Modelling the flexural properties of filled epoxy: Effects of volume fraction

Sugiman Sugiman[1*], *Salman* Salman[1], *Agus* Dwi Catur[1], and *Yuli* Panca Asmara[2]

[1]Department of Mechanical Engineering University of Mataram Mataram, Indonesia
[2]Faculty of Engineering and Quantity Surveying, INTI International University Nilai Negeri Sembilan, Malaysia

Abstract. The effects of volume fraction on the flexural characteristics of epoxy materials filled with cement, fly ash, and CaCO3 are discussed in this work. At a temperature of 50oC, water was used to soak the filled epoxies. It was discovered that the flexural modulus rose with the volume fraction for all fillers. However, the flexural strength of fly ash and CaCO3-filled epoxies tended to decrease with the increase in volume percent. The flexural strength of cement-filled epoxy somewhat improved with the increment volume fraction. According to those data, cement has a stronger interface than fly ash and CaCO3. In comparison to those in the dry condition, the flexural modulus and strength of all the epoxy systems dramatically decrease for the aged specimen. Epoxy that has been filled appears to lessen the reduction in flexural properties compared to that of neat epoxy. Again, the cement-filled epoxy performs better than fly ash and CaCO3. Halpin-Tsai and Pukánszky models have been successfully applied to model the flexural modulus and strength in the dry condition, respectively, but both models failed to predict those mechanical properties in wet condition.

1 Introduction

The epoxy resin highly contributes to developing high-performance composites, adhesives and coating [1]. Nevertheless, epoxy is prone to water attacks which could affect its performance when operating in a moist environment. Water can degrade the physical and mechanical properties of epoxy, so it is necessary to improve the water-resistance of epoxy.

One of the attempts to improve the water-resistance of epoxy is by adding filler. Various fillers can be used to enhance the water-resistance of epoxy such as silica [2], calcium carbonate [3], fly ash [4], talc [5], carbon black [6] and silicon carbide [7], clay, and carbon nanotube [8]. Besides filler size, the effectiveness of filler also depends on the interaction of filler with matrix and the reactivity of filler to water. Filler size contributes to the diffusion path length that affects the diffusivity. Interaction of filler/matrix indicates the ability of water to attack the interface of filler/matrix. When fillers are well-bonded with matrix, the water resistance of its composites could be improved significantly. However, the interaction of the filler/matrix depends on the filler's surface functionality and the matrix's functional group. During ageing, the surface functionality can change as water molecules interact with the filler, affecting the bonding between the filler and matrix. Our previous research [9] indicated that the composites filled with filler with different reactivity had different responses to the water absorption and their tensile properties. In this paper, the study is aimed at the effect of the volume fraction of filler having different reactivity to water on the flexural properties of filled epoxy systems. Modelling of the effects of filler volume fraction on the flexural properties was carried out.

2 Experimental Method

2.1 Materials

The matrix used here was epoxy resin based on epichlorohydrin of bisphenol-A with the hardener of polyaminoamide. The fillers used were Portland cement, fly ash, and CaCO3. The average particle size of Portland cement, CaCO3 dan fly ash was 30, 15, and 74 μm, respectively.

2.2 Specimen fabrication, ageing and testing

The detail of the specimen fabrication and ageing were as described in our published paper [9] so they were not discussed further here. This study focused on flexural properties in dry (unaged) and wet (aged) conditions. The specimen followed the ASTM D790 [10]. Ageing of the specimen was carried out by soaking them in distilled water at a temperature of 50oC. After 30 days, the specimens were taken out to be tested in bending. In this ageing time, epoxy has reached saturation [9].

The flexural test was conducted using a Tensilon testing machine. The span length to the specimen thickness ratio was kept at 16. The displacement rate of the flexural test was 2 mm/min. The flexural strength

* s.sugiman@unram.ac.id

(σf) and the flexural modulus (Ef) were calculated using Eq. (1) and Eq. (2), respectively.

$$\sigma f = \frac{3PmaxS}{2bh^2} \quad (1)$$

$$Ef = \frac{S3m}{4bh^2} \quad (2)$$

where Pmax is the maximum load, b and h are respectively the width and the specimen thickness, S is the span length, and m is the slope of the load-deflection curve at the elastic region.

3 Findings and Discussion

3.1 Experimental results

Figure 1 shows the typical flexural stress-strain of the unaged (dry) and aged (wet) samples. The stress-strain in a dry condition for filled epoxy (Fig. 1a) was mostly dominated by the linear portion with very limited plastic deformation before the break. However, the flexural stress-strain for neat epoxy showed softening after peak stress. Even for the neat epoxy, the specimen did not break after the strain reached 5%, and the test was stopped at the strain of 10% without a break [10]. In wet condition (see Fig. 1b), all the epoxy systems showed softening after peak load, and the test was halted after the strain reached at least 10%.

