Water Absorption and Fracture Toughness of Hybrid Calcium Carbonate/Rubber Particle/Epoxy Composites

Sugiman Sugiman[1](✉), L. Hasfari Firmansyah[1], Paryanto Dwi Setyawan[1], and Hafiz T. Ali[2]

[1] Department of Mechanical Engineering, Faculty of Engineering, University of Mataram, Nusa Tenggara Barat, Mataram 83125, Indonesia
s.sugiman@unram.ac.id

[2] Department of Mechanical Engineering, College of Engineering, Taif University, Taif 21944, Saudi Arabia

Abstract. The study investigated the effects of ageing on the fracture toughness of the nano Calcium Carbonate/ground rubber particle hybrid composites. The rubber particles content was 0, 5, 10 and 15 wt%, while the calcium carbonate contents was fixed 2 wt% of the epoxy resin. Aging was carried out in distilled water at a temperature of 50 °C. Water absorption and fracture toughness properties of an epoxy-containing a hybrid of rubber particles and Calcium Carbonate were carried out. It was observed that the water absorption increased after adding ground rubber particle and calcium carbonate. The fracture toughness increased after adding rubber particles and the optimum fracture toughness was obtained at the rubber particle content of 10%. Adding calcium carbonate in the epoxy containing rubber particles reduced the fracture toughness but improved the fracture toughness of the aged specimens.

Keywords: Epoxy · Calcium carbonate · Ground rubber particle · Fracture toughness · Water absorption

1 Introduction

Epoxy is a thermosetting polymer that attracts materials engineer to be used as matrix of fibrous composites. In addition, epoxy have gained diverse applications such as for coating and adhesives, due to high mechanical properties, high adhesion, and low shrinkage [1]. Nevertheless, epoxy is able to absorb water significantly, which then have negative effects on the mechanical properties (i. e. tensile and elastic modulus), as well as the fracture toughness. Water also has detrimental effects on the physical properties such as the glass transition temperature (Tg) [2, 3]. Swelling [4–6] and irreversible degradation such as leaching of the low-molecular-weight in epoxy backbone [7, 8] are often reported. The detrimental effects of water limit the application of epoxy in engineering structures.

S. Sugiman et al. (Eds.): MIMSE-M-E 2022, AER 216, pp. 334–342, 2023.
https://doi.org/10.2991/978-94-6463-078-7_31

Other limitation of epoxy is its low fracture toughness. This is due to high cross-link in its structure. Many attempts have been reported to enhance the fracture toughness of epoxy such as introducing low elastic modulus of rubber particles. Hard particles from silica, glass bead, mica and other inorganic particles also can improve the fracture toughness [9]. Although significantly improve the fracture toughness, soft rubber particles reduce the elastic modulus significantly, on the other hand the hard particles can enhance the elastic modulus but are limited in fracture toughness improvement. Hybridization of both kind particles might have a compromised enhancement between elastic modulus and fracture toughness [10]. To name a few, Carolan et al. reported fracture toughness of epoxy could be enhanced (by 900%) by hybridization of rubber particles (8%) and nano-silica (8%); however, it must be paid by lowering the elastic modulus by about 15% [11]. Alavitabari et al. reported that the toughness HDPE/nano Clay nanocomposite decreased, however the addition small amount of nano calcium carbonate prevents the drastic drop in the toughness [10]. Micro and nano CaCO3 are low-cost fillers that have been utilized to modify polyurethane [12], polylactic acid [13], stearic acid [10], and epoxy [14] [16].

Rubber particles can be obtained from tire rubber waste, which has good mechanical properties. Although the use of ground tire rubber to fill the polymer has been reported; however, the study of hybrid $CaCO_3$ and ground tire rubber are limited, both on mechanical properties and water absorption behaviour. Therefore, the objective of this paper is to investigate the water absorption and its fracture toughness of hybrid of nano calcium carbonate -ground rubber particles after being aged in distilled water. Surface morphologies after fracture toughness test were also reported.

