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Micro-crack behavior of carbon fiber reinforced thermoplastic modified epoxy composites for cryogenic applications

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ABSTRACT

Three different types of thermoplastics, poly(ether imide) (PEI), polycarbonate (PC), and poly(butylene terephthalate) (PBT) were used to modify epoxy for cryogenic applications. Carbon fiber reinforced thermoplastic modified epoxy composites were also prepared through vacuum-assisted resin transfer molding (RTM). Dynamic mechanical analysis (DMA) shows that the storage moduli of PEI, PC, and PBT modified epoxies are 30%, 21%, and 17% higher than that of the neat epoxy respectively. The impact strength of the modified epoxies at cryogenic temperature increases with increasing thermoplastic content up to 1.5 wt.% and then decreases for further loading (2.0 wt.%). The coefficient of thermal expansion (CTE) values of the PBT, PEI, and PC modified epoxies also decreased by 17.76%, 25.42%, and 30.15%, respectively, as compared with that of the neat epoxy. Optical microscopy image analysis suggests that the presence of PEI and PC in the carbon fiber reinforced epoxy composites can prevent the formation of micro-cracks. Therefore, both the PEI and PC were very effective in preventing micro-crack formation in the composites during thermal cycles at cryogenic condition due to their low CTE values and high impact strength.

1. Introduction

Epoxy is one of the most important types of thermosetting resin due to its high specific strength and stiffness, low curing shrinkage, good chemical and corrosion resistances, high adhesion and dimensional stabilities [1–4]. Epoxies have a wide range of applications in fuel tank fabrication, aerospace, electrical, electronic, and automobile industries [1–7]. However, these resins are quite brittle, showing poor resistance to crack propagation, especially at cryogenic temperature. Cryogenic liquids, such as liquefied oxygen and hydrogen are used in fuel cells for power generation. These kinds of liquefied fuels normally cause aging of cryogenic fuel tanks during thermal cycles from cryogenic to room temperature (RT) and vice versa. An internal stress inside the matrix is generated due to the change in temperature (thermal cycles between RT to room temperature) and leads to the formation of micro-cracks in epoxy based materials. In order to overcome this kind of micro-crack formation and allow the use of epoxy based materials under cryogenic condition, the co-efficient of thermal expansion (CTE) of the epoxy at cryogenic temperature should be kept as small as possible. For this purpose, the epoxy is usually modified by introducing various toughening agents, such as inorganic fillers, block copolymer, hyperbranched polymer, reactive diluents, reactive liquid rubber, and thermoplastic [8,9]. Previous studies have shown that thermoplastics such as polycarbonate (PC) [10,11], poly(ether imide) (PEI) [12,13], and poly(butylene terephthalate) (PBT) [14,15] can toughen epoxy at room temperature without sacrificing its glass transition temperature (T_g) or other desirable properties. Chen et al. investigated the toughening behavior of an epoxy modified by commercial polyetherimide (PEI) [16]. The commercial grade PEI was modified by nitric acid prior to blend preparation. The improvement in mechanical properties is due to the homogeneous miscibility of the epoxy and nitrated PEI. Kim et al. investigated the multiple autocatalytic reaction of the epoxy/amine terminated PEI/NMA system by molecular modeling [17]. Chen et al. [18] studied the miscibility and fracture behavior of an epoxy/PC blend. According to their observations, the blend is miscible and shows improved mechanical properties at room temperature. However, investigations of the properties of epoxy-based

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materials and their composites at cryogenic temperature, especially their CTEs and micro-crack resistance, have so far been quite limited.

The objective of this work is to explore the behaviors of different thermoplastic toughened epoxies at cryogenic temperature and the effect of carbon fiber/epoxy composites on the micro-crack resistance. Therefore, commercial grade PEI, PC, and PBT were used to modify epoxy in the present work. Modified epoxy/carbon fiber laminates were also prepared to investigate the dual effect of carbon fiber and thermoplastic modifiers on the cryogenic toughening and micro-crack resistance behavior under cryogenic thermal cycling. It is anticipated that the prepared composites may be useful for the fabrication of space shuttles and cryogenic fuel tanks.

