Investigation of the Relationship Between Morphology and Tribological Properties of an Epoxy Resin Based on Tetraglycidyl 4,4′-Diaminodiphenylmethane Modified with Polyetherimide Oligomers

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ABSTRACT: In this paper, polyetherimides (PEI) with two different calculated number-average molecular weights (M_n) of 5000 and 10,000 g/mol were synthesized and used to modify tetraglycidyl 4,4′-diaminodiphenylmethane. Three different morphologies (separated phase, bi-continuous phase, and phase inversion structure) were obtained by controlling molecular weights and content of PEI. Thermal and mechanical characterizations showed that addition of PEI resulted in an increase in thermal stability and tensile strength. Tensile strength of samples with bi-continuous phase was higher than those with separated phase or phase inversion structure. Influence of morphologies on tribology properties were studied by a ring-on-block wear tester. Higher wear resistance was achieved from samples with bi-continuous phase. It was found that wear life of samples with bi-continuous phase was almost 100% higher than that of samples with separated phase. This is clearly related to the change in thermal and mechanical properties caused by the change of morphologies. Scanning electron microscope observations of worn surfaces and wear debris of the tested samples showed that tribological behaviors and wear mechanisms were heavily dependent on morphologies. © 2013 Wiley Periodicals, Inc. J. Appl. Polym. Sci. **2014**, *131*, 39863.
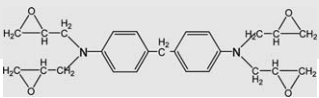
INTRODUCTION

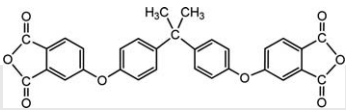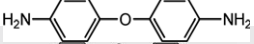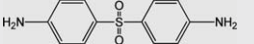Epoxy resins are a kind of high-performance thermosetting resin with high bonding strength, excellent thermal resistance, high mechanical strength, and outstanding dielectric and aging characteristics. For the reason, epoxy resins are widely used in many fields ranging from high-performance composites to electric and electronic insulation, protective coatings, and structural adhesives.[1–3] However, epoxy resins are brittle as well as sensitive to moisture, and they exhibit poor tribology properties, which greatly limit the application of them.[1] To address these defects, much attention is drawn to improve the overall performance of epoxy resins.[4–7] Especially, extensive works have been done to improve the mechanical[8–11] and tribological properties.[12–17] One of the most successful methods of improving their toughness is to incorporate a second phase of rubbery particles[5,18,19] or engineering thermoplastics.[8,20] It has been shown that the addition of rubbery materials to epoxy resin enhances their fracture toughness, while at the same time goes against the improvement of the performance of glass transition temperatures (T_gs), thermal stability, and the other mechanical properties.[21–25] Compared with rubbery materials, it has been reported that engineering thermoplastics improves the toughness of epoxy resin without decreasing most of the other mechanical properties and thermal stability. As a result, engineering thermoplastics, such as polyethersulfone (PES),[26,27] polysulfone (PSF),[28–30] poly(ether ether ketone),[31–33] and polyetherimide (PEI)[34,35] have been used as toughening agents of epoxy resin or other thermosetting resins.

The key point to improve the mechanical properties of epoxy resin by introducing a thermoplastics phase into the primary epoxy phase is controlling morphology.[36] Generally speaking, there are three morphologies: separated phase structure, bi-continuous phase structure, and phase-inversion structure. Girard-Reydet[36] found that epoxy resin was effectively toughened only when the thermoplastic and epoxy form a bi-continuous phase (bi-continuous phase structure), or the thermoplastic forms a continuous phase with the epoxy spherical domain (phase-inversion structure).

Table I. Chemical Formulas of the Materials Used in This Study

Materials	Chemical formulas
TGDDM	
BPADA	
PA	
4,4′-ODA	
DDS	

Different morphologies can be obtained by the following methods: changing thermoplastics content and curing agents, varying chain structure and molecular weight of thermoplastics, altering curing temperatures and time.[37–41]

On the basis of the studies above, we conclude that the tribology properties of epoxy resin can be improved by controlling the morphologies to bi-continuous phase or phase inversion structure. However, as far as we know, there is no report on the relationship of morphology and tribological properties. From this point of view, in this article, PEIs with two different M_n are used to modify tetraglycidyl 4,4′-diaminodiphenylmethane TGDDM/4,4′-diaminodiphenylsulfone (DDS) system. Morphologies of the cured products are observed by scanning electron microscope (SEM). Thermal stability, tensile strength, and tribological properties of the cured products are investigated by thermo gravimetric analysis (TGA), universal testing machine, and ring-on-block wear tester. Wear mechanism are studied by observing the worn surfaces and wear debris of the tested samples.

EXPERIMENTAL

Materials
TGDDM was supplied by Changzhou Olong Electrical Insulation Materials Co., Ltd. 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°C under vacuum prior to use. Phthalic anhydride (PA) 4,4′-oxydianiline (4,4′-ODA), DDS, triethylamine, acetic anhydride, dimethyl acetamide (DMAc), and dichloromethane were purchased from Sinopharm Group Chemical Reagent Co., Ltd. In addition, 4,4′-ODA was recrystallized from ethanol/water (1 : 1) prior to use. Ethanol was purchased from Shanghai First Chemical Factory. All the reagents were used as received. The chemical structures of the materials are shown in Table I.

Synthesis of PEI
PA terminated PEI with different calculated M_n was synthesized using BPADA, 4,4′-ODA, and PA. The molar ratios of BPADA, 4,4′-ODA and PA for the target molecular weights of 5000 and 10,000 g/mol are shown in Table II. PEI with molecular weights of 5000 and 10,000 g/mol were named as PEI-5k and PEI-1w, respectively, in this article. To prepare the polyetheramide acid (PEAA) oligomers, the monomers were allowed to react at room temperature (RT) in DMAc for 6 h. Triethylamine and acetic anhydride were added to the PEAA solution as per procedure. The solution was allowed to stir at 60°C for 2 h. The resultant mixture was then poured into ethyl alcohol to yield the precipitate (PEI). The solid was collected by filtration, followed by washing by deionized water for three times. The collected solid was dried at 120°C in an air oven for 12 h and then moved to a vacuum oven at 80°C for 24 h to remove all of the water.

Preparation of the Bulk Specimens
PEI was first dissolved in dichloromethane at room temperature and the obtained solution was incorporated into epoxy resin (TGDDM). The mixture was mechanically stirred at room temperature for 10 min to get a homogeneous solution. The obtained solution was stirred at 60°C for 2 h to remove dichloromethane. After completely removing dichloromethane, DDS was added to the mixture with mild stirring. The mixture was then poured into a mold. After being degassed in a vacuum oven, the mixture was allowed at 150°C for 6 h to completely cure. The sample designation is shown in Table III. It should be pointed out that phr used in this paper means per-hundred weight of epoxy resin (TGDDM).