2 Materials and Methods

2.1 Materials

The epoxy resin and hardener were respectively a diglycidyl ether of bisphenol-A and polyamidoamine, supplied by Justus Kimia Raya, Surabaya, Indonesia. Ground tire rubber particles were obtained by scrapping the tire rubber (without thread), screening and sieving using a sieve of size 200 mesh (0.075 mm) and less, while nano $CaCO_3$ (NCC) was commercially purchased from RW Chemical Ltd, China. The size of these fillers was about 60–80 nm.

2.2 Rubber Treatments

The rubber particles were treated with a stearic acid solution with concentration of 1wt% in acetone solution. The 100 g of rubber particles were immersed in a stearic acid solution with rubber to stearic solution weight ratio of 1: 2 for 2 h at room temperature. The treated particles were then filtered and dried at 50 °C in an oven for 24 h. The dried rubber was stored in a sealed container before use.

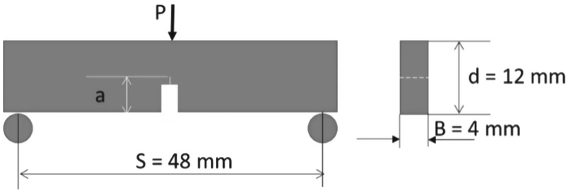

Fig. 1. A single edge notch bend (SENB) specimen.

2.3 Sample Preparations

In the manufacture of single-edge notch bend (SENB) specimens, the filler (NCC and GTR) was mixed with epoxy resin, with the ratio of NCC to GTR was is 0/0 (neat epoxy), 0/5, 0/10, 0/15, 2/0, 2/5, 2/10, and 2/15 (wt%). For clarity, the samples were coded as neat epoxy, NCC0R5, NCC0R10, NCC0R15, NCC2R0, NCC2R5, NCC2R10 and NCC2R15, where CC dan GTR were denoted for NCC and GTR, respectively. The mixture was stirred using a hand mixer for 20 min and then degassed in a vacuum chamber for 30 min to remove air bubbles trapped in the mixture. Epoxy hardener was added to the mixture with epoxy resin to hardener ratio of 60: 40. The resin system and hardener mixture was stirred manually in a clockwise direction, degassed for 30 min and then poured into a silicone rubber mold. The mixture was then left at room temperature for 24 h for curing.

After cured, the specimens were machine to get a notch and pre-crack using fresh sharp blade as shown in Fig. 1.

2.4 Aging and Fracture Toughness Test

Before conducting fracture toughness test, the specimens were conditioned into two conditions: dry dan wet specimens. For the dry condition, specimens were tested in dry condition, but for the wet condition, specimens were immersed in distilled water at a temperature of 50 °C prior to being tested. Water uptake studies were also carried out using the SENB specimen directly. The SENB specimens were weigh periodically until they reached the saturation level, indicating by no significant water absorption observed with time. After reaching the saturation level, they were taken out for fracture toughness test. The fracture toughness test was conducted using a Tensilon testing machine with a displacement rate of 10 mm/min and with a 10 kN load cell. Fracture toughness was determined according to ASTM D4055. Scanning electron microscopy was performed to examine the fracture morphology with operating at 10 kV using a JEOL 6510 LA machine.

3 Results and Discussion

3.1 Water Uptake

Water absorption behaviour of hybrid NCC-GTR/epoxy composites can be seen in Fig. 2. It is observed that in general, water absorption increases faster initially and then slows down after reaching the saturation level. This water uptake curves are typical for Fickian diffusion law [15].

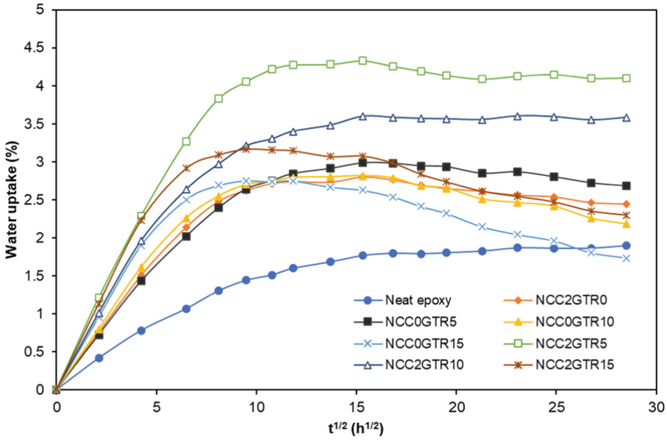

Fig. 2. Water uptake vs aging time for epoxy systems.

