in glass transition temperature (Tg), tensile strength and microhardness. The tribological properties of PEI specimens were evaluated on a reciprocating friction and wear testing machine. Higher wear resistance was achieved by the incorporation of phenylethynyl terminated agent. Furthermore, wear rate of modified PEI prepared from the oligomers with the calculated Mn of 5000 g/mol was about five times lower than that of unmodified PEI. At least for the range of this study, while increasing calculated Mn of oligomers, wear rate of modified PEI initially decreased sharply and then increased slightly. This is clearly related to the change in the macro- and micro-mechanical properties. Scanning electron microscope (SEM) observations of worn surfaces showed that type of wear changed from abrasive wear of unmodified PEI into fatigue wear.

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1. Introduction

Aromatic polyimide (PI) resins exhibit a number of outstanding physical and chemical properties, such as excellent thermal and thermo-oxidative stability, solvent resistance, as well as mechanical, anti-wear and electrical properties. These excellent properties widely broaden the applications in automotive, bearings, micro-electronic appliances, aerospace materials and railway transport systems [1–3]. According to the increase in the demand for the industrial applicability, significant efforts have been focused on preparing PI resins with superior mechanical and tribological properties.

In previous literatures, many researchers have investigated various factors affecting tribological behaviors of PI, including type of atmosphere, temperature and contact stress [4–6]. Furthermore, the addition of traditional micro-fillers, such as graphite, MoS2 and fiber, could enhance tribological and mechanical properties [7–10]. Samyn and Schoukens [8] have proposed some tribological mechanisms of thermoplastic PI modified PTFE. What is more, a great variety of nano-particles, such as metal oxidation nanoparticles, carbon nanotubes (CNTs), silicon compounds and some other nano-particles could largely improve the tribological properties of PI as well as mechanical properties [11–17]. Sinha and coworkers [16] have investigated the influence of single walled carbon nanotubes (SWCNTs) addition on the tribological properties of the PI films and found that the incorporation of the SWCNTs obviously enhanced the load-bearing capacity of the PI composites. On the other hand, only a few reports, however, have been available on the improvement of tribological behaviors of PI modified by changing macromolecule structures. Chitsaz-Zadeh and Eiss [18] have changed the diamine groups into structures with different elasticity modulus and found that flexible chain configurations with a high toughness led to a positive effect on the wear rates of PI films. In our team group, Tian et al. [19] investigated the tribological properties of fluorinated PI. Experimental results indicated that the friction coefficient and wear rate decreased with increasing fluoride monomer ratio. These above researches have indicated that mechanical and tribological properties were depended heavily on the structures of PI. Thereby, an in-depth knowledge of the relationship between structures and properties of PI becomes imperative for further understanding related mechanism and improving mechanical and tribological properties. From this point of view, it is potential way to enhance the related properties by the incorporation of some latent cross-linkable groups, which may thermally react to provide cross-links.
Previous works on the imide oligomers have been focused on the phenylethyln terminated oligomers [20–24]. Compared with nadic terminated oligomers, this kind of oligomers possesses good processability without evolution of volatiles during the thermal curing process [25,26]. Despite enormous reports on the performance of imide oligomers, no investigations, to date, have ever been investigated the tribological, macro- and micro-mechanical properties of modified polyetherimide (PEI) prepared from phenylethyln terminated etherimide (PT-EI) oligomers.

Herein, the objective of this study was aimed to investigate the effect of phenylethyln terminated agent on the tribological, macro- and micro-mechanical properties of PEI. 4-phenylethylnylphthalic anhydride (4-PEPA), as the phenylethyln terminated agent, was added to synthesize a series of PT-EI oligomers, according to different calculated $M_n$. Modified PEI resins were prepared by the thermal curing reaction of PT-EI oligomers. For comparison, unmodified PEI was also prepared. In order to further investigate the relationship between mechanical properties and wear resistance, mechanical properties of PEI were examined at both macro-level and micro-level. Furthermore, appropriate calculated $M_n$ of oligomers was investigated by a comparison, which was made in the thermal stability, mechanical and tribological properties of modified PEI. In addition, worn surfaces and wear debris were characterized to understand the related tribological mechanisms.

