Water absorption and tensile properties of the hybrid of fly ash-CaCO$_3$/epoxy composites

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Abstract. The paper presents water absorption and its effect on the tensile properties of hybrid of fly ash-CaCO$_3$-filled epoxy. The total filler content was 20wt%, with the fly ash to CaCO$_3$ ratios were 20/0, 15/5, 10/10, 5/15 and 0/20. Adding fillers into epoxy decreased the water uptake in the ranges of 15 - 22%, where the lowest and the highest water uptake of the hybrid systems belonged to the fly ash/CaCO$_3$ ratios of 15/5 and 20/0, respectively. The tensile strength and elastic modulus continued to decrease with aging time for all epoxy systems. At the saturation level, the tensile strength and elastic modulus of filled epoxies were improved compared to the unfilled epoxy, except for the hybrid of fly ash/CaCO$_3$ of 15/5. The fracture strain as well as the tensile toughness were considerably increased at the equilibrium. A scanning electron microscopy revealed that in dry condition the fly ash was well bonded with the matrix, but not for the CaCO$_3$ particles. In the semi equilibrium and equilibrium states, the fly ash and CaCO$_3$ were mostly detached from the epoxy. The hybrid of fly ash/CaCO$_3$ of 15/5 was not recommended as it decreased the tensile properties more than the other hybrid compositions.

1. Introduction

The increasing use of epoxy in coating, polymeric matrix composites and structural adhesives [1] has attracted the material engineers to improve the property in order to fulfill a specific requirement such as high stiffness and water resistance. Hard inorganic fillers, such as mica, silica, and glass bead have been extensively used to fill the thermoset such as unsaturated polyester and epoxy resin [2,3] and often they acted individually to improve the stiffness and/or toughness. Filler can effectively improve a specific property such as elastic modulus, while other fillers can improve the other aspects, such as water resistance. Therefore, hybridization of fillers may improve many aspects required for increasing the performance of thermosetting polymers.

Hybridization can include nano dan micro-fillers, soft and hard particles and different type of fillers. Imai et al. [4] investigated hybridization of micro-silica and layered silicate to improve the thermal expansion dan insulation breakdown properties of epoxy. The results indicated that the thermal expansion was low and the insulation properties were improved. Javni et al. [5] used micro- and nano-silica to fill the rigid and flexible polyurethane. They found that the nano-silica improved the hardness and compressive strength but decreased the rebound resilience. In the contrary, micro-silica decreased the hardness and compressive strength and increased the rebound resilience. Carolan et al. [6] investigated the hybrid of soft rubber particles and nano silica to improve the toughness as well as to maintain the stiffness of epoxy. They found that at the hybrid content of 8% rubber particles and 8%
nano-silica increased the toughness by about 900% compared to unmodified epoxy, but the elastic modulus decreased by about 15%.

Among the micro-fillers, fly ash and CaCO\(_3\) are low cost fillers. Fly ash is a spherical particle as waste of coal combustion in a thermal power plant. Fly ash has been extensively studied to fill the epoxy resin [7,8], the unsaturated polyester resin [9], while micro- and nano-CaCO\(_3\) particles have been utilized to modify the polyurethane [10], polylactic acid [11] and epoxy [8,12,13]. Our previous study [8] revealed that the fly ash improved the tensile strength and the toughness of epoxy better than the CaCO\(_3\) particles. On the other hand, CaCO\(_3\) particles reduced the water absorption and increased the elastic modulus of epoxy more than that of the fly ash particles. Therefore, it is interesting to hybridize both particles to improve the mechanical properties as well as to reduce water absorption of epoxy. The paper investigates the water absorption and its effect on the tensile properties of epoxy as well as the morphologies of the fracture surfaces.

2. Methods

2.1. Materials
Epoxy was based on a diglycidyl ether bisphenol-A with a hardener of poliamideamino. As filler, fly ash and calcium carbonate (CaCO\(_3\)) were used. Fly ash particles were obtained from Paiton’s thermal power plant with the particle size of 200 mesh and less, while CaCO\(_3\) was commercially purchased from a local store with the particles size of 800 mesh.