Table 1. The diffusion properties of the epoxy systems.

Specimen	Water uptake ± SD (%)	Diffusion rate ± SD (mm^2/h) (× 10^{-3})
Neat epoxy	2.82 ± 0.08	1.66 ± 0.18
NCC0R5	2.94 ± 0.07	2.09 ± 0.20
NCC0R10	2.80 ± 0.05	2.52 ± 0.04
NCC0R15	2.73 ± 0.16	3.25 ± 0.09
NCC2R0	2.77 ± 0.16	1.81 ± 0.14
NCC2R5	4.25 ± 0.15	1.66 ± 0.05
NCC2R10	3.58 ± 0.04	1.41 ± 0.08
NCC2R15	3.14 ± 0.37	4.04 ± 0.60

R is ground tire rubber.

As seen in Fig. 2 and Table 1, without NCC, the equilibrium water uptake at the GTR content of 5% increase and then decrease at the GTR content of 10 and 15% compared to that of neat epoxy. With the 2wt% NCC, the water uptakes of epoxy were even higher than that of neat epoxy, but the trend of water uptake due to increasing GTR was similar. The water uptake at the GTR content of 5% was the highest. Without NCC, the diffusion rate of epoxy filled with GTR increase with the increased of GTR content, compared to that of neat epoxy; however, with addition of 2wt% NCC, the diffusion rate decreased with the increase of GTR up to 10%. At GTR content of 15%, the diffusion rate was much higher than others epoxy systems. It appeared that the addition of GTR increase the water absorption, although GTR had been treated to become hydrophobic. The hybrid NCC and GTR further increased water absorption, which might due to the increase of fillers content. This is a synergistic effect of the hybrid that have negative effect on the amount of water absorbed. Other researchers [17, 18] also reported the

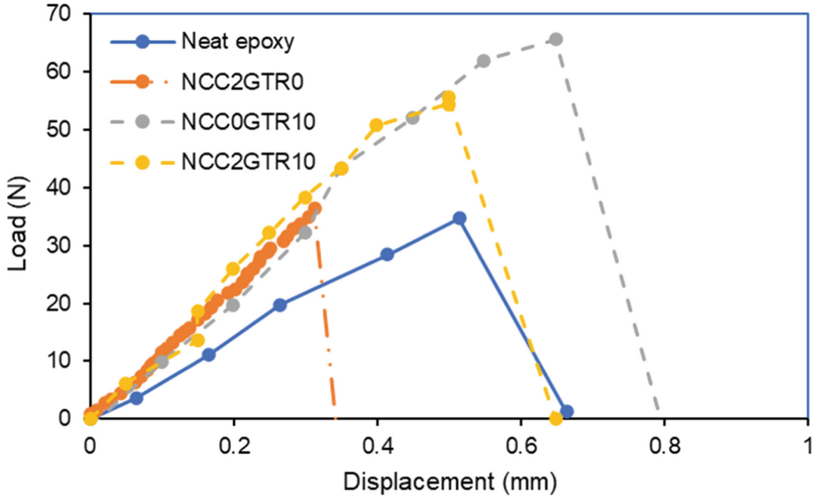

Fig. 3. Typical load vs displacement of composites in dry condition.

increase of water absorption with addition of hydrophobic nanoparticles such as nano $CaCO_3$ and carbon black. It can be seen that the decrease of water absorption after a certain time was observed for GTR content of 10 and 15% without NCC. This was due to leaching of the loosed bonded GTR. Adding NCC reduced the leaching but increased water absorption significantly.