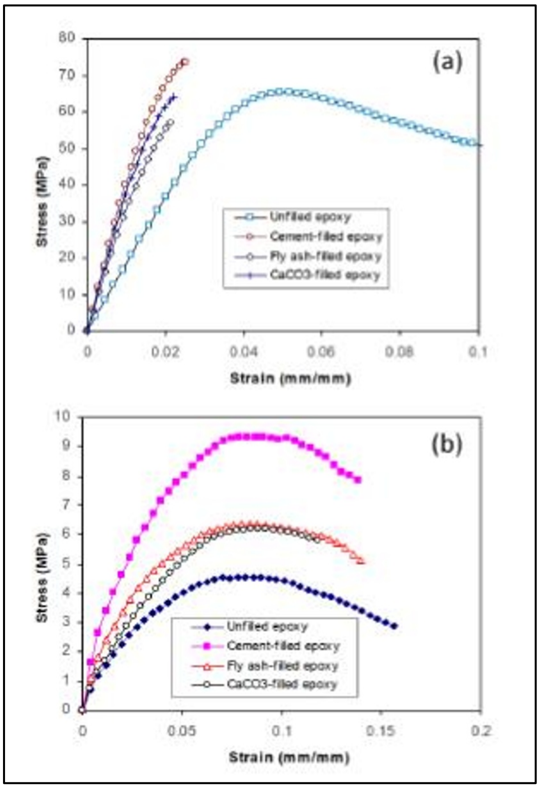

Fig. 1. Typical stress-strain of filled epoxies in (a) dry condition, (b) wet condition.

Figure 2a shows the curves of flexural modulus vs. the filler volume fraction in dry condition. The flexural modulus increased with the filler volume fraction increment for all three filled epoxies. It is expected that, based on the rule of mixture, hard filler with high elastic modulus improved the elastic modulus of epoxy. As seen in Fig. 2a, the flexural elastic modulus for all fillers was not much different, indicating that the interaction of filler/matrix did not contribute to the elastic modulus. It agrees with the report of [11].

According to numerous researchers [11], [12], adding micro-size filler typically causes the tensile strength to drop. The bonding strength between the filler and matrix [11] and the filler's distribution affect the filled epoxy's tensile strength. Similarly, as shown in Fig. 2b, the flexural strength of epoxies filled with fly ash and calcium carbonate declined as the filler volume fraction increased, but it tended to slightly rise for epoxies filled with cement. The flexural strength of 10% fly ash-filled epoxy, showed the highest, which might be due to the better dispersion. The improved flexural strength of cement-filled epoxy could be due to the better interfacial strength and the better dispersion compared to other studied fillers.

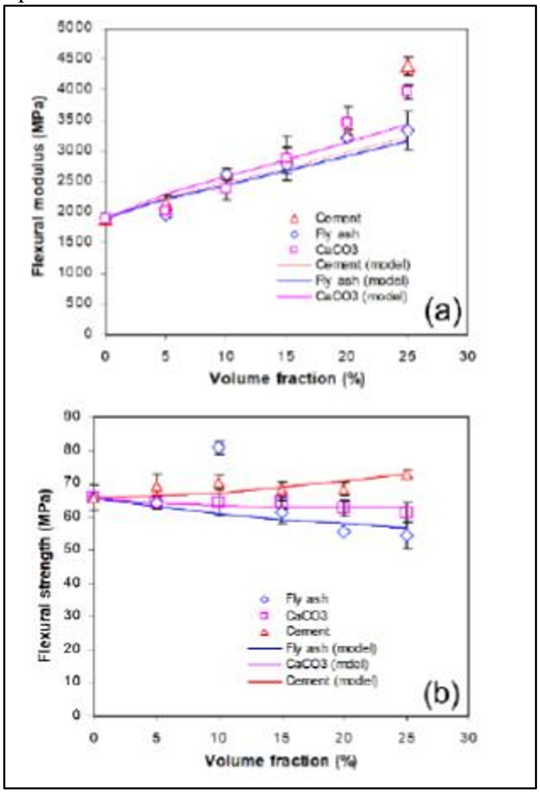

Fig. 2. (a) Flexural modulus, (b) flexural strength in dry condition.

Figure 3a shows the flexural modulus of specimens after being aged for 30 days. The flexural modulus significantly decreased compared to those in the dry state after 30 days of ageing. Flexural modulus decreased by 87% for unfilled epoxy. When cement filler was added, the flexural modulus was reduced to 52% at a volume fraction of 5%, nevertheless greatly improved compared to unfilled epoxy. The increase in filler volume fraction did not significantly affect the flexural modulus. Meanwhile, the addition of fly ash and $CaCO_3$ only slightly improved the flexural modulus compared to the neat epoxy. Cement is very reactive to water and hydration reaction with water resulted in tobermorite which might improve the interaction with epoxy matrix. For the aged condition, plasticization of the epoxy matrix played the main role on the reduction of the elastic modulus.

