Physicochemical properties of modified epoxy used for reinforcing concrete by carbon fiber reinforced polymer

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Abstract. This work is an experimental investigation about the properties of sand-powder adhesive subjected to high temperature. Thus, three main mixtures were tested. These mixes contain three different sand to adhesive ratios; 0:1, 1:1 and 1.5:1. The Simultaneous Thermal Analyzers (STA); represent real-time measurement, change of sample weight analysis and heat flow were investigated. The results indicated that the physicochemical properties (residual mechanical properties, residual weight, weight losing rate, glass transition temperature (Tg), Carbonate point or extrapolated onset temperature (To), and heat flow) have been remarkably enhanced by the addition of sand-powder. The addition of sand resulted in increased epoxy resistance to high heat. When the sand-powder exposed to 550 °C, the weight loss of the epoxy was 52%, 30% and 25% for sand to adhesive ratios equal to 0, 1, and 1.5 % respectively. In other words, the epoxy containing a high proportion of sand retained 25% of its weight under the influence of a high temperature degree. Adding sand increases the temperature and time necessary to reach the first and second carbonation point. Adding sand to adhesive increase the temperature needed to reach the glazing point Tg and the point of reversal in the curve derived from loss of weight.

Keywords: Adhesive, CFRP, Sand, STA.

1. Introduction
Epoxy adhesives have been used to paste fibers on various substrates such as concrete or steel, as it is available in different types due to the manufacturers. Usually, epoxy comprises two parts namely resin and hardener. The strengthening for concrete structures using epoxy bonded with carbon fibers reinforcing polymers (CFRP) was verified for being an effective strengthening technique. Thus, with epoxy adhesive some drawbacks such as thermal inconsistently to the concrete base, diffusion closeness, working circumstances and minimum temperature of application as stated by Täljsten B
and Blanksvärd T [1]. Thus, these disadvantages put limits on using the epoxy adhesives or their effectiveness.

Several studies were conducted to address the effect of heat and weather conditions on the adhesive, where the Camata et al. [2] observed that heating influence cycles up to 100 °C on exposure concrete model reinforcing by carbons sheet. The study reported that heating cycles affected all kinds of epoxy.