Preparation of the Friction Specimens
The mixture obtained above was first dissolved in a dichloromethane–acetone (with a molar ratio of 1 : 1) mixed solvent. The samples used for friction and wear tests were prepared by spraying the prepared solutions with 0.15 MPa nitrogen gas on a clean steel plate polished by metallographic abrasive paper using a spray gun. The steel plate was heated at 60°C in an air oven before spraying. After spraying, the samples were degassed in a vacuum oven, and then cured at 150°C for 6 h in an air oven.

Friction and Wear Tests
A ring-on-block wear tester (MHK-3, Jinan Testing Machine Factory, China) was used to evaluate the friction and wear performance of the cured products. The contact schematic of the frictional couple is shown in Figure 1. An AISI-C-52100 steel ring (HardnessHv850) of 48.95 mm in diameter and 12.05 mm in thickness was rotated against the cured products at a speed of 1.28 m/s and a load of 100 N. Before each test, the steel ring

Table II. Molar Ratios of BPADA, 4,4′-ODA and PA and M_n of the Resultant PEI

	Monomers (molar ratios)			
Sample name	BPADA	4,4′-ODA	PA	Calculated M_n (g/mol)
PEI-5k	0.86	1	0.28	5000
PEI-1w	0.93	1	0.14	10,000

Table III. Sample Designations

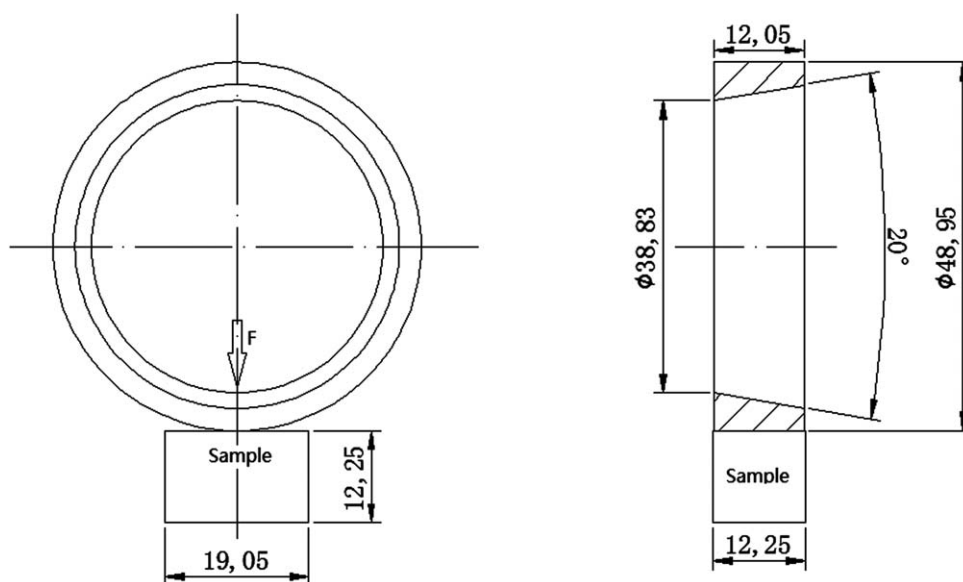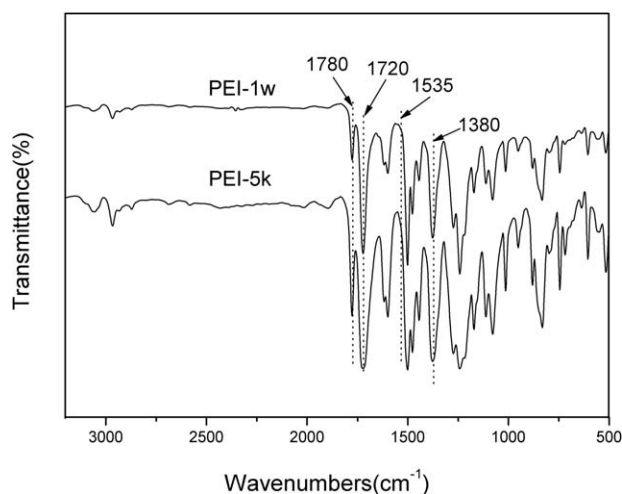| Sample designation	TGDDM (g)	DDS (phr[a])	PEI content (phr[a]) 5k	PEI content (phr[a]) 1w
TD	100	49.6	0	0
TP5k-6.4	100	49.6	6.4	0
TP5k-12.8	100	49.6	12.8	0
TP5k-19.2	100	49.6	19.2	0
TP5k-25.6	100	49.6	25.6	0
TP5k-32.0	100	49.6	32.0	0
TP5k-38.4	100	49.6	38.4	0
TP1w-6.4	100	49.6	0	6.4
TP1w-12.8	100	49.6	0	12.8
TP1w-19.2	100	49.6	0	19.2
TP1w-25.6	100	49.6	0	25.6
TP1w-32.0	100	49.6	0	32.0

[a] phr means per-hundred weight of epoxy resin (TGDDM).

was abraded with 800 grade abrasive paper and polished by metallographic abrasive paper, after which the steel ring was cleaned with acetone followed by drying. At the end of each test, the width of the wear scar was measured with a measuring microscope, and the wear life of the specimen was calculated from the following equation:

$$WL = t / \left\{ r - \sqrt{[r^2 - (d/2)^2]} \right\} \times 10^3$$

Where WL is wear life (s/μm), t is the tested time (s), r is the radius of the counterpart ring (mm), and d is the width of the wear scar (mm).

All the friction and wear tests were carried out at about 25°C and a relative humidity of about 40%. All the data presented in the current work were the averages of three replicate measurements.

Figure 2. Results of FTIR analysis.

Analysis Methods

A Fourier transform infrared spectroscopy spectrometer (FT-IR, NEXUS-470, Thermo Nicolet Co., USA) was applied to characterize the resultant PEI. Samples were tableted into KBr pellets before FTIR analysis.

The morphology of the fracture surfaces of the cured samples were observed by a TS 5136MM SEM (Tescan Co., Czech). Before the observation, the cured samples were fractured in liquid nitrogen and coated with a layer of gold.

The glass transition temperature (T_g) was obtained via a dynamic mechanics analyzer (DMA 242C, NETZSCH Co. Ltd., German) in the scanning temperature mode. It was performed in the range of 50–300°C, at a heating rate of 3°C/min, with an oscillation frequency of 1 Hz. The geometry of deformation was the tension mode. Cured samples with a size of 10.0 mm × 3.5 mm × 0.2 mm were prepared for the experiment.