2. Experimental

2.1. Materials

2,2'-bis[4-(3,4-dicarboxyphenoxy)phenyl]-propanedianhydride (bisphenol-A dianhydride, BPADA) was purchased from Shanghai Research Institute of Synthetic Resins and dried at 120 $^\circ$C under vacuum prior to use. 4,4'-oxydianiline (4,4'-ODA) and acetic anhydride were supplied by Sinopharm Group Chemical Reagent Co., Ltd. In addition, 4,4'-ODA was recrystallized from ethanol/water (1:1) prior to use. 4-phenylethylnylphthalic anhydride (4-PEPA) was provided by Changzhou Sunlight Pharmaceutical Co., Ltd and purified by vacuum desiccation. N, N-dimethylformamide (DMF) and triethylamine were obtained from Shanghai Qiangshun Chemical Agent Co., China. Ethanol was purchased from Shanghai First Chemical Factory. All the reagents were used as received.

2.2. Synthesis of polyetheramide acid, phenylethynyl terminated etheramide acid and etherimide oligomers

The phenylethyln terminated etheramide acid (PTAA) oligomers based on BPADA, 4,4'-ODA and 4-PEPA with different calculated $M_n$ were synthesized, according to Scheme 1. The molar ratios of BPADA, 4,4'-ODA and 4-PEPA for the target molecular weight (3000, 5000, 8000 and 10000 g/mol) are shown in Table 1. The PTAA oligomers were prepared by allowing the monomers to react at room temperature (RT) in DMF for 5 h. For comparison, the polyetheramide acid (PAA) was also prepared by the solution condensation between BPADA and 4,4'-ODA with the molar ratios as 1:1, according to the previous amide acid route [12]. The PTAA and PAA solutions were kept in a freezer until use. The PT-EI oligomers were obtained via chemical synthesis route. After the preparation of the PTAA solution, triethylamine and acetic anhydride were added as per procedure described elsewhere [27]. The solution was allowed to stir overnight at room temperature. The resultant mixture was then poured into hot water to yield precipitate. The solid was collected by filtration, and then dried at 120 $^\circ$C in vacuum for 24 h to afford an off-white solid.

2.3. Preparation of the film specimens

The PT-EI oligomer powder was dissolved in DMF to get a homogenous solution at a concentration of 35 wt%. The PT-EI solution was cast onto a glass substrate, and then was heated at 100, 150 and 200 $^\circ$C for 1 h to get rid of volatile, followed by the thermally curing at 320 $^\circ$C for 2 h. Modified PEI films were obtained by the thermal curing reaction of the corresponding

<table>
<thead>
<tr>
<th>Scheme 1. Synthesis of phenylethyln terminated etherimide oligomers.</th>
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![Scheme 1](image-url)
PT-EI solutions with different calculated $M_n$. For comparison, unmodified PEI (PEI-0) film was also prepared by the thermal imidization of the PAA solution. The thickness of the resulting thin films was about 0.05 mm. The details and the designations of the film specimens are given in Table 2.

2.4. Preparation of the friction specimens

The samples for friction and wear tests were prepared by casting PT-EI solutions onto a stainless steel plate. Prior to coating the PT-EI solutions onto the steel plate, the stainless steel plate was ground with abrasive papers of various grit sizes in sequence. These specimens were thermally cured in an air convection oven, according to the given temperature procedure as described above. For comparison, unmodified PEI (PEI-0) specimen was also prepared. The details and designations of the friction specimens are given in Table 2.

2.5. Friction and wear tests

The tribological tests were conducted on a reciprocating friction and wear testing machine (HS-2M, Lanzhou Zhongke Kaihua Technology Development Co., Ltd.). The contact schematic diagram of the frictional couple is shown in Fig. 1. A 9Cr18 stainless steel ball of diameter 6.0 mm was used as the counterpart. The roughness of the stainless ball used is 20 nm, as provided by the supplier. The test was performed under ambient conditions (temperature: 23 ± 2 °C, relative humidity: 50 ± 10%) at a reciprocating frequency of 5 Hz and an applied load of 6 N. The length of stroke in one cycle is 8 mm. Each friction and wear test was carried out for 10 min. Before each test, the surfaces of the friction specimens and the counterpart ball were cleaned with acetone followed by drying.