Similar to the flexural modulus, for the aged condition, the flexural strength significantly decreased due to plasticization (see Figure 3b). The effect of fly ash dan $CaCO_3$ fillers seemed not significant, but indeed the cement filler reduced the degradation of the flexural strength, particularly at the lower volume fraction (5%).

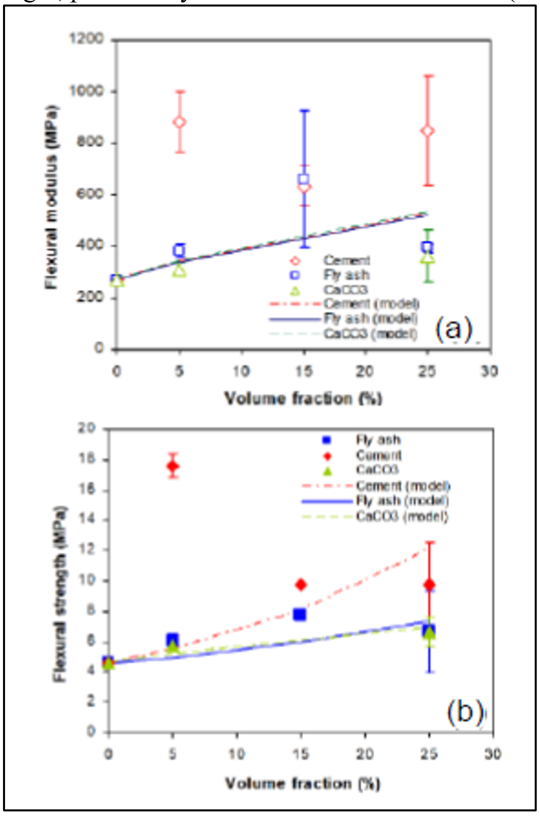

Fig. 3. (a) Flexural modulus, (b) flexural strength in wet condition

3.2 Modelling the flexural properties

Halpin-Tsai's model (Eqs. (3)-(4)) was chosen as it has been successfully applied to model the elastic modulus of filled polymers [13]-[15].

$$Ef = \frac{1+\xi\eta Vp}{1-\eta Vp} * Em \quad (3)$$

$$\eta = \frac{\left(\frac{Ep}{Em}\right)-1}{\left(\frac{Ep}{Em}\right)+\xi} \quad (4)$$

Where E_f is the flexural modulus of composites, E_p is the elastic modulus of particle, E_m is the elastic modulus of matrix, respectively, and V_p is the volume fraction of particles. The shape factor, ξ, depends on the geometry, and it was taken as 2 for spherical particles.

To model the flexural strength (σ_f), a model developed by Pukanszky et al. [16] was applied here, given in Eq. (5).

$$\sigma f = \left[\left(\frac{1-Vp}{1+2.5Vp}\right)\sigma m\right] exp(BVp) \quad (5)$$

Where V_p is the volume fraction of the particle, σ_m is the strength of the matrix, and B is an empirical constant. The B value is dependent on the interfacial bonding energy, particle density and the surface area of particles. The B value started from 0 for very weak adhesion to a higher value, according to the adhesion strength.

In a dry environment, the elastic moduli of cement, fly ash, and $CaCO_3$ were 135 GPa [17], (17 GPa] [18], and (35 GPa) [19]. The B values for cement, fly ash, and $CaCO_3$ were determined to be 3.5, 2.5, and 2.9, respectively, in the dry state and 7, 6.1, and 6, respectively, in the wet condition. Due to hydration process, the cement's elastic modulus in a wet state decreased to 25 GPa [17]. The elastic modulus of fly ash and $CaCO_3$ particles was the same in the wet state because there is little to no chemical reaction with water. Those B values indicate that the adhesion strength order from the highest to the lowest was cement, fly ash, and $CaCO_3$.

In dry condition, the predicted flexural modulus, especially at a high-volume fraction, were underestimated for all filled epoxies. In contrast, the agreement between the predicted flexural strength and the experimental data was reasonably good (see Figure 2a). In the wet condition, the Halpin-Tsai and Pukanszky et al. models failed in estimating the flexural modulus and strength, respectively (see Figures 3a dan 3b). This might be due to the excessive plastic deformation of the matrix as the epoxy matrix absorbed water in saturation and induced plasticization.

4 Conclusions

Unaged and aged cement-, fly ash- and $CaCO_3$-filled epoxies have been studied to determine the impact of filler volume percent on their flexural characteristics. No matter the type of filler, increasing the filler volume percentage improved the flexural modulus of epoxy. The type of filler did, however, have an impact on the flexural strength when it came to the filler volume percentage. While the fly ash and $CaCO_3$-filled epoxy tended to weaken with an increase in volume percent, the flexural strength of cement filler epoxy tended to marginally improve. Halpin-Tsai and Pukanszky models have been successfully modelled the flexural modulus and strength successfully in dry condition. However, both models fail to do so for the aged samples as the matrix experiences excessive plastic deformation due to plasticization having absorbed water. Cement filler, which is very reactive to water, improved epoxy's flexural modulus and strength.

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