2. Experimental

2.1. Preparation of thermoplastic filled epoxies

The epoxy YD-128 (DGEBA, Kukdo Chemical Ltd., Korea) with an epoxide equivalent weight (EEW) of 185–190 eq^{-1} was used for the present study. The curing agent was polyoxypropylenediamine (Jeffamine D-230) (New Seoul Chemical Ltd., Korea). The thermoplastics used to modify the epoxy were commercial grade poly(ether imide) (PEI, GE Ultem 1000, GE Plastic, MI, USA), polycarbonate (PC, TRIREX 3022IR, Samyang Kasei Co., Korea) and poly(butylene terephthalate) (PBT, TRIBIT 1500, Samyang Co., Korea). The filler content was expressed as a percentage of the total weight of the blend (i.e., wt.%). Fig. 1 shows the chemical formulae of the individual thermoplastics. Unidirectional carbon fiber (CARBONEX CF-730, Hankuk Carbon Ltd., Korea) was used as reinforcement for the composites. Dichloromethane with a purity of 99% (Aldrich, USA) was used as a solvent.

2.2. Modification of epoxy and preparation of carbon fiber/modified epoxy composites

The PEI or PC was dissolved in an excess of dichloromethane. The mixture was stirred into the epoxy at room temperature and de-gassed overnight in a vacuum oven at 80 °C. The curing agent was then added and the mixture was stirred for 15 min. The mixture was then poured into an open silicon mold. The epoxies were cured at 80 °C for 4 h and then allowed to cool naturally to room temperature. For the modification of epoxy with PBT, the PBT was added into the epoxy directly and heated at 170 °C for 20 min. The curing agent was added and the mixture was stirred for 15 min. Then, the mixture was cast into an open silicon mold. The blends were cured at 80 °C for 4 h and were allowed to cool naturally to room temperature.

Carbon fiber reinforced epoxy laminates of about 15.24 cm × 15.24 cm in size were prepared by the method of vacuum-assisted resin transfer molding (VARTM). The symmetric laminates consisted of nine plies of carbon fabric in a $[0^{\circ}_{3}, 90^{\circ}_{3}]_s$ configuration.

2.3. Characterization

The impact properties of the epoxy/thermoplastic blends were tested using notched Izod impact testing according to the ASTM D-256 specification. Specimens for impact testing were immersed in liquid nitrogen at the temperature of 77 K for over 30 min before being mounted onto the impact tester. The pendulum of the impact tester was released immediately against the notch after the specimen was mounted onto the impact tester and each impact test was completed in a couple of seconds to avoid the change of temperature inside the specimens. At least five specimens were tested for each blend. The thermal expansions of the neat resin and the

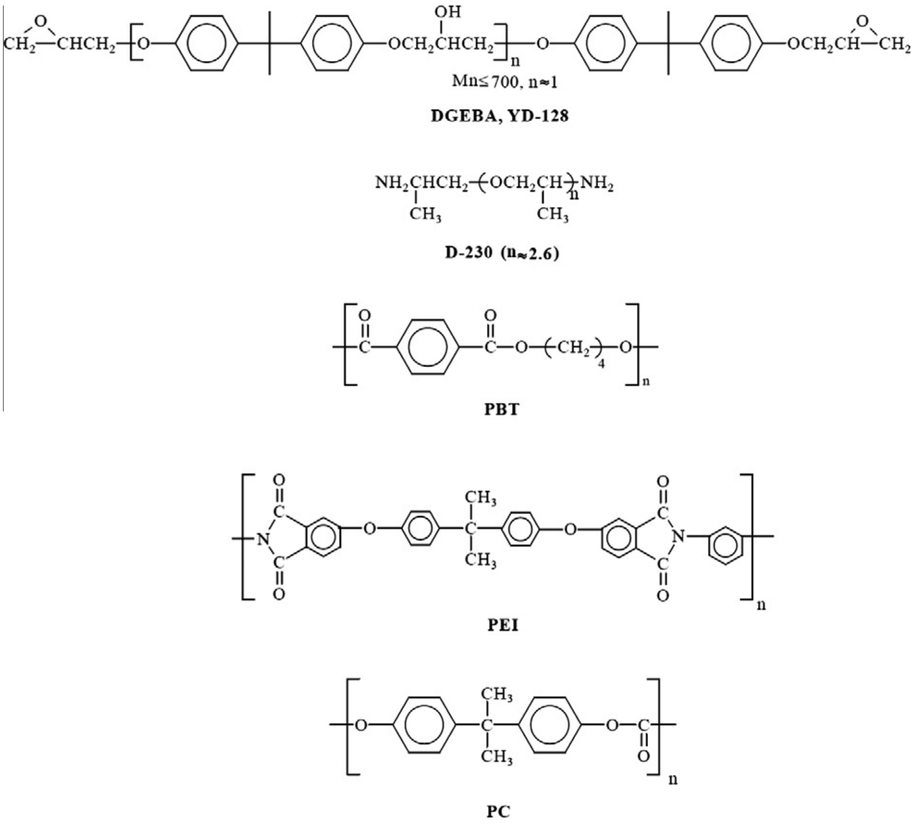

Fig. 1. Chemical structures of epoxy, D-230, PBT, PEI and PC.