The friction coefficient was obtained by the computer automatically. At the end of each test, the depth of the wear scar was measured with a stylus surface profiler (Dektak 150, Veeco instruments Inc., USA), and then the wear volume ($\Delta V$, mm$^3$) of the specimen was calculated according to the following equation:

$$
\Delta V = \frac{L}{2} \left[ \frac{r^2 \arccos \frac{r^2 - d^2 - (r-d)^2}{2 r d}}{r} + 2 \int_0^d \pi \sqrt{r^2 - (r-d)^2} d \left( \sqrt{r^2 - (r-d)^2} \right) \right]
$$

where $\Delta V$ is the wear volume (mm$^3$), $d$ the depth of the specimen (mm), $L$ the length of stroke in one cycle (mm), and $r$ the radius of the counterpart ring (mm). The wear rate ($K$, mm$^3$/Nm) of the specimen was calculated from the following equation:

$$
K = \frac{\Delta V}{F t v}
$$

where $F$ is the applied load (N), $t$ the experimental duration (s), $v$ the reciprocating frequency (Hz) and $L$ the stroke length in one cycle (m). In this work, five replicates of friction and wear tests were carried out to minimize data scattering, and the average results were reported in this article.

2.6. Analysis methods

Fourier transform infrared spectroscopy (FTIR, Nexus-470, Nicolet Co., USA) was utilized to identify the ethynyl groups in the PT-EI oligomers, and also was carried out to confirm that the ethynyl groups disappear after the thermally curing procedure. Nuclear magnetic resonance (NMR) spectra were obtained on a Varian Mercury plus 400 M instrument (Varian Co., USA) using chloroform-d as solvents. $^1$H-NMR and $^{13}$C-NMR spectra were used to confirm the success of synthesis and the existence of the ethynyl groups.

Intrinsic viscosity measurement was conducted at a concentration of 0.5 g/dL in DMF at 25 °C, using an Ubbelohde cannon-type viscometer.

The glass transition temperature ($T_g$) was measured by a dynamic mechanical analyzer (DMA, 242, Netzsch Co., Germany). A tension mode was employed on thin film specimens. The temperature scans were run from 100 to 280 °C at a heating rate of 5 °C/min. The tests were conducted at a frequency of 1 Hz, vibration amplitude being set to 120 μm, static compressive stress 4 N.

The decomposition behaviors of the PEI films were investigated by using thermal gravimetric analysis (TGA, Pyris 1, Perkin Elmer Co., USA). The measurement was conducted in flowing nitrogen atmosphere (40 cm$^3$/min) at a heating rate of 20 °C/min.

Tensile properties tests were carried out according to ISO 527-3:1995 standard, using a universal testing machine (CMT4104, Shenzhen Sans Testing Machine Ltd., China) at a crosshead speed of 2 mm/min. The parallel segment of the dumbbell-shaped specimens for tensile tests was 20 × 4 × 0.05 mm. The average value of five replicated measurements was adopted as the final result.

Nanoindentation tests were conducted with an ultra nanoindentation tester (CSM Instruments, Switzerland) using a Berkovich diamond indenter. After contacting with the surface, the indenter was approached into the friction specimens with a constant strain rate of 0.05 s$^{-1}$ until 2000 nm of depth was reached, held at the maximum load for 50 s, and then withdrawn from the surface with the same rate as loading. At least five indents were performed on each specimen and the average value was finally adopted. The hardness was calculated by the Oliver and Pharr method [28,29].

In order to investigate the related tribological mechanisms, the morphologies of worn surfaces and debris were observed by using scanning electron microscope (SEM, 5136MM, Tescan Co., Czech). All specimens were sputter coated with a thin gold layer prior to SEM observation.