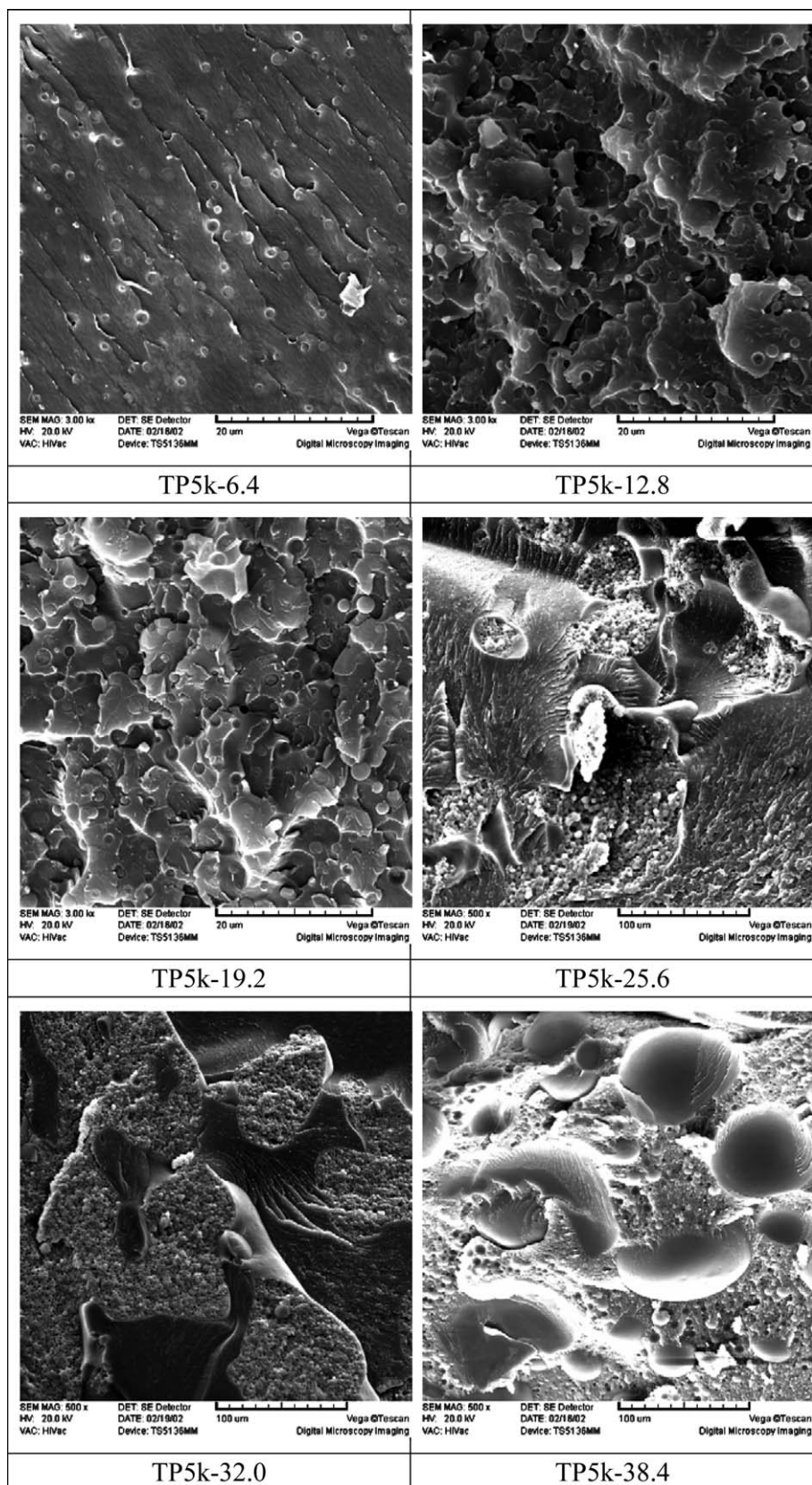**Figure 1.** Contacting schematic for the frictional couple.

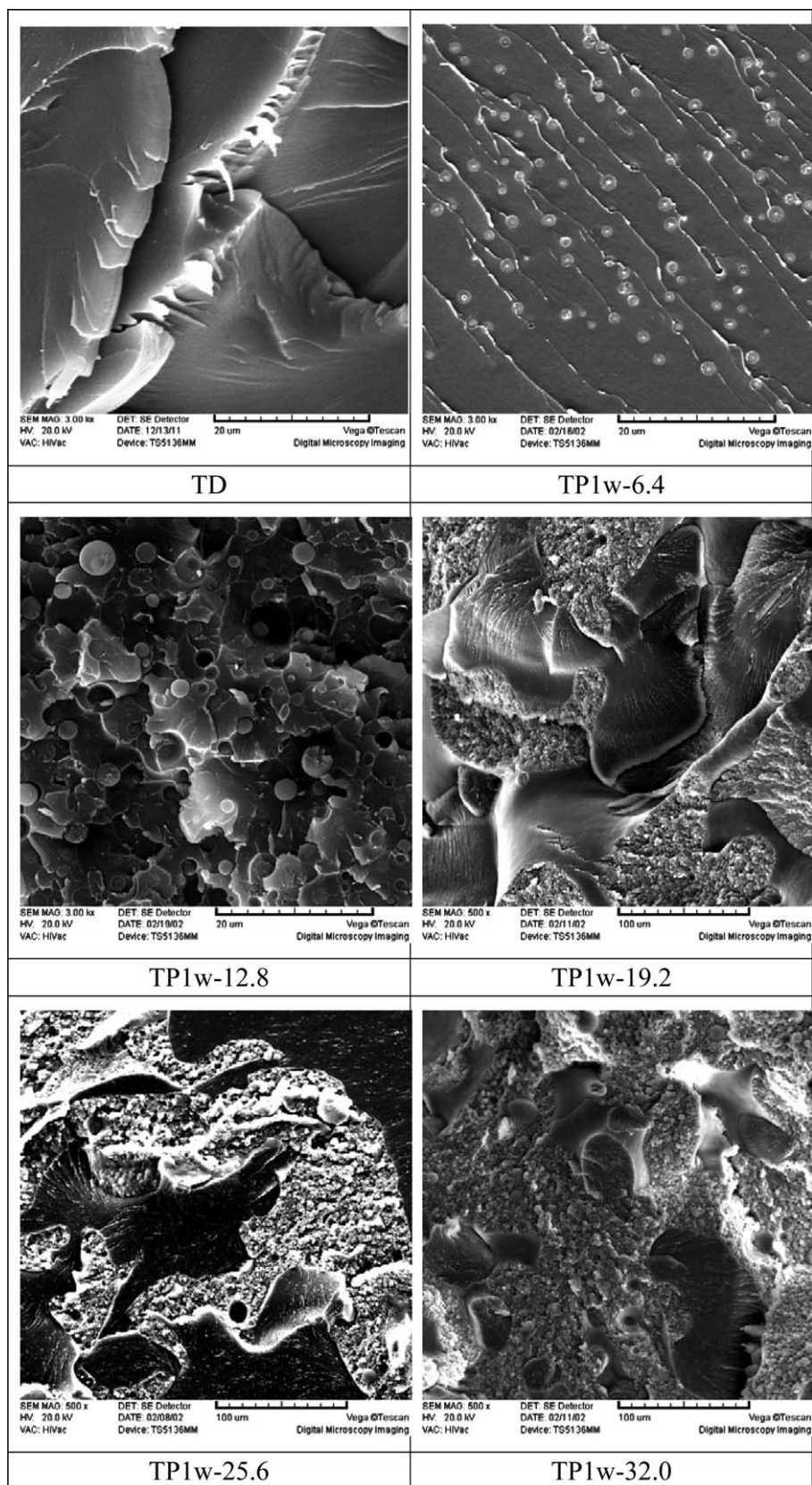**Figure 3.** Morphologies of PEI-5k modified TGDDM/DDS system.