3.2 Fracture Toughness

Figure 3 shows the load-displacement curves of the SENB test for neat and NCC-GTR filled epoxies both in dry and wet conditions. Test was carried out when the SENB specimens reached the saturation level, after 34 days of immersion. It appears that all the load-displacement curves show a linear elastic behaviour up to the peak load, as expected. According to ASTM D5045, fracture toughness was determined using the maximum load.

As seen in Fig. 4, in dry condition, with and without NCC, fracture toughness of epoxy increased with the increase of GTR, but the maximum increase occurred at the GTR content of 10%. Without GTR, adding 2wt% NCC did not affect the fracture toughness of epoxy, but after adding GTR, the fracture toughness decreased compared to that without NCC at same GTR content, about 10.7, 4.6 and 5.8%, respectively for GTR content of 5, 10 and 15wt%. However, if being compared to neat epoxy, the increased fracture toughness was 64, 89 and 82% for GTR content of 5, 10 and 15%, respectively.

In a wet condition, the fracture toughness of neat epoxy increased about 38% compared to that at dry condition. Adding 2wt% NCC into epoxy further increasing the fracture toughness to 52%. Without NCC, the fracture toughness increased about 13–14% at the GTR content in range of 5–10% and then decreased to only 4% at the GTR content of 15%, compared to neat epoxy. The Moreover, the fracture toughness's were lower than those in the dry condition. But adding 2 wt%, the fracture toughness did not

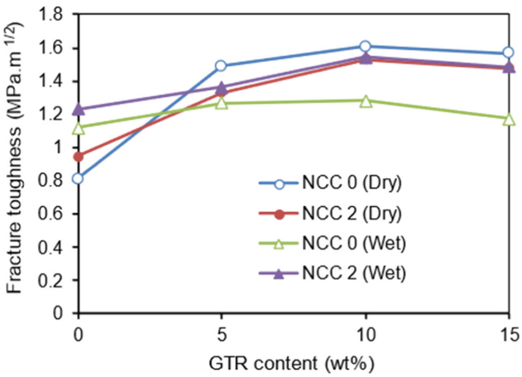

Fig. 4. Fracture toughness of filled epoxy systems.

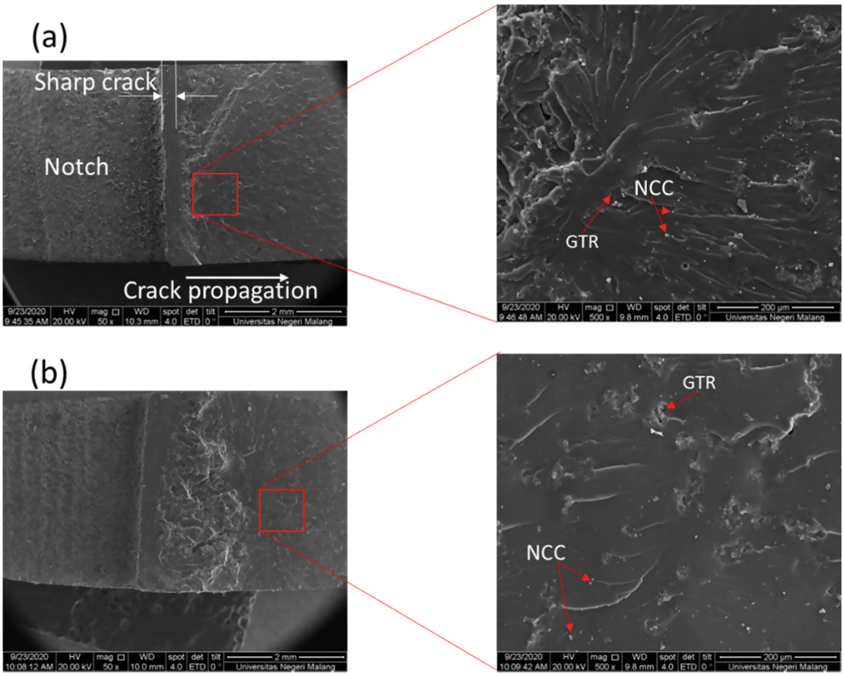

Fig. 5. The Scanning electron microscope micrographs of fracture surface of SENB at (a) dry and (b) wet conditions for epoxy filled with 2 wt% NCC and 10 wt% GTR.

decrease event slightly increased compared to those at the dry condition, under the same GTR content. Here NCC maintained the fracture toughness oh hybrid NCC-GTR/epoxy even the epoxy had been saturated with water. There is a constructive synergistic effect between NCC and GTR operated in wet environment of the fracture toughness. Some researchers [19] reported that in the saturation condition, the fracture toughness was lower than those in the dry condition.