![Fig. 1. Schematic diagram of the contact configuration of the reciprocating friction and wear testing machine.](image-url)
3. Results and discussion

3.1. Characterization of the PT-EI oligomers and PEI

The FTIR spectra of modified PEI prepared from different calculated \( M_n \) of oligomers and a typical PT-EI oligomer are shown in Fig. 2. In order to avoid duplication, the PT-EI oligomer with the calculated \( M_n \) of 5000 g/mol is chosen to represent. The FTIR spectrum of unmodified PEI is also presented in Fig. 2. It can be found that there are several of the same characteristic absorption bands on the spectra among the PT-EI oligomer and PEI (specimens from PEI-0 to PEI-4). The bands at about 1778 and 1720 cm\(^{-1}\), which belong to the asymmetric and symmetric stretching vibrations of imide \( C=O \), are clearly observed. The bands at about 1378 and 745 cm\(^{-1}\), which are assigned to the stretching and blending of imide \( C-N \), are also detected. In addition, the PT-EI oligomer exhibits the characteristic band around 2213 cm\(^{-1}\), which is attributed to the stretching vibration of ethynyl \( C\equiv C \) in the modified PEI (specimens from PEI-1 to PEI-4) disappears, which demonstrates that the PT-EI oligomers have been fully thermally cured after the multistage heating schedule. Thus, from characteristic peaks discussed above, it was roughly proved that the expected chemical structures have been obtained according to Scheme 1.

Figs. 3 and 4 show \(^1\)H-NMR and \(^{13}\)C-NMR spectra of the PT-EI oligomer (represented by the calculated \( M_n \) of 5000 g/mol), respectively. It can be seen that the PT-EI oligomer has been prepared successfully, according to the \(^1\)H-NMR spectrum and \(^{13}\)C-NMR spectrum. Moreover, the \(^{13}\)C-NMR spectrum shows the integrals of the carbons in the backbone (\( -\text{CH}_3, \delta = 31 \) ppm) and the end-capping group (\( -\text{C}\equiv\text{C}, \delta = 88 \) and 94 ppm). Thus it is further demonstrated that the PT-EI oligomers have been synthesized successfully according to Scheme 1.

Molecular weight control was achieved by utilizing 4-PEPA as an end-capping agent. As shown in Table 1, the intrinsic viscosity of the PAA and PTAA solutions was measured by Ubbelohde viscometer at a concentration of 0.5 g/dL in DMF at 25 °C. It can be found that different calculated \( M_n \) is corresponding to different intrinsic viscosity, which is consistent with previous reports of other researchers \([23,30]\). Therefore, it can be proved indirectly that the PT-EI oligomers with different calculated \( M_n \) have been synthesized by the phenylethynyl terminated agent.

3.2. Macro-mechanical properties of PEI

Fig. 5 shows the effect of phenylethynyl terminated agent on the tensile strength and elongation at break of PEI. As shown in Table 1, the PT-EI oligomers with different calculated \( M_n \) were prepared according to different addition of phenylethynyl terminated agent. The PEI-0 and modified PEI (specimens from PEI-1 to PEI-4) have been prepared, respectively, according to Table 2. It can be clearly seen that the incorporation of phenylethynyl terminated agent significantly enhances the tensile strength of PEI and causes a reduction in elongation at break. It is worth noting that the highest tensile strength is obtained at the calculated \( M_n \) of 5000 g/mol and this is ca. 20% higher than that of the PEI-0 (87.14 MPa).
When the calculated $M_n$ is above 5000 g/mol, however, the tensile strength of modified PEI decreases slightly and the elongation at break improves. This implies that the calculated $M_n$ of oligomers plays an important role in the macro-mechanical properties of PEI. The difference in the changes in the tensile strength as a function of calculated $M_n$ of oligomers can be possibly explained by the difference in the backbone composition and crosslink density what we will discuss below. Apparently, it is found that appropriate calculated $M_n$ of oligomers can markedly improve the tensile strength of PEI.