Figure 4. Morphologies of sample TD and PEI-1w modified TGDDM/DDS system.

Table IV. Results of Tensile Strength and Elongation at Break

PEI content (phr[a])	Tensile strength (MPa)		Elongation at break (%)	
	5k	1w	5k	1w
0	51.2		1.7	
6.4	58.7	59.9	1.9	2.0
12.8	56.7	54.3	1.8	2.1
19.2	54.4	74.5	1.9	2.6
25.6	65.9	72.1	2.3	2.6
32.0	62.3	58.1	2.4	2.8
38.4	53.6	-	2.6	-

[a] phr means per-hundred weight of epoxy resin (TGDDM).

A TGA (Model 951, Perkin Elmer Co., USA) was applied to investigate the thermal stability of the cured samples in nitrogen atmosphere (flow rate 40 mL/min). Powdered samples of 3 ± 1mg scraped carefully from the cured samples and a heating rate of 20 °C/min were used in every experiment.

Tensile strength test was conducted with a universal testing machine (CMT4104, Shenzhen Sans Testing Machine Ltd., China). The gauge length and crosshead speed of tensile strength test were set as 20 mm and 5 mm/min, respectively. Samples with sizes of 30.0 mm × 5 mm × 0.2 mm were prepared for tensile strength test.

In order to investigate the tribological mechanisms, morphologies of the wear debris and worn surfaces were also observed by using TS 5136MM SEM (Tescan Co., Czech). The wear debris and worn surfaces were coated with a layer of gold before observation.

RESULTS AND DISCUSSION

Characterization of PEI

The PEI synthesis method used in this work has been successfully and widely used in many published work.[42–44] As result, we believe that FTIR analysis is enough to confirm that PEI is successfully synthesized. The result of FTIR analysis is shown in Figure 2. There were strong peaks at 1780 cm^{-1} (C=O asym-

Table V. T_g of the Tested Samples

PEI content (phr[a])	T_g (°C)	
	PEI-5k	PEI-1w
0	245	
6.4	160.5/249.5	140.9/249.2
12.8	154.8/250.8	140.9/249.1
19.2	148.0/247.0	143.4/187.0
25.6	144.6/240.9	143.0/184.0
32.0	143.2/197.2	138.1/181.4
38.4	143.5/197.5	–

[a] phr means per-hundred weight of epoxy resin (TGDDM).

Table VI. Results of TGA Analysis

PEI content (phr[a])	T_5[b] (°C)		T_{10}[c] (°C)		R_w[d] (%)	
	5k	1w	5k	1w	5k	1w
0	347.20		373.81		23.04	
6.4	350.77	355.37	377.20	374.96	25.52	22.54
12.8	349.51	361.12	378.17	379.71	26.98	22.48
19.2	352.35	361.44	382.13	382.50	26.39	23.71
25.6	354.09	360.32	384.26	384.78	26.73	23.00
32.0	356.86	353.56	384.21	374.82	26.56	24.79
38.4	358.30	–	385.68	–	27.39	–

[a] phr means per-hundred weight of epoxy resin (TGDDM).
[b] T_5: the temperature at 5% weight loss.
[c] T_{10}: the temperature at 10% weight loss.
[d] R_w: residual weight retention at 800°C.

metric stretching of aromatic imides), 1720 cm^{-1} (C=O symmetric stretching of aromatic imides) and 1380 cm^{-1} (C—N stretching of aromatic imides) in the spectra of PEI-5k and PEI-1w. There was no band at 1535 cm^{-1} (in-plane bending vibration of secondary amide N—H).[45,46] On the basis of the results above, it could be confirmed that PEI was successfully synthesized.

Morphologies

Morphologies of the samples were observed using SEM, shown in Figures 3 and 4. In all images presented here, the dark regions correspond to the epoxy-rich phase, whereas the bright regions correspond to the PEI-rich phase.

For sample with no PEI (sample TD), a homogenous phase was observed, indicating that no phase separation occurred during curing process. For samples with PEI with a molecular weight of 5000 g/mol (PEI-5k), many fine PEI-rich globules can be observed in the PEI-rich phase (separated phase structure) when the content of PEI was less than 19.2 phr. Sizes of the globules increased with the increasing PEI content. When the content of PEI was 25.6–32.0phr, large and continuous PEI-rich
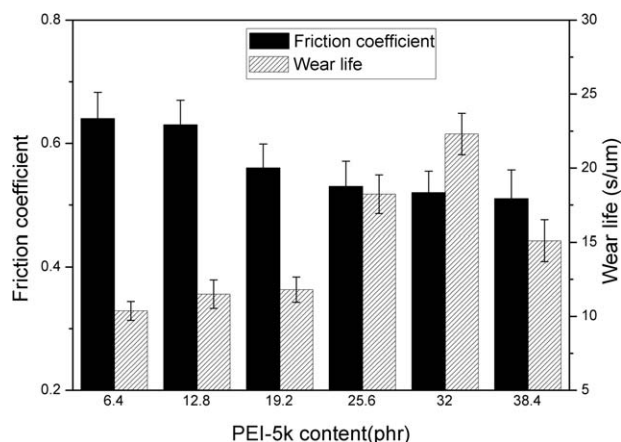
Figure 5. Friction coefficient and wear life of PEI-5k modified TGDDM/DDS system.
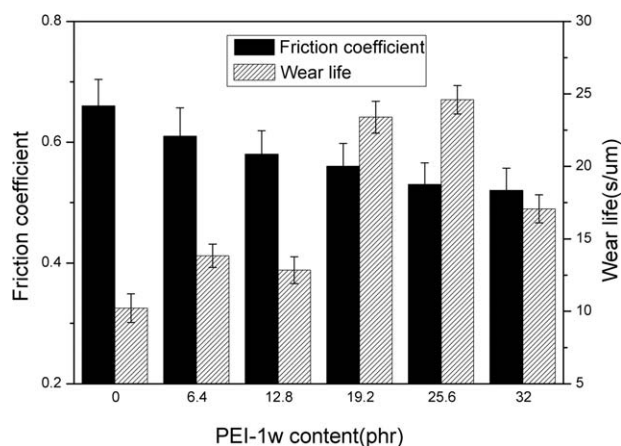
Figure 6. Friction coefficient and wear life of sample TD and PEI-1w modified TGDDM/DDS system.

domains dispersed in an epoxy-rich continuous phase (bi-continuous phase structure). However, in sample with PEI of 38.4phr, many large epoxy-rich globules can be observed in the PEI-rich continuous phase (phase-inversion structure).