thermoplastic modified epoxies were tested using a TMA Q 400 (TA Instrument, USA) at a heating rate of 10 °C min^{-1} and a preload force of 0.5 N. Dynamic mechanical analysis (DMA) was performed using a Q 800 DMA (TA instruments, USA) in the fixed frequency mode at 1 Hz with an amplitude of 0.40 mm. Rectangular DMA specimens with dimensions of 60 × 10 × 3 mm^3 were cut and polished to a uniform size. Thermogravimetric analysis (TGA) was carried on a TA instrument (Q50, USA). The samples were scanned from 30 °C to 600 °C at heating rate of 10 °C min^{-1}. The fracture surfaces of the specimens after impact testing were examined by field emission scanning electron microscopy (FE-SEM, JEOL JSM-6701F). Prior to the examination, the fracture surfaces were coated with a thin evaporated layer of gold to improve conductivity. In order to check the micro-cracks in the carbon fiber reinforced epoxy composite laminates, the samples were allowed to equilibrate at 22 °C and then placed in a liquid nitrogen bath (77 K) for 10 min. After exposure to liquid nitrogen the samples were placed inside a desiccators and allowed to return to room temperature. Each sample was exposed to a minimum of five thermal cycles until optical microscopy revealed no micro-cracks. Three specimens from each laminate were cycled at cryogenic temperature. Each sample was examined prior to cycling to ensure that there were no initial cracks or defects on the surface. After each material had reached thermal equilibrium in a desiccator it was examined at ×160 magnification using an optical microscope.

3. Results and discussion

3.1. Impact strength of epoxies modified with different thermoplastics

The impact strengths at 77 K and room temperature of epoxies modified with different thermoplastics are listed in Table 1. The error bars denote the standard deviation of the impact strength. It has been found that the impact strengths of the thermoplastics (PC, PBT, and PEI) modified epoxies are higher than that of a neat epoxy at both cryogenic and room temperature. The impact strength of the modified epoxy at room temperature increases as the thermoplastic content increases up to 1.5 wt.% and then decreases with further loading. On the contrary, the impact strength at cryogenic temperature is higher than that of neat epoxy for the entire range of thermoplastic loadings. The PEI modified epoxy shows the highest impact strength value at cryogenic temperature, which is 45% more than that of neat epoxy. This indicates that the PEI modified epoxy shows good impact resistance at cryogenic temperature. It is also noteworthy that PEI can improve the impact strength of epoxy at −200 °C [19]. On the contrary, PC and PBT do not improve the impact strength of the epoxy matrix at cryogenic temperature. This is attributed to the brittle nature of PC and PBT at −100 °C. The impact strength of PEI modified epoxy at room temperature has been found to increase by about 59% as compared to neat epoxy. This indicates that PEI can improve the impact resistance of the epoxy matrix both at cryogenic and room temperature. Therefore, it is anticipated that the thermoplastic modified epoxy can resist micro-cracking under cryogenic thermal cycling and can be considered as a useful material for cryogenic applications.