3.3. Micro-mechanical properties of PEI

Fig. 6 shows the effect of phenylethynyl terminated agent on the typical loading-hold-unloading curves and microhardness of PEI. On loading, the force increases with increasing depth. It can be seen that the loading-hold-unloading curve of PEI obviously shifts upwards because of the incorporation of phenylethynyl terminated agent, indicating that modified PEI (specimens from PEI-1 to PEI-4) specimens’ resistance to indentation significantly increases comparing with PEI-0. It is well noting that the deformations of modified PEI specimens are similar after unloading and are less than that of PEI-0. While the curves of modified PEI initially shift upwards with increasing calculated $M_n$, and then go down clearly when the calculated $M_n$ is above 5000 g/mol. The values of microhardness of PEI show a significant increase from 397.7 to 548.2 MPa because of the incorporation of phenylethynyl terminated agent. Obviously, the above results suggest the idea that the appropriate calculated $M_n$ of oligomers by the addition of 4-PEPA causes the improvement in micro-mechanical properties of PEI.

Surprisingly, the change trend of microhardness among the PEI is completely the same as that of tensile strength. It indicates that the influence of the incorporation of phenylethynyl terminated agent on the macro- and micro-mechanical properties displays the same effect, which is due to an essential factor that the changes in the macromolecular structures of PEI.

3.4. Thermal properties of PEI

The thermal properties of PEI, which were thermally cured, were evaluated by DMA and TGA. The thermal data of PEI based on TGA and DMA are summarized in Table 3. It is obviously found that the glass transition temperature ($T_g$) of modified PEI (specimens from PEI-1 to PEI-4) is enhanced significantly in different levels, compared with that of the PEI-0. This phenomenon may be well explained that the incorporation of the phenylethynyl terminated agent offers some latent cross-linkable groups, which makes the polymer backbone more rigid after the thermally curing process.

Moreover, the PEI-2 shows the highest $T_g$ of 238.2$^*\text{C}$, which is ca. 20$^*\text{C}$ higher than that of the PEI-0 (216.7$^*\text{C}$). Combining with macro- and micro-mechanical characterization above, it can be inferred that the optimal calculated $M_n$ of the PT-EI oligomers can be 5000 g/mol.

Comparing the weight retentions between the PEI-0 and modified PEI, it is found that the incorporation of phenylethynyl terminated agent improves the weight retentions of modified PEI, and these values are higher than 54.1%. In addition, the modified PEI specimens exhibit excellent thermal stability with 5 and 10 wt% of weight loss in the range of 537–547.5 and of 549.9–559.6$^*\text{C}$ in nitrogen atmosphere, respectively. This indicates that modified PEI specimens still keep excellent thermal stability after the incorporation of phenylethynyl terminated agent.

3.5. Friction and wear properties of PEI

The friction coefficient and wear rate of PEI specimens were conducted under a load of 6 N, a reciprocating frequency of 5 Hz and dry condition. Fig. 7 presents the effect of phenylethynyl terminated agent on the friction coefficient and wear rate of PEI specimens.

Compared with the PEI-0, the wear rate of modified PEI (specimens from PEI-1 to PEI-4) shows lower values clearly. What is more, the wear rate of the PEI-2 prepared from the oligomer

<table>
<thead>
<tr>
<th>Samples</th>
<th>$T_a^a$ ($^\text{C}$)</th>
<th>$T_a^b$ ($^\text{C}$)</th>
<th>$R_w^c$ (%)</th>
<th>$T_g$ ($^\text{C}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PEI-0</td>
<td>546.9</td>
<td>558.1</td>
<td>51.3</td>
<td>216.7</td>
</tr>
<tr>
<td>PEI-1</td>
<td>537.0</td>
<td>549.9</td>
<td>54.1</td>
<td>224.2</td>
</tr>
<tr>
<td>PEI-2</td>
<td>543.3</td>
<td>555.7</td>
<td>57.6</td>
<td>238.2</td>
</tr>
<tr>
<td>PEI-3</td>
<td>541.2</td>
<td>552.4</td>
<td>54.6</td>
<td>231.7</td>
</tr>
<tr>
<td>PEI-4</td>
<td>547.5</td>
<td>559.6</td>
<td>58.2</td>
<td>228.3</td>
</tr>
</tbody>
</table>