For samples with PEI with a molecular weight of 10,000 g/mol (PEI-1w), separated phase structure was observed when the content of PEI was less than 12.8 phr; bi-continuous phase structure was observed when the content of PEI was 19.2–25.6 phr; phase inversion took place when the content of PEI was more than 32.0 phr.

It was found that less PEI-1w was needed to get bi-continuous phase or phase-inversion structure compared with PEI-5K, which agreed well with elsewhere.[34,38,41]

Mechanical Properties
Results of tensile strength test are shown in Table IV. It was obvious that tensile strength heavily depended on morphologies of cured products. For samples with PEI-5k, when the content of PEI-5k was 25.6–32.0phr, tensile strength was higher than those with other content. However, for samples with PEI-1w, the best tensile strength was obtained when the content of PEI-1w was 19.2–25.6phr. Apparently, samples with bi-continuous phase structure had better tensile strength than those with separated phase and phase-inversion structure. According to Girard-Reydet,[36] it could be explained that high degree of interaction between phases in bi-continuous morphologies may facilitate a more uniform stress distribution in the material under load and thereby avoid premature failure by localized stress concentrations, and hence that results in a higher tensile strength. Elongation at break of samples with bi-continuous phase was higher than those with separated phase; however the change was very slight. This is attributed to the high crosslinking density of TGDDM/DDS, leading to the high rigidity. And the rigid phase (TGDDM/DDS) plays a more important role in determining the elongation at break than flexible phase (PEI). As a result, the changes of elongation at break are not significant even when there is PEI continuous phase in the cured products.

Thermal Properties
Thermal properties of the cured samples were evaluated by DMA and TGA, in order to give an insight to the relationships

of morphologies and thermal properties. The thermal data of the cured samples based on DMA and TGA are summarized in Tables V and VI.

There was only one tan δ peak at 245°C for sample TD. Two tan δ peeks were found for all samples modified with PEI, peak at lower temperature corresponding to the glass transition of PEI-rich phase, the one at higher temperature corresponding to the glass transition of epoxy-rich phase. It was also found that the glass transition temperature (T_g) of epoxy-rich phase decreased when bi-continuous phase or phase-inversion structure formed. It could be explained that epoxy resin and PEI in two phases of the cured products have different T_gs, and hence results in two tan δ peaks. Significant influence of PEI on T_gs of epoxy-rich phase came to exist when there is a continuous PEI-rich phase in the cured products.

For PEI-5k modified TGDDM/DDS systems, it was found that T_g of PEI-5k rich phase decreased firstly (6.4–19.2 phr) and then stayed the same (25.6–38.4 phr) with increasing PEI-5k content. For PEI-1w modified TGDDM/DDS systems, T_g of PEI-1w rich phase almost stayed unchanged with PEI-1w content increasing. On the basis of the morphology analysis, it could be found that T_g value of the PEI rich phase decreased with the size of PEI rich phase increasing; and when the size of PEI rich phase was larger than a certain value, T_g of the PEI rich phase remained the same. It could be explained that epoxy molecules dispersed into thermoplastic rich phase, which acted as a plasticizer.[31] This led to the decrease of T_g of the PEI rich phase.[47] More epoxy molecules dispersed into PEI rich phase with the size of PEI rich phase increasing, resulting in the decrease of the T_g value of the PEI rich phase. When the size of PEI rich phase was larger than a certain value, it was likely that the influence of epoxy molecules getting into PEI rich phase on T_g of PEI rich phase stayed almost unchanged. The size of PEI separated phase in samples TP5k-6.4, TP5k-12.8, TP5k-19.2, TP1w-6.4, and TP1w-12.8 are 1.20 μm, 1.37 μm, 1.51 μm, 1.78 μm, and 2.68 μm respectively. It was obvious that the size of PEI-1w separated phase is larger than that of PEI-5k separated phase, and PEI continuous phase is much larger than PEI separated phase. As a result, T_g of PEI-5k rich phase decreased firstly and then remained the same with increasing size of PEI-5k rich phase; however, T_g of PEI-1w rich phase almost stayed unchanged with PEI-1w content increasing.