2.2. Specimen preparation.
For fabricating the tensile specimens, epoxy resin was mixed with fillers with total filler content of 20wt%. The ratios of fly ash (FA) to CaCO\(_3\) (CC) were 20/0, 15/5, 10/10, 5/15, 0/20 (by weight), which were named as FA20/CC0, FA15/CC5, FA10/CC10, FA5/CC15 and FA0/CC20, respectively. The mixture was stirred using a hand mixer for 30 min. The mixture then was degassed in a vacuum chamber to release the air bubble trapped during mixing. Hardener was added to the mixture (with epoxy resin to hardener ratio of 1/1), stirred slowly to avoid significant air bubbles and then degassed again. The mixture then was transferred into a dog bone shaped-silicon rubber mould with dimension according to ASTM D638 [14]. The mould was left to cure for at least 24 hours.

2.3. Conditioning and testing
Conditioning was carried out by immersing the specimens in distilled water at a temperature of 50\(^\circ\)C. The water uptake studies were performed for each specimen using the dog-bone specimen directly. Weighing of the specimens were conducted at every three hours during the first day and once a day for the following days. Conditioning was grouped as dry, semi-equilibrium and equilibrium. For the aged specimens, after the water content of the specimen reached approximately the semi equilibrium (144 hours) and the equilibrium states (2479 hours), they were taken out for tensile testing. The tensile test for the dry, semi equilibrium and the equilibrium specimens was conducted using a Tensilon testing machine with displacement rate of 5 mm/min. Scanning electron microscopy was performed to examine the fracture surface morphologies using a JEOL 6510 LA machine operating at 10 kV.

3. Results and Discussion

3.1. Water uptake
Figure 1 shows the water uptake vs. square root of aging time for the epoxy systems. It can be seen that the water uptakes were initially linear and then slowing down when reached close to the equilibrium (saturation). The non-linear water uptake at the very beginning stage might be caused by the difficulty of water diffused into the very smooth surfaces, as the specimen surface was not abraded.
before aging. It was also observed by another researcher [15]. The water uptakes seemed to follow the Fickian diffusion law as also reported by Sugiman and Salman [8].

![Figure 1](image)

**Figure 1.** Water uptake vs. square root of aging time for epoxy systems.

**Table 1.** The diffusion properties of the epoxy systems.

| Specimen       | Water uptake ± SD (%) | Diffusion rate ± SD (mm²/h) (×10⁻³) |
|----------------|------------------------|------------------------------------|
|                | At semi-equilibrium     | At equilibrium                     |                                |
| Neat epoxy     | 2.51 ± 0.13            | 7.60 ± 0.07                        | 3.60 ± 0.41                    |
| FA20/CC0       | 2.05 ± 0.03            | 5.90 ± 0.01                        | 3.03 ± 0.03                    |
| FA15/CC5       | 2.41 ± 0.34            | 6.42 ± 0.09                        | 3.13 ± 0.05                    |
| FA10/CC10      | 2.09 ± 0.14            | 6.05 ± 0.04                        | 3.14 ± 0.13                    |
| FA5/CC15       | 1.87 ± 0.14            | 6.01 ± 0.10                        | 3.34 ± 0.52                    |
| FA0/CC20       | 2.15 ± 0.16            | 6.06 ± 0.01                        | 3.10 ± 0.02                    |