3.2. Morphological analysis

FE-SEM analysis was conducted to examine the morphology of the fracture surfaces of the neat epoxy and thermoplastic modified epoxies. Fig. 2 shows the FE-SEM images for pure epoxy and thermoplastic (1.5 wt.%) modified epoxy samples. The fracture surface of neat epoxy (Fig. 2a) is smooth with many “wavelike” traces, which are caused by rapid crack propagation [31]. The fracture surface of 1.5 wt.% PBT modified epoxy is quite different from that of the neat epoxy, as shown in Fig. 2b. In comparison to the neat epoxy, the lubricated mirror plane has been replaced by numerous dichotomous micro-cracks in the modified resin. The formation of micro-cracks is thought to result from the absorption of impact energy or the emergence of the deflection of crack propagation near the PBT domain [32]. A smooth surface with elongated material can be observed in the PC modified epoxy (Fig. 2c). The PC seems to show good bonding with the epoxy matrix. The toughening may arise from the chemical reactions that most probably took place between the epoxy and the polymeric modifier, which is partially soluble in the epoxy matrix [33]. Furthermore, the features reveal some plastic deformation due to the epoxy matrix, which can lead to higher energy absorption during the crack propagation process. A micrograph of an epoxy with 1.5 wt.% of PEI is presented in Fig. 2d, in which a phase separated morphology is clearly visible. The microstructure consists of homogenously dispersed spherical domains of PEI in the epoxy matrix. The average diameter of the separated phases has been determined to be 1.0 μm. It has been assumed that the PEI spherical domains are formed in situ during curing and that deformation occurs near the PEI-rich phase [34]. This indicates that PEI particles serve as sites of stress concentration and have good interfacial bonding with the epoxy matrix at cryogenic temperature [35].

3.3. Thermomechanical analysis

The thermal expansions of the neat epoxy and modified epoxies are shown in Fig. 3. The glass transition temperature (T_g) has been determined from the dramatic turning point on the thermal-expansion curve. Table 2 lists the T_g values of neat epoxy and the various modified epoxies. The T_g values of thermoplastic modified epoxy are clearly higher than that of the neat epoxy. This increase in T_g of the modified epoxies possibly arose from the interaction between the epoxy molecules and the thermoplastic molecules. The structure of these three thermoplastics is similar to that of the epoxy and therefore they have good compatibility with the epoxy. These three thermoplastics all have higher T_g values than cured epoxy. Therefore, adding thermoplastic into the epoxy can increase the T_g value [20,21]. The T_g values of PEI, PBT, and PC are 217 °C, 165 °C and 150 °C, respectively, with the result that the T_g temperature of PEI modified epoxy is higher than those of PBT and PC modified epoxies [10–16].

The coefficient of thermal expansion (CTE) quantifies the thermal expansion of the solid. The coefficient can be volumetric or linear according to whether the measurement is determined by the change of the volume or length of the sample. The CTE of the

Table 1
Impact strengths of the neat and modified epoxies with various thermoplastic modifiers.

Modifier		PBT		PC		PEI	
Temperature		77 K (J/m)	293 K (J/m)	77 K (J/m)	293 K (J/m)	77 K (J/m)	293 K (J/m)
Contents	0	26.4 ± 3.5	54.2 ± 2.3	26.4 ± 3.5	54.2 ± 2.3	26.4 ± 3.5	54.2 ± 2.3
	0.5	27.6 ± 3.2	56.4 ± 2.2	31.5 ± 4.0	64.7 ± 2.8	36.5 ± 2.6	66.5 ± 2.4
	1.0	33.2 ± 1.6	59.3 ± 1.9	35.5 ± 2.1	65.8 ± 2.5	38.1 ± 4.3	73.7 ± 2.5
	1.5	34.5 ± 2.5	64.7 ± 2.7	36.01 ± 3.2	69.4 ± 1.8	39.8 ± 2.1	79.8 ± 1.7
	2.0	33.5 ± 1.4	69.9 ± 1.6	35.4 ± 1.8	75.5 ± 1.7	38.5 ± 3.3	86.1 ± 2.1