3.3 Fractography

After the scanning electron microscopy (SEM) of selected samples, the results of the SEM test with 2% $CaCO_3$ and 10% rubber particle (wt %) both in dry and wet conditions are shown in Figs. 5. In dry condition, as seen in Fig. 5a, the fracture surface was rough and if the selected region was magnified, it is seen that the GTR acted as crack deflector, while NCC were functioned as obstacles resulting in crack branching. Both contributed to the increase of fracture toughness. However, GTR is more effective in improving the fracture toughness than NCC. Adding NCC increased the stiffness of hybrid composites so adding 2 wt% NCC slightly decreased the fracture toughness compared to those without NCC at the same GTR content.

In wet condition, the fracture surfaces at the slow propagation region seems rougher than that in the dry condition (see Fig. 5b); however, at the faster propagation (indicated and magnified) the fracture surface appears to be smoother than that in the dry condition. This due to the lower tensile strength in wet condition than in the dry condition. In wet condition, the fracture toughness was lower than that in the dry condition as it was observed GTR and NCC were debonded from the matrix and then reduced the effectivity of particles to deflect and branch the crack propagation.

4 Conclusions

The water absorption and fracture toughness of neat and nano calcium carbonate (NCC) and ground rubber particles (GTR)-filled epoxies were investigated. It was found that water absorption increased after adding either NCC or GTR. Hybrid of NCC and GTR further increased water absorption from 2.82 for neat epoxy to 4.25% for hybrid of 2wt% NCC and 5 wt% GTR. In general, adding 10wt%GTR improved fracture toughness of epoxy by about 90% compared to that of neat epoxy. NCC also slightly improved epoxy fracture toughness but hybrid with GTR slightly decreased than fracture toughness compared with those without NCC. However, NCC maintained the fracture toughness of aged epoxy. The increase of fracture toughness was attributed by crack deflection and crack branching induced by GTR and NCC.

Acknowledgement. This work was supported by DRPM, Ministry of Education, Culture, Research, and Technology, Republic of Indonesia under grant number 3938/UN18/PP/2021.

References

1. Kong, J., Ning, R., Tang, Y.: Study on modification of epoxy resins with acrylate liquid rubber containing pendant epoxy groups (2006). https://doi.org/10.1007/s10853-005-1862-6.
2. De'Nève, B., Shanahan, M.E.R.: Water absorption by an epoxy resin and its effect on the mechanical properties and infra-red spectra. Polymer (Guildf). 34, 5099–5105 (1993). https://doi.org/10.1016/0032-3861(93)90254-8.
3. Zhou, J., Lucas, J.P.: Hygrothermal effects of epoxy resin. Part I: the nature of water in epoxy. Polymer (Guildf). 40, 5505–5512 (1999). https://doi.org/10.1016/S0032-3861(98)00790-3.