It was found that the thermal stability of the cured products was slightly improved because of the introduction of PEI. For samples with PEI-5k, temperatures of the 5% and 10% weight loss increased from 347.2 (without PEI) to 358.3°C (38.4 phr PEI) and 373.8 (without PEI) to 385.7°C (38.4 phr PEI) respectively. However, for samples with PEI-1w, temperatures of the 5% (and 10%) weight loss increased from 347.2°C (and 373.8°C) to 361.4°C (and 384.8°C), and then decreased to 353.7°C (and 374.8°C) with PEI content increasing from 0 to 32.0 phr. Residue weight at 800°C slightly increased with PEI content increasing, both for PEI-5k and PEI-1w. Moreover, Residue weights of samples with PEI-5k were about 3% higher than samples with PEI-1w. In accordance with our former work,[45,46] it could be explained that the crosslinking density of
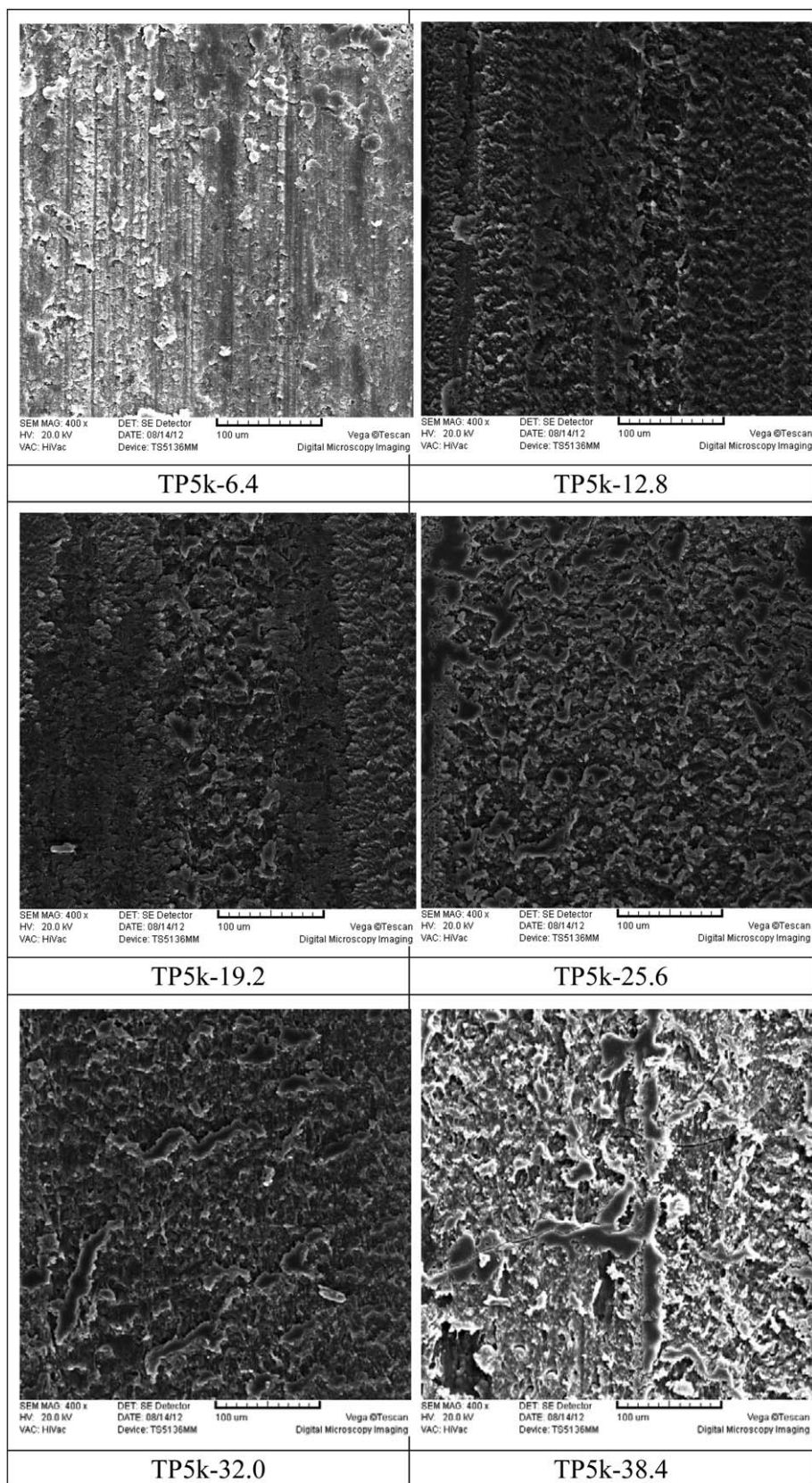
Figure 7. SEM images of worn surfaces of PEI-5k modified TGDDM/DDS system.
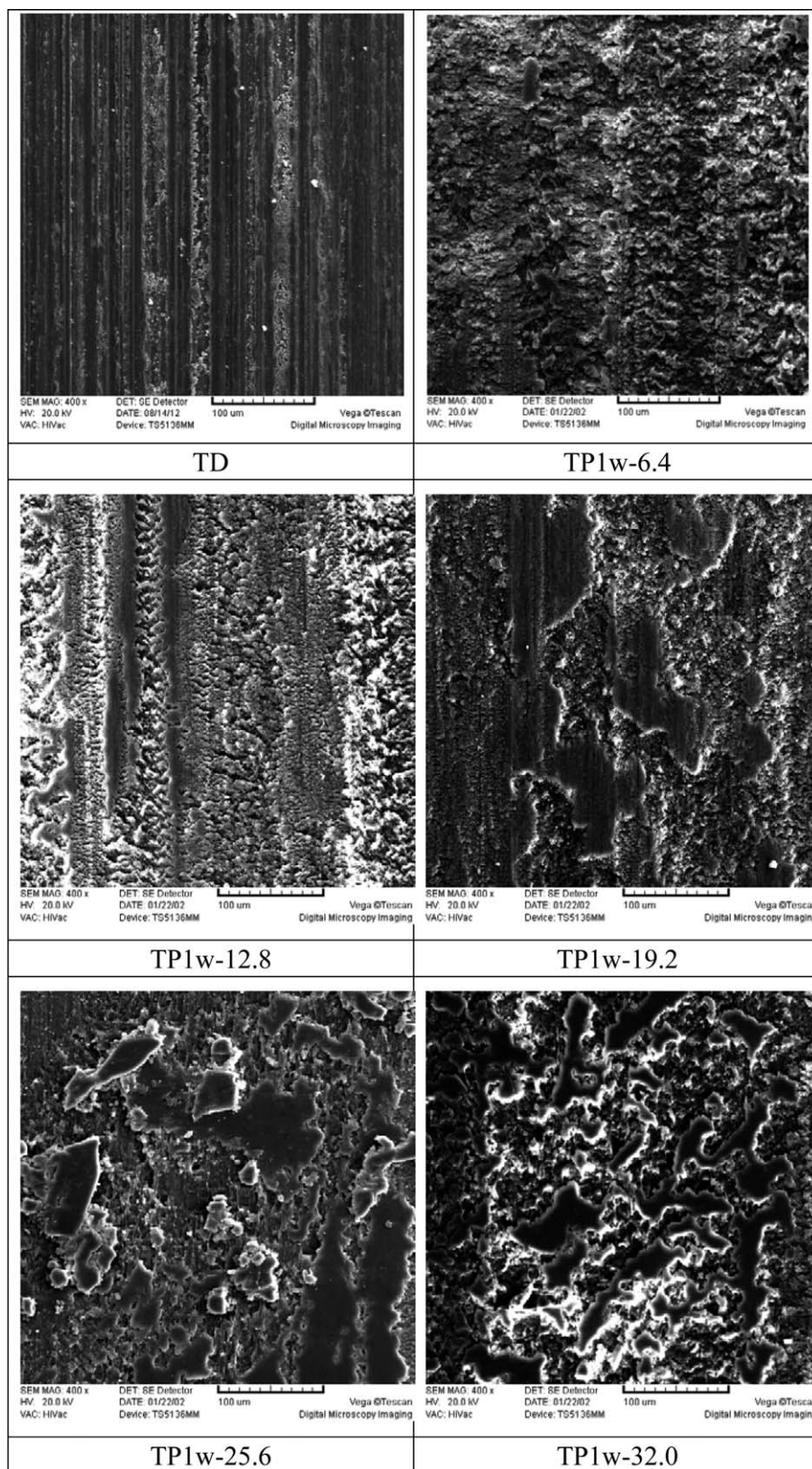
Figure 8. SEM images of worn surfaces of sample TD and PEI-1w modified TGDDM/DDS system.