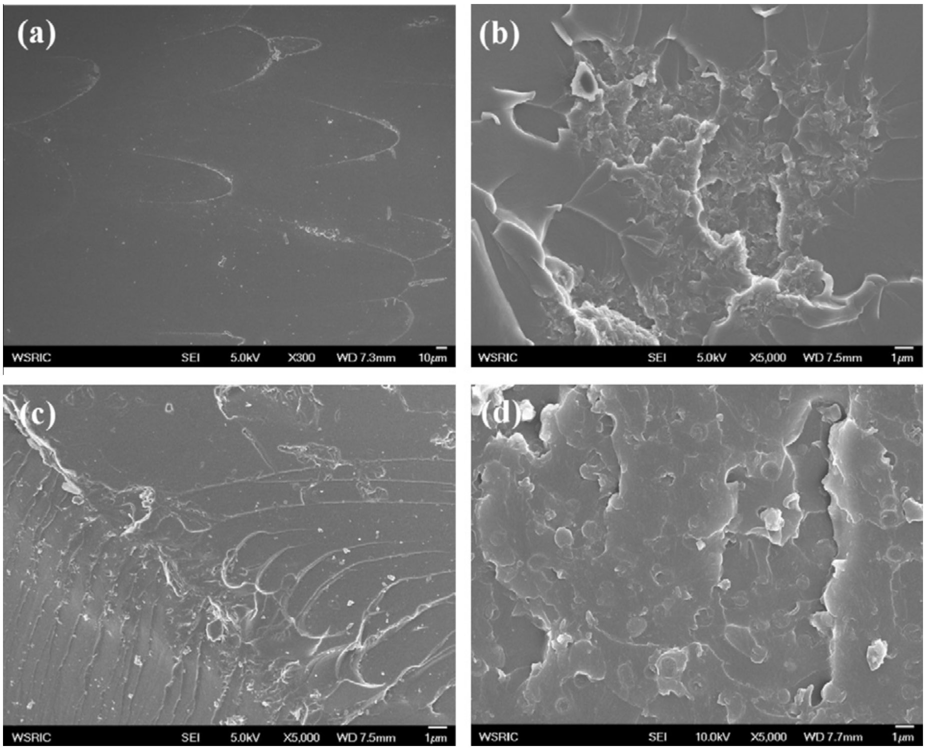

Fig. 2. SEM micrographs of fractured surfaces of (a) neat epoxy, (b) PBT modified epoxy, (c) PC modified epoxy and (d) PEI modified epoxy.

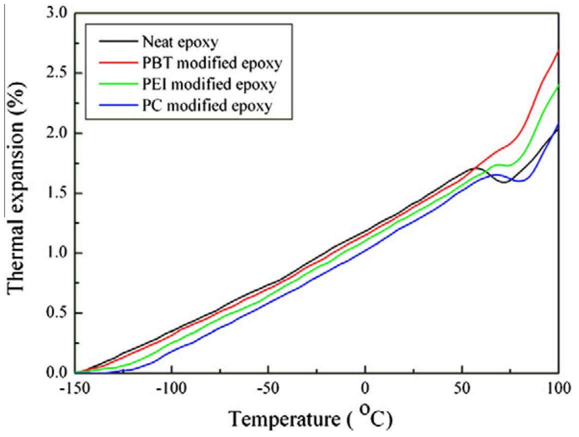

Fig. 3. Variation of thermal expansion of neat epoxy and the modified epoxies with temperature.

Table 2
Glass transient temperatures of the neat epoxy and thermoplastic modified epoxies.

Sample	Neat epoxy	PC-epoxy	PBT-epoxy	PEI-epoxy
T_g (°C)	77.98	80.65	81.77	82.13

samples can be calculated based on the dimension change curves as shown in Fig. 4. The CTE values of the thermoplastic modified epoxies are lower than that of the neat epoxy. In comparison to the neat epoxy, the PBT, PEI and PC modified epoxies show CTE reductions of 14%, 17% and 23%, respectively. The magnitude of the CTE depends on the structure of the materials. For single-phase materials, the CTE is determined by the atomic bonding, molecular structure, and molecular assembly. An elevated temperature would increase thermal energy and lead to an increase in the atomic movement. Weak atomic bonding owing to the increased inter-atomic distance would show a large CTE values [22,23]. For multiphase materials, such as composites, the CTE is dependent on each component phase and also on the interactions between each phase. However, weak interfacial bonding between the phases cannot effectively incorporate the contributions of each component, while strong interfacial bonding can reduce the thermal-expansion properties significantly [24,25]. Therefore, an inspection of the reduction in CTE values of the modified epoxies suggests that PC and PEI can effectively enhance the micro-crack behavior of the carbon fiber reinforced modified epoxy composites (under cryogenic thermal cycling) for cryogenic applications.

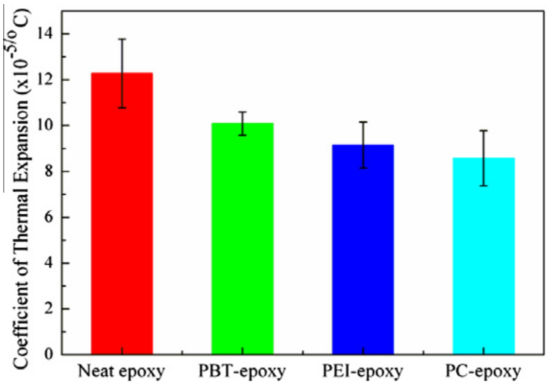

Fig. 4. CTE values of neat epoxy and thermoplastic modified epoxy.