$^a$ $T_a$: the temperature at 5 wt% of weight loss was recorded by TGA with a heating rate of 20 $^\text{C}$/min under $N_2$ atmosphere.
$^b$ $T_a$: the temperature at 10 wt% of weight loss was recorded by TGA with a heating rate of 20 $^\text{C}$/min under $N_2$ atmosphere.
$^c$ $R_w$: residual weight retention was recorded by TGA at 800 $^\text{C}$ with a heating rate of 20 $^\text{C}$/min under nitrogen atmosphere.
with the calculated $M_n$ of 5000 g/mol reaches the minimum value and the lowest wear rate is $3.8 \times 10^{-5}$ mm$^3$/Nm, which means that the wear resistance of the PEI-2 is ca. five times more than that of the PEI-0. The degree of substantial improvement in the wear resistance of the PEI is similar to that obtained in some previous studies [11–15]. In addition, it can be seen that the wear rate of modified PEI initially decreases sharply and then increases slightly with increasing calculated $M_n$. Therefore, the optimum calculated $M_n$ of oligomers is 5000 g/mol considering the wear resistance of PEI.

As shown in Fig. 7, the incorporation of phenylethynyl terminated agent obviously causes to increase the friction coefficient of PEI. It is also found that the friction coefficient is 0.51 at the maximum value when the calculated $M_n$ reaches 5000 g/mol.

3.6 Worn surfaces and wear debris observations

To make clear the tribological mechanisms of PEI, worn surfaces and wear debris of the PEI-0 and modified PEI were investigated with SEM.

The SEM images of the worn surfaces of the PEI-0 and modified PEI under experimental conditions are shown in Fig. 8a, c, e, g and j. It can be seen that the wear width of modified PEI (specimens from PEI-1 to PEI-4) is much smaller compared with that of the PEI-0 (0.66 mm). This demonstrates that the incorporation of phenylethynyl terminated agent can obviously enhance the wear resistance of PEI. Furthermore, it is also found that the wear width...
of modified PEI first reduces and then increases with increasing calculated \( M_\text{n} \). The wear width is at its smallest value when the calculated \( M_\text{n} \) is 5000 g/mol. Apparently, the change trend of wear rate as discussed above is well consistent with the change in the wear width.

In addition, it can be seen in Fig. 8 that the worn surface of the PEI-0 is relatively smoother than those of modified PEI (specimens from PEI-1 to PEI-4) and shows signs of light adhesion and abrasive wear. However, the worn surfaces of modified PEI are rough, displaying deep scuffed and furrowed marks. Moreover, it is obviously seen that fatigue deformations on the worn surfaces of modified PEI are severer to some extent compared with that of the PEI-0, indicating that the type of wear changed from abrasive wear into fatigue wear. Surprisingly, the change trend of surface roughness of worn surfaces (Fig. 8a, c, e, g and j) is roughly consistent with the change trend of friction coefficient of the corresponding PEI. This might be inferred that the surface roughness of worn surface is one of the most important factors that govern the friction coefficient of materials.

Debris is a product of friction experiments. Therefore, its analysis can be helpful to understand the related friction and wear mechanism. The SEM images of wear debris of PEI specimens are given in Fig. 8b, d, f, h and k. Both wear debris of the PEI-0 and modified PEI almost consists of flakes. Nevertheless, debris of modified PEI (specimens from PEI-1 to PEI-4) is considerably smaller than that of the PEI-0. Furthermore, it is also found that the size of debris first decreased with increasing calculated \( M_\text{n} \), however, the debris size of modified PEI increases when the calculated \( M_\text{n} \) exceeds 5000 g/mol. It is worth noting that the wear debris of the PEI-2 turns to be small sized platelets or particles. The size of the debris agrees well with the wear resistance of the corresponding PEI specimens, considering the relationship between the debris size and wear rate.