As seen in Figure 1 and Table 1, the equilibrium water uptakes and the diffusion rate of the filled epoxies decreased compared to the neat epoxy. Compared to the neat epoxy, the decreases of the equilibrium water uptake were 22, 15, 20, 21 and 20% for FA20/CC0, FA15/CC5, FA10/CC10, FA5/CC15 and FA0/CC20, respectively. Meanwhile for the diffusion rate, the decreases were in the range of 12-16%, compared to the neat epoxy. For the filled epoxy systems, the diffusion of water took longer route due to the existence of particles. Individually (not hybridized), fly ash and CaCO₃ fillers acted the similar way as the equilibrium and the diffusion rate was about the same. The hybridization with the composition of FA10/CC10 and FA5/CC15 also did not significantly affect the diffusion properties compared to the fly ash- dan CaCO₃-filled epoxies. However, at the composition of FA15/CC5, the effectivity in reducing the equilibrium and the diffusion rate of neat epoxy was less than the other compositions. A fly ash particle contained some elements such as silicone (Si), aluminium (Al), magnesium (Mg), iron (Fe), potassium (K), and calcium (Ca) [8]. The elements of Na and Ca are soluble to water forming NaOH and Ca(OH)$_2$ respectively [16], while SiO$_2$ reacted to water forming silica acid [17]. The existence of a small amount of CaCO₃ together with the hydrolysed fly ash might be favourable for forming the calcium silicate hydrates that more consumed water than the other compositions [18].
3.2. Tensile properties

3.2.1. Tensile strength. Figure 2 shows the tensile strength of the epoxy systems in the dry, semi equilibrium and the equilibrium states. In the dry condition, compared to the neat epoxy the significant decrease of the tensile strength, by about 15% was observed for the FA15/CC15 composition, while the tensile strength of other compositions did not differ significantly (based on the analysis of variance). After being aged until the semi equilibrium state, the tensile strength for all epoxy systems decreased significantly. The highest decrease was also observed for the FA15/CC5 compositions, while for the other compositions, the tensile strength did not significantly differ to that of the neat epoxy. The decrease of the tensile strength for the neat epoxy, FA20/CC0, FA15/CC5, FA10/CC10, FA5/CC15- and FA0/CC20-filled epoxies were about 28, 32, 54, 33, 34 and 33%, respectively. Further aging to the equilibrium state, the tensile strength significantly decreased and the decreases were 83, 76, 85, 79, 80, and 79% compared to those in the dry condition for each epoxy system. Again, the highest decrease was observed for the FA15/CC5-filled epoxy. In this case, plasticization of the matrix was the main cause in decreasing the tensile strength for the neat epoxy [8,15]. For the filled epoxies, in addition to the plasticization, particles debonding also contributed to the decrease of the tensile strength [8]. This effect was clearly seen in the FA15/CC5 filled epoxy, while for the other compositions, it was not observed as the tensile strength did not significantly differ with that of the neat epoxy. Nevertheless, the hybrid composition of FA5/CC15 was preferred as it has the highest tensile strength in the dry condition and has relatively the modest reduction in the wet condition.

![Figure 2. The tensile strength of the epoxy systems in various conditions.](image1)

![Figure 3. The elastic modulus of the epoxy systems in various conditions.](image2)

3.2.2. Elastic modulus. Figure 3 shows the elastic modulus of the epoxy systems in various conditions. In the dry condition, the elastic modulus increased compared to the neat epoxy. This was expected as the elastic modulus of fillers was much higher than the epoxy matrix. The increase of the elastic modulus for the FA20/CC0-, FA15/CC5-, FA10/CC10-, FA5/CC15- and FA0/CC20-filled epoxies were 26, 14, 33, 33 and 33%, respectively. It was seen that when the content of CaCO₃ was higher than 10% in the total filler content, the elastic moduli were about the same. The elastic modulus for the FA was about 17 GPa [19], while the elastic modulus of CaCO₃ was about 35 GPa [20], so it was expected that high content of CaCO₃ increased the elastic modulus more than that of the fly ash. Similar to that in the tensile strength, compared to the neat epoxy, the increase of the elastic modulus for FA15/CC5 was the lowest among the other compositions.
For the specimens aged until the semi equilibrium state, compared to the dry condition, the elastic moduli decreased and the reductions were 26, 10, 34, 10, 6 and 10% for the neat epoxy, FA20/CC0-, FA15/CC5-, FA10/CC10-, FA5/CC15- and FA0/CC20-filled epoxies, respectively. The elastic moduli for the filled epoxies were still higher than that of the neat epoxy; except the elastic modulus of the FA15/CC5-filled epoxy, which was lower than that of the neat epoxy. After aging until the equilibrium, the elastic moduli of the epoxy systems had the similar trend to those of the semi equilibrium. The elastic modulus at the equilibrium state were dropped by 92, 87, 96, 87, 90 and 88% for the neat epoxy, FA20/CC0-, FA15/CC5-, FA10/CC10-, FA5/CC15- and FA0/CC20-filled epoxies, respectively, compared to those in the dry condition. This was caused by plasticization effect that increased with the increase of aging time (or water content). For the filled epoxies, the effect of plasticization was compensated by the particles by hindering plastic deformation, so the decrease of the elastic moduli was not as high as that for the neat epoxy. It seemed that the effect of plasticization on the elastic modulus was more pronounced than the effect on the tensile strength [15].