3.4. Dynamic mechanical analysis

Dynamic mechanical analyses were performed to measure the mobility of the epoxy chain segments and to study the inter-phase properties of the neat epoxy and thermoplastic modified epoxies.

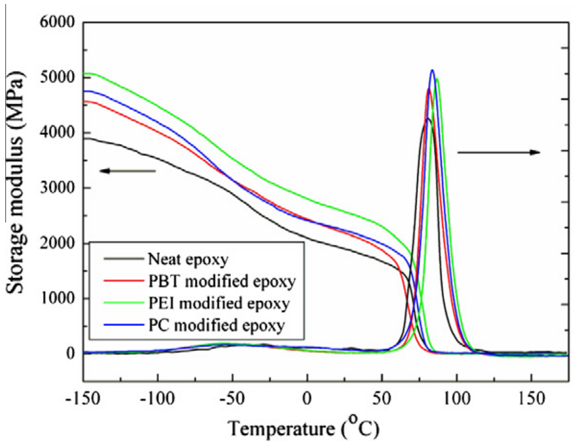

Fig. 5. DMA curves of neat epoxy and thermoplastic modified epoxy.

The content of the thermoplastic was 1.5 wt.%. An oscillatory force was applied to the specimens at constant frequency. The storage modulus and tan δ of the pure epoxy and the modified epoxies are shown in Fig. 5. Evidently, the storage modulus of the thermoplastic modified epoxies in the glassy region is higher than that of the neat epoxy. The storage moduli of PEI, PC, and PBT modified epoxy are 5025 MPa, 4733 MPa, and 4539 MPa, respectively, which are approximately 30%, 21%, and 17% higher than that of the neat epoxy at the −150 °C. The increase in storage modulus in the glassy region suggests that the thermoplastics were well dispersed in the epoxy matrix and have good interfacial bonding with the epoxy matrix [26]. Therefore, the storage modulus of the thermoplastic modified epoxy is higher than that of the neat epoxy at T_g, which implies cryogenic toughening of the epoxy matrix.

The graph clearly shows similar trends in the T_g values of both the neat epoxy and the thermoplastic modified epoxies. In all the thermoplastic modified epoxies, T_g appears at higher temperatures (3–6 °C) than that of the corresponding neat epoxy. The results are in good agreement with the CTE curves. As mentioned in other studies [27], the addition of a thermoplastic can affect the curing reaction by selectively removing certain components from the thermosetting network, leading to a change in T_g. With the addition of PEI, PC, and PBT this effect is relatively small, and the observed T_g values are only slightly higher than that of the neat epoxy.

3.5. Thermogravimetric analysis

TGA was used to investigate the thermal stability of the neat epoxy and the thermoplastic modified epoxy. The TGA curves (Fig. 6) show the decomposition temperatures of pure epoxy and thermoplastic (1.5 wt.%) modified epoxy. At 300 °C, the weight loss of pure epoxy, PBT modified epoxy, PC modified epoxy, and PEI modified epoxy are 1.76%, 1.65%, 1.32%, and 0.85%, respectively. It has been reported that the thermal stabilities of the modified epoxy are attributed to the presence of thermoplastics in the modified resin [28–30]. Thermal stability can be increased by increasing the thermoplastic content. The results suggest that the increase in thermal stability at the onset of decomposition is due to the higher thermal stability of the thermoplastics. However, the decomposition rate is dominated by the properties of the cured epoxy when the temperature reaches about 350 °C. It has been found that both the thermoplastic modified epoxies and pure epoxy show a rapid weight loss at around 350 °C. However, the rate of decomposition of the pure epoxy is faster than those of the modified epoxies. This is attributed to the good thermal stability of the thermoplastics. After complete decomposition, the neat epoxy has the smallest residual weight. The residual weight is determined by both the thermoplastic type and the epoxy properties, which suggest that the thermoplastic can increase the thermal stability of the epoxy.