3.7. Discussion

It is worth pointing out that mechanical and tribological properties of a material is dependent on a number of factors, which includes macromolecule structures, composition for blends, processing, surface tension, interfacial adhesion, etc. In the case of modified PEI in this study, macromolecule structures were modified by the incorporation of phenylethynyl terminated agent. The PT-EI oligomers are rich in ethynyl groups (cross-linkable groups) (Fig. 2). Upon the thermal curing reaction, the ethynyl groups have undergone a complex reaction involving chain extension, branching and crosslinking without the evolution of volatile by-products, which makes the polymer backbone more rigid [21–23]. Although the definite structure of modified PEI (specimens from PEI-1 to PEI-4) is not well known, modified PEI specimens exhibit an excellent combination of properties that include higher \( T_g \), tensile strength and microhardness, compared with PEI-0. Moreover, there definitely exists a close relationship between mechanical properties and wear resistance of PEI. In other words, the improvement in macro- and micro-mechanical properties of PEI contributes to obtain better wear resistance.

In addition, SEM observations of wear debris (Fig. 8) indicate that modified PEI with higher tensile strength and microhardness shows relatively small flakes or particles. According to Ratner-Lancaster [42,43], it could be explained that the material may be more difficult to be peeled off because of more excellent mechanical properties, and hence that results in a lower wear.

By making further comparison among the properties of modified PEI (specimens from PEI-1 to PEI-4), it is apparently found that the best performances, including \( T_g \), mechanical and tribological properties, are obtained when the calculated \( M_\text{n} \) is 5000 g/mol. In other words, the calculated \( M_\text{n} \) which is greater or less than 5000 g/mol goes against the improvement of the performance of PEI. It may be explained as follows: First, the PT-EI oligomers would be rich in ethynyl groups when the calculated \( M_\text{n} \) is relatively small. The backbone composition of the PEI might mainly consist of carbon chain (alkene C=C) after the thermal curing. The carbon backbone is generally much weaker than the aromatic backbone. Second, there would be poor in cross-linkable groups when the calculated \( M_\text{n} \) is relatively large. That would result in low crosslink density after the thermal curing, which is also demonstrated by Hergenrother et al. [44]. Therefore the backbone composition and crosslink density are important factors, which influence the performances of PEI.

4. Conclusion

Modified PEI resins were prepared by the thermal curing reaction of PT-EI oligomers. The incorporation of 4-PEPA was utilized to synthesize a series of PT-EI oligomers, according to different calculated \( M_\text{n} \). The tribological properties of PEI specimens were investigated by a reciprocating friction and wear testing machine. The macro- and micro-mechanical properties were evaluated to further understand the relationship between mechanical and tribological properties. The friction and wear mechanism was discussed by analyzing the worn surfaces and wear debris. The major conclusions can be summarized as follows:

(1) The incorporation of phenylethynyl terminated agent increases \( T_g \), tensile strength and microhardness of PEI. Modified PEI prepared from the oligomer with the calculated \( M_\text{n} \) of 5000 g/mol shows the highest tensile strength, which is ca. 20% higher than that of the PEI-0. Moreover, the weight retentions of modified PEI are improved gently compared with that of the PEI-0.

(2) The incorporation of phenylethynyl terminated agent contributes to a significant improvement on the tribological properties. The wear rate of modified PEI specimens initially decreases sharply and then increases slightly with increasing calculated \( M_\text{n} \). It is worth noting that modified PEI prepared from the oligomer with the calculated 5000 g/mol shows the best wear resistance, which is ca. five times more than that of unmodified PEI. SEM observations of worn surfaces show that type of wear changed from abrasive wear into fatigue wear.

(3) The improvement in macro- and micro-mechanical properties of modified PEI contributes to obtain better wear resistance. 

(4) The calculated \( M_\text{n} \) of oligomers is one of significant factors which affect \( T_g \) mechanical and tribological properties. Apparently, modified PEI shows the best performance when the calculated \( M_\text{n} \) is 5000 g/mol.

References