3.2.3. Fracture strain. Figure 4 shows the fracture strains of the epoxy systems under various conditions. In contrast to the tensile strength and the elastic modulus, in the dry condition, the fracture strains of the filled epoxies were slightly lower than that of the neat epoxy. However, after being aged until the semi equilibrium state, compared to those in the dry condition, the fracture strains increased by about 64, 61, 110, 32, 9, and 19% for the neat epoxy, FA20/CC0-, FA15/CC5-, FA10/CC10-, FA5/CC15- and FA0/CC20-filled epoxies, respectively. Further aging to the equilibrium state, the increases of fracture strains were remarkably, by about 588, 602, 531, 557, 544 and 623% for the neat epoxy, FA20/CC0-, FA15/CC5-, FA10/CC10-, FA5/CC15-, and the FA0/CC20-filled epoxies, respectively, compared to those in the dry condition. The remarkable increase of the fracture strain indicated that the aged epoxy systems became very ductile due to the plasticization effect.

![Figure 4](image1.png)

**Figure 4.** The fracture strain of the epoxy systems in various conditions.

![Figure 5](image2.png)

**Figure 5.** The tensile toughness of the epoxy systems in various conditions.

3.2.4. Tensile toughness. Figure 5 shows the tensile toughness of the epoxy systems in various conditions. The toughness was obtained by measuring the area underneath the tensile stress-strain curve, which indicated the amount of energy absorbed for breaking [21]. Referring to Figures 3 and 4, it seemed that the toughness was the opposite to the elastic modulus, and it was proportional to the fracture strain. As seen in Figure 5, in the dry condition, the toughness did not differ significantly among the epoxy systems (based on the analysis of variance); however, they tended to increase after being aged until the semi equilibrium and further increased with increasing aging time up to the equilibrium state. The highest toughness belonged to FA20/CC0 composition, which was the fly ash-
filled epoxy. Sugiman and Salman [8] also reported that the fly ash-filled epoxy had higher fracture toughness than the CaCO$_3$-filled epoxy. Nonetheless, the other compositions except FA15/CC5 also indicated high toughness after aging and they were higher than that of the neat epoxy.

![Figure 6](image-url)

**Figure 6.** Optical micrograph of the fracture surfaces of (a) neat epoxy, (b) FA20/CC0, (c) FA15/CC5, and (d) FA0/CC20. The magnification is 50×.

3.3. Fracture morphologies

Figure 6 shows the optical micrographs of the fracture surfaces of the selected compositions in the dry, semi equilibrium and the equilibrium states. For brittle fracture like epoxy, the fracture surfaces consisted of three regions; mirror, mist and final fracture regions [22,23]. The mirror region is an area surrounding the crack source. The mist region is the transition between the mirror and the final fracture regions. The surface roughness is smooth like mirror in the mirror region and gradually increases into the transition region and very rough in the final fracture region [22,23]. It was seen in Figure 6a that for the neat epoxy, the mirror, mist and the final fracture regions were distinguishable,
indicated by marks 1, 2 and 3, respectively. As seen in Figure 6a, in the dry condition, the mirror region (in the red dashed line, indicated by mark 1) was clearly seen, but the mist region was not. In the semi equilibrium state, the mirror and the mist regions were obvious. In this condition, the mechanical properties between the inner and outer of the bulk specimen were different, as at the outer layer the water content was higher than the inner part of the bulk. Due to plasticization, the outer layer was more ductile than the inner; therefore, this affected the fracture mechanism leading to the different appearances of the fracture surfaces. In the equilibrium state, the fracture surface was smooth, where the mirror, mist and the final fracture regions were hardly distinguished. In this condition, the bulk of epoxy has reached the saturation level, so the difference in the mechanical properties between the outer and the inner of bulk might be small, similar to that in dry condition. The area of mirror region increased with the increase of aging time (water content), due to increasing the plasticization effect [24].