3.6. Laminate micro-cracking

Carbon fiber reinforced epoxy laminates prepared by VARTM were used to study the micro-crack morphology and to determine the crack density. The optical photomicrographs of the micro-crack

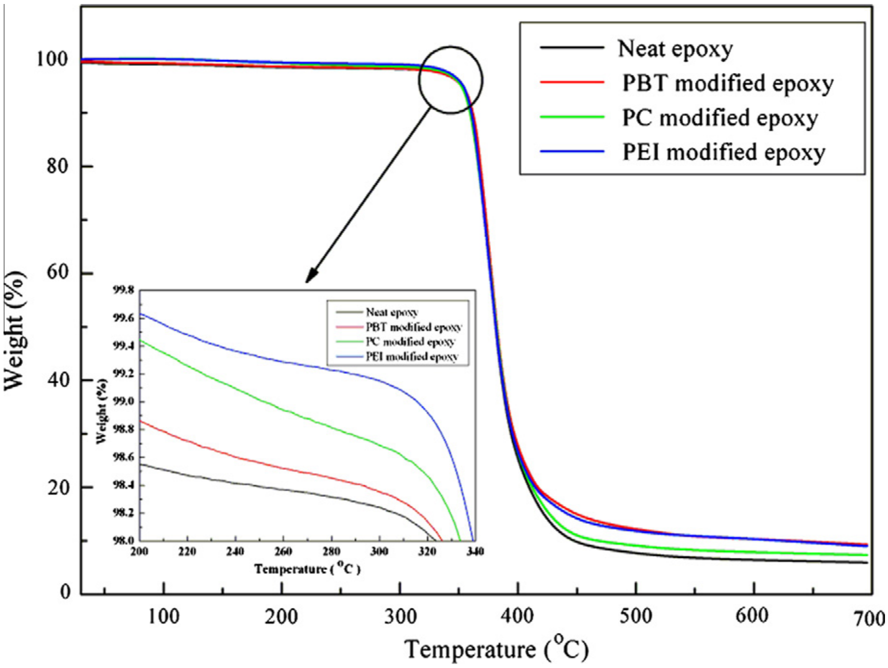

Fig. 6. TGA curves of neat epoxy and thermoplastic modified epoxy.

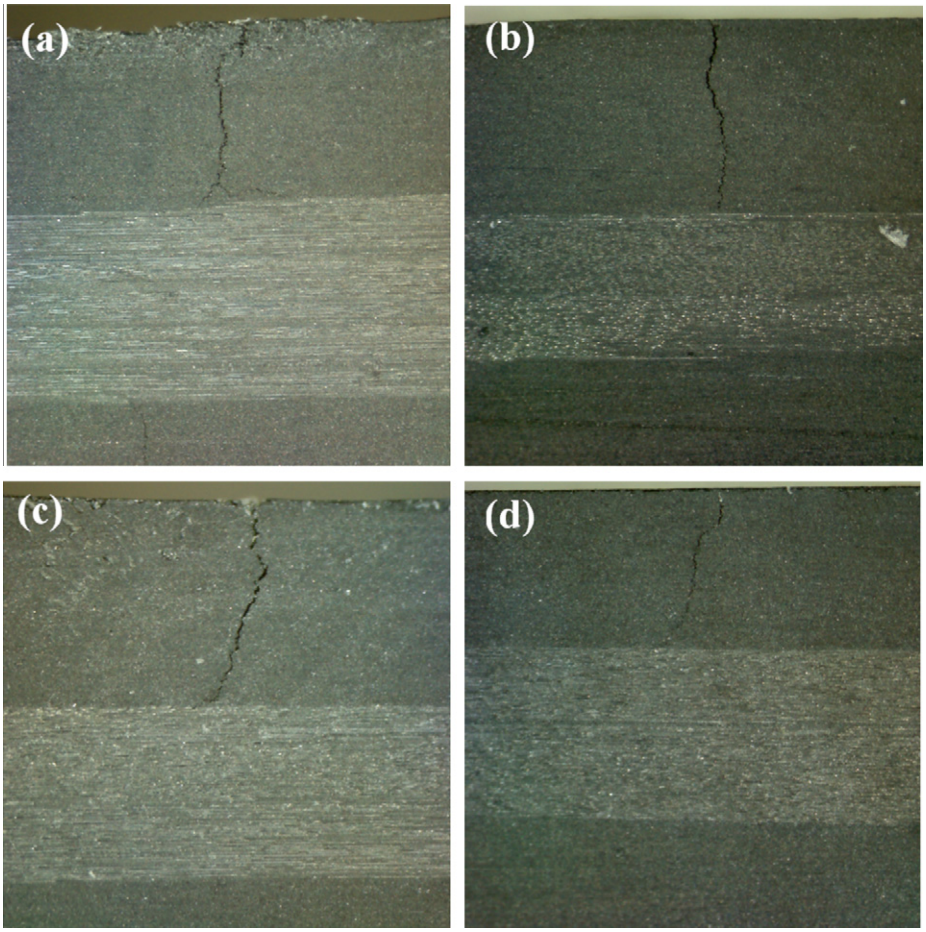

Fig. 7. Reflected optical micrographs of cryogenically cycled carbon fiber/epoxy laminates: (a) carbon fiber/neat epoxy, (b) carbon fiber/PBT modified epoxy, (c) carbon fiber/PC modified epoxy, and (d) carbon fiber/PEI modified epoxy laminates.