the samples with PEI-1w may be lower than these with PEI-5k, due to the higher viscosity of PEI-1w compared with PEI-5k, and thereby resulting in some hydrogen- or oxygen-rich groups (such as hydroxy) leaving in the crosslinking network of TGDDM/DDS. This finally led to the lower residue weights of TGDDM/DDS modified with PEI-1w compared with PEI-5k.
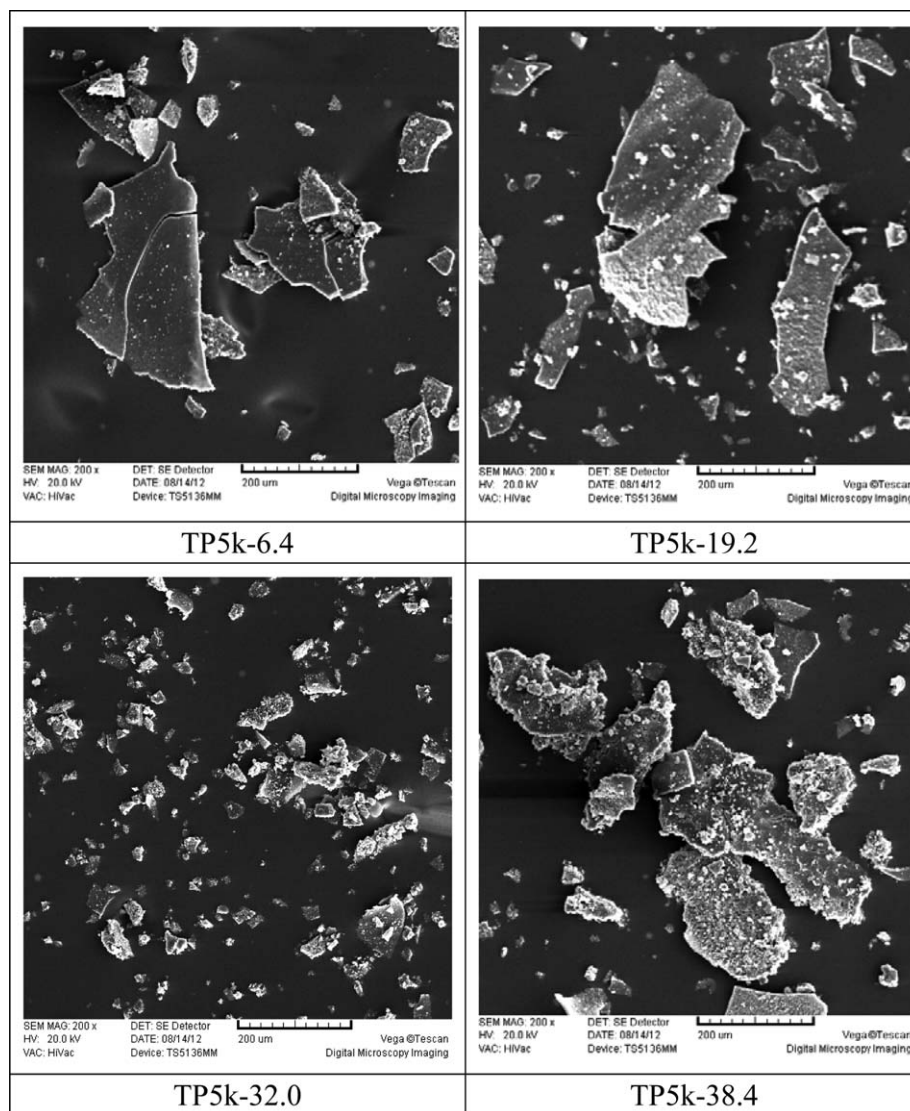
Figure 9. SEM images of wear debris of PEI-5k modified TGDDM/DDS system.

Additionally, the residue weights of PEI-5k and PEI-1w used in this work are 48.2% and 46.8% respectively, resulting in a higher residue weights of PEI-5k modified TGDDM/DDS system than that of PEI-1w modified TGDDM/DDS system.

Friction and Wear Properties

The results of the tribological tests are shown in Figures 5 and 6. It should be pointed out that herein we used wear life to characterize the wear resistance of the samples. The longer wear life means the higher wear resistance. Apparently, wear resistance of the PEI modified samples was higher than that of the unmodified samples. Moreover, wear resistance greatly depended on phase structures.

For samples with separated PEI-5k-rich phase, wear life slightly improved with PEI-5k content increasing. However, wear life of samples with separated PEI-1w-rich phase structure decreased slightly with increase of PEI-5k content. For samples with bi-continuous phase structure, wear life was significantly higher than those with other phase structure, and slightly improved

with PEI-5k or PEI-1w content increasing respectively. In addition, it was found that the wear life of samples with bi-continuous phase composed of PEI-1w and epoxy resin was slightly higher than those composed of PEI-5k and epoxy resin. Compared with samples with bi-continuous phase structure, significant decreases of wear life were observed for samples with phase-inversion structure. But still higher than those with separated PEI-5k (or PEI-1w)-rich phase structures. Friction coefficient decreased with PEI content increasing both for samples with PEI-5k and PEI-1w.