For the filled-epoxy systems, the fracture surfaces also showed the three regions, although they were not as obvious as that for the neat epoxy. The fracture surfaces were rougher than those of neat epoxy due to the fillers that acted as loci of microcrack initiation, crack branching, crack pinning and void growth [2,3,8]. As seen in Figures 6(b-d), the fracture surfaces for the filled epoxies in the same conditions (dry, semi equilibrium and equilibrium) seemed similar. The area of mirror region increased with aging time, which was consistent with that in the neat epoxy.

![Figure 7](image_url)

**Figure 7.** The scanning electron microscopy (SEM) micrograph of the fracture surfaces of FA15/CC5-filled epoxy in (a) dry, (b) semi equilibrium, and (c) equilibrium states.

The scanning electron microscopy (SEM) was conducted on the selected composition, which was FA15/CC5-filled epoxy, as this composition have the lowest properties in all conditions. As seen in Figure 7, the fracture surface in the dry condition was rougher than the other conditions. In dry condition (Figure 7(a)), the fly ash particles were well bonded by the epoxy matrix; however, the CaCO$_3$ particle appeared to debond, as void was observed around the CaCO$_3$ particle. Similar results on this behaviour were reported in Ref. [8]. The debonded CaCO$_3$ particle might initiate the microcrack that could propagate causing the failure. This might cause the lower properties of the FA15/CC5-filled epoxy. After being aged in the semi equilibrium and the equilibrium states, the matrix plasticized, and
water might attack the interface filler-matrix. When the filler has a weak interface bonding with epoxy matrix, water may displace the particle from the matrix and upon loading, and then the particles debonded from the matrix. This decreased further the tensile strength. The debonded fly ash particles after being aged in the semi-equilibrium and equilibrium are shown in Figures 7b and 7c, respectively. It can be seen that the fly ash particle debonded from the matrix and the void grew upon loading. The matrix void growth became wider after aging to the equilibrium state, where the matrix plasticization was massive.

4. Conclusions

Investigation of water absorption and its effect on the tensile properties of the neat and the hybrid of fly ash (FA)-CaCO₃ (CC)-filled epoxies have been undertaken. The total filler content was 20wt%, and the hybrid compositions were FA20/CC0, FA15/CC5, FA10/CC10, FA5/CC15, FA0/CC20. It can be concluded as follows:

- The hybrid of fly ash-CaCO₃-filled epoxy decreased the equilibrium water uptake and the diffusion rate of epoxy resin. The decrease of the water uptake was about the same (20-22%), but for the composition of FA15/CC5, it was about 15%. While the decrease of the diffusion rate was about 12-16%.
- The tensile strength of the hybrid of fly ash-CaCO₃-filled epoxy did not differ significantly to that of the neat epoxy, except the composition of FA15/CC5, where the tensile strength decreased by about 15%. Meanwhile, the hybrid of fly ash-CaCO₃ significantly increased the elastic modulus of epoxy.
- Aging in distilled water at temperature of 50°C caused deleterious effect on the tensile strength and the elastic modulus for all of the studied epoxy systems; however, the fracture strain and the toughness increased considerably. Again, the effect of aging has the highest impact on the composition of FA15/CC5, so it is not recommended for hybridizing the fly ash and CaCO₃ with the fly ash to CaCO₃ ratio was close to 15/5, but the hybrid composition of FA5/CC15 was recommended.

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