morphologies developed as a result of cryogenic cycling are shown in Fig. 7. The micro-cracks propagate normal to the carbon fibers along their length, beginning at the outer edge of the laminates and ends at the 0°/90° ply interface. It is seen that the micro-cracks did not appear to change with the thermoplastic type. It is noteworthy that the micro-cracks appear to be narrower in the thermoplastic modified epoxy laminate, as shown in Fig. 7b–d, the spacing between micro-cracks is smaller than in the neat epoxy laminate as shown in Fig 7a. It can also be noted that more micro-cracks formed on the outer side of the laminate. This phenomenon has been noted in other works and may be attributed to the roughness of the back side, which might have contributed more crack initiation sites than the tool side [36,37].

Significant variations in the micro-crack density of the laminates are observed as the type of thermoplastic is changed. The variations of micro-crack density in carbon fiber reinforced epoxy laminates are shown in Fig. 8 according to the type of thermoplastic used to modify the epoxy. The addition of thermoplastic can improve the micro-crack resistance of the laminates. This may be due to the reinforcing efficiency of the thermoplastic, which lowers the thermal stress present in the carbon fiber–epoxy laminate by reducing the matrix CTE. It has been found that the toughening caused by PBT can slightly improve the micro-crack resistance of the laminates. On the contrary, the dispersed PEI and PC can reduce the crack density by ~37%. From the previous results we can see that PEI and PC can reduce the CTE of the epoxy matrix more effectively than PBT. Therefore, all these observations are in good agreement with each other in suggesting that PEI and PC are good toughening materials for epoxy.

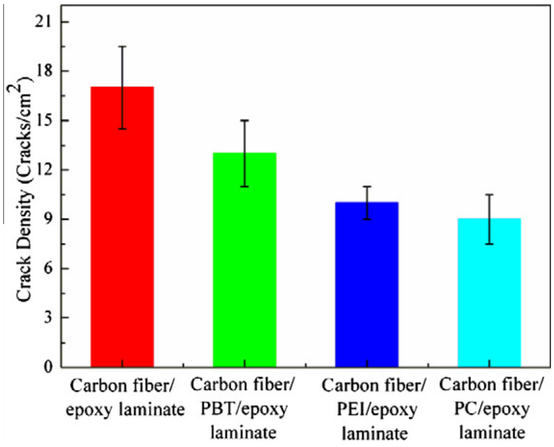

Fig. 8. Average crack densities of the various systems.

4. Conclusion

In this work, three types of thermoplastic were used to modify epoxy at cryogenic temperature (77 K). The properties, such as the impact strength and CTE values, of the modified epoxies were characterized at cryogenic temperature. The method of VARTM was adopted to prepare carbon fiber reinforced epoxy laminates and the effect of thermoplastic additions on the micro-crack resistance of the laminates was investigated. The results show that the presence of thermoplastic can increase the impact strength of epoxy and decrease the CTEs of the epoxy matrix. In comparison to the neat epoxy, the impact strength and CTEs of epoxy with 1.5 wt.% of PEI, at cryogenic temperature increased by 45% and decreased by 23%, respectively. The storage modulus in the glassy region of the thermoplastic modified epoxy is higher than that of the neat epoxy. The storage moduli of PEI, PC, and PBT modified epoxy are 5025 MPa, 4733 MPa and 4539 MPa, respectively, which are approximately 30%, 21%, and 17% higher than that of the neat epoxy. The TGA results suggest that thermoplastic can increase the temperature of the onset of decomposition. Optical micrographs show that thermoplastic modified epoxy laminates have good micro-crack resistance at cryogenic temperature. Therefore, both PEI and PC were very effective for preventing the formation of micro-cracks in the carbon fiber reinforced epoxy composites during cryogenic thermal cycles due to their low CTE values and the high impact strengths of the modified epoxies.

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