According to Xu et al.,[48] it could be explained that may be the size of the separated PEI phase affected mechanical properties, too large size of the separated PEI phase results in decrease of mechanical properties, and hence that results in a lower wear life. Higher degree of interaction between phases in bi-continuous morphologies[36] made samples with bi-continuous morphologies have better wear resistance than those with other morphologies. It was likely that wear resistance of PEI-1w continuous phase was higher than that of the PEI-5k continuous
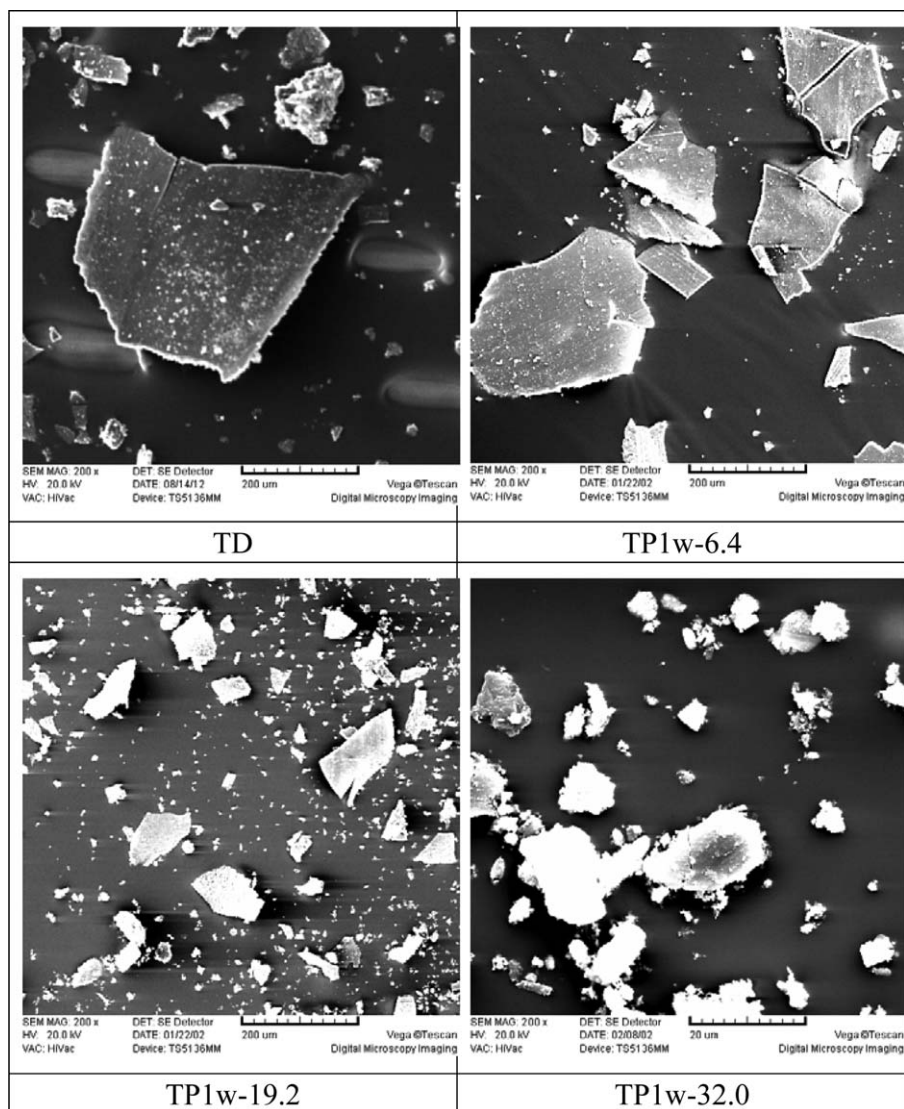
Figure 10. SEM images of wear debris of sample TD and PEI-1w modified TGDDM/DDS system.

phase, due to the higher intermolecular force of PEI-1w than that of the PEI-5k. Therefore, samples with bi-continuous of PEI-1w exhibited better wear resistance than PEI-5k.

Wear Behavior and Mechanism

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

The SEM images of worn surfaces of the tested samples are shown in Figures 7 and 8.

It could be seen that there were deep scuffed and furrowed marks on the worn surfaces of samples TD, TP5k-6.4, TP5k-12.8, TP5k-19.2, TP1w-6.4, and TP1w-12.8 (morphology of these samples are separated phase), indicating that the dominating wear behaviors was abrasive wear. It was likely that the contact surface of these samples cracked and the wear debris broke away from the contact surfaces more easily than the other samples due to its poor toughness of the continuous phase (cured

TGDDM/DDS). The exfoliated fragments between the samples and the steel ring scratched the contact surface of the samples, leading to traces of plough on worn surfaces of these samples. Moreover, it was obviously seen that the amount and depth of the furrowed marks on the worn surfaces of these samples decreased with PEI-5k content increasing, and slightly increased with PEI-1w content increasing.

No furrowed marks were seen on worn surfaces of samples TP5k-25.6, TP5k-32.0, TP1w-19.2, and TP1w-25.6 (bi-continuous phase); however, there was obviously plastic deformation and flow, indicating that the main wear behavior was fatigue wear.[17] PEI is a kind of thermoplastic resin with lower T_g than that of the cured TGDDM/DDS in this article. Once a PEI-continuous phase formed, obviously plastic deformation of PEI took place during the friction and wear process.

More heavily plastic deformation was observed on worn surfaces of samples TP5k-38.4 and TP1w-32.0 (phase-inversion structure), indicating the main wear behavior was fatigue wear. For

samples with phase-inversion structure, there is much more PEI-continuous phase than samples with bi-continuous phase. Consequently, severer plastic deformation took place during the friction and wear process.

The SEM images of wear debris of the tested samples are shown in Figures 9 and 10.

Typically, wear debris with two different morphologies were observed in the figures: flakiness-like wear debris with relatively smooth surfaces and trim edges (named type one wear debris) and that with relatively rough surfaces and edges (named type two wear debris). For samples with homogenous phase and separated PEI-5k (1w)-rich phase structures, only wear debris of type 1 was seen; for samples with bi-continuous phase structure, both type 1 and type 2 wear debris were seen; for samples with phase-inversion structure, it was found that most of the wear debris was type 2 wear debris. It was likely that wear debris of type 1 was the cured epoxy resin peeled off the wear surfaces; however, main component of wear debris of type 2 was the PEI peeled off the wear surfaces because of the plastic deformation. Additionally, it could be seen that sizes of the wear debris of samples with bi-continuous phase structure was considerably smaller than those with separated phase or phase-inversion structures. The size of the debris agrees well with the wear resistance of the corresponding specimens, considering the relationship between the debris size and wear resistance. It was likely that materials may be more difficult to be peeled off because of more excellent mechanical properties, and hence that results in a lower wear.[12] In this study, for samples with PEI-rich separated phase structure, epoxy resin continuous phase was peeled off the wear surfaces due to its poor mechanical strength. However, for samples with bi-continuous phase, mechanical strength was improved according to section "Mechanical properties," consequently, it was more difficult for epoxy resin continuous phase to be peeled off the wear surfaces than samples with separated phase structure.

CONCLUSIONS

A systematic work has been done to make a thorough inquiry of the relationship of morphologies and tribological properties of PEI modified TGDDM/DDS system. Three different morphologies (separated phase, bi-continuous phase, and phase inversion structure) were obtained by controlling molecular weights and content of PEI. Tensile strength, thermal, and tribological properties of samples with different morphologies were studied. The major conclusions obtained in this article can be summarized as follows:

1. PEI modified TGDDM/DDS are possessed of better thermal stability, higher tensile strength than that of the unmodified TGDDM/DDS. Samples with bi-continuous phase show the highest tensile strength, which are ca. 23% and 46% higher than that of the unmodified TGDDM/DDS, for PEI-5k and PEI-1w, respectively.
2. Tribological properties of TGDDM/DDS are improved due to the addition of PEI. Wear life of samples with bi-continuous phase is almost 25 s/μm, significantly higher than those with other phase structures (10–16 s/μm).

3. SEM observations of worn surfaces show that wear behavior of samples with PEI-separated phase is abrasive wear. For samples with bi-continuous and phase inversion structure, the dominant wear behavior is fatigue wear. It is worth noting that samples with phase inversion structure show severe fatigue wear than those with bi-continuous phase.
4. Phase structure is one of the significant factors that affect tensile strength, and especially tribological properties. It is apparent that samples with bi-continuous phase exhibit best performance. However, it looks like that there is no significant influence of phase structure on thermal stabilities.

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