4. Xiao, G.Z., Shanahan, M.E.R.: Swelling of DGEBA/DDA epoxy resin during hygrothermal ageing. Polymer (Guildf). 39, 3253–3260 (1998). https://doi.org/10.1016/S0032-3861(97)10060-X.
5. VanLandingham, M.R., Eduljee, R.F., Gillespie Jr., J.W.: Moisture Diffusion in Epoxy Systems. J Appl Polym Sci. 71, 787–798 (1999). https://doi.org/10.1002/(SICI)1097-4628(19990131)71:5<787::AID-APP12>3.0.CO;2-A.
6. Li, Y., Miranda, J., Sue, H.J.: Hygrothermal diffusion behavior in bismaleimide resin. Polymer (Guildf). 42, 7791–7799 (2001). https://doi.org/10.1016/S0032-3861(01)00241-5.
7. Xiao, G.Z., Shanahan, M.E.R.: Water absorption and desorption in an epoxy resin with degradation. J Polym Sci B Polym Phys. 35, 2659–2670 (1997). https://doi.org/10.1002/(SICI)1099-0488(19971130)35:16<2659::AID-POLB9>3.0.CO;2-K.
8. Shanahan, M.E.R., Auriac, Y.: Water absorption and leaching effects in cellulose diacetate. Polymer (Guildf). 39, 1155–1164 (1998). https://doi.org/10.1016/S0032-3861(97)00277-2.
9. Bartczak, Z., Argon, A.S., Cohen, R.E., Weinberg, M.: Toughness mechanism in semicrystalline polymer blends: II. High-density polyethylene toughened with calcium carbonate filler particles. Polymer (Guildf). 40, 2347–2365 (1999). https://doi.org/10.1016/S0032-3861(98)00444-3.
10. Alavitabari, S., Mohamadi, M., Javadi, A., Garmabi, H.: The effect of secondary nanofiller on mechanical properties and formulation optimization of HDPE/nanoclay/nanoCaCO<inf>3</inf> hybrid nanocomposites using response surface methodology. Journal of Vinyl and Additive Technology. 27, 54–67 (2021). https://doi.org/10.1002/vnl.21783.
11. Carolan, D., Ivankovic, A., Kinloch, A.J., Sprenger, S., Taylor, A.C.: Toughening of epoxy-based hybrid nanocomposites. Polymer (Guildf). 97, 179–190 (2016). https://doi.org/10.1016/j.polymer.2016.05.007.
12. Donate-Robles, J., Martín-Martínez, J.M.: Addition of precipitated calcium carbonate filler to thermoplastic polyurethane adhesives. Int J Adhes Adhes. 31, 795–804 (2011). https://doi.org/10.1016/j.ijadhadh.2011.07.008.
13. Kumar, V., Dev, A., Gupta, A.P.: Studies of poly (lactic acid) based calcium carbonate nanocomposites. Compos B Eng. 56, 184–188 (2014). https://doi.org/10.1016/j.compositesb.2013.08.021.
14. Sugiman, S., Salman, S.: Hygrothermal effects on tensile and fracture properties of epoxy filled with inorganic fillers having different reactivity to water. J Adhes Sci Technol. 33, 691–714 (2019). https://doi.org/10.1080/01694243.2018.1558492.
15. Eskizeybek, V., Ulus, H., Kaybal, H.B., Şahin, Ö.S., Avcı, A.: Static and dynamic mechanical responses of CaCO<inf>3</inf> nanoparticle modified epoxy/carbon fiber nanocomposites. Compos B Eng. 140, 223–231 (2018). https://doi.org/10.1016/j.compositesb.2017.12.013.
16. Atta, A.M., Al-Lohedan, H.A., Ezzat, A.O., Al-Hussain, S.A.: Characterization of superhydrophobic epoxy coatings embedded by modified calcium carbonate nanoparticles. Prog Org Coat. 101, 577–586 (2016). https://doi.org/10.1016/j.porgcoat.2016.10.008.
17. Sugiman, S., Salman, S., Anshari, B.: Hydrothermal ageing of hydrophobic nano-calcium carbonate/epoxy nanocomposites. Polym Degrad Stab. 191, (2021). https://doi.org/10.1016/j.polymdegradstab.2021.109671.

18. Starkova, O., Chandrasekaran, S., Prado, L.A.S.A., Tölle, F., Mülhaupt, R., Schulte, K.: Hydrothermally resistant thermally reduced graphene oxide and multi-wall carbon nanotube-based epoxy nanocomposites. Polym Degrad Stab. 98, 519–526 (2013). https://doi.org/10.1016/j.polymdegradstab.2012.12.005.
19. Sugiman, S., Putra, I.K.P., Setyawan, P.D.: Effects of the media and ageing condition on the tensile properties and fracture toughness of epoxy resin. Polym Degrad Stab. 134, 311–321 (2016). https://doi.org/10.1016/j.polymdegradstab.2016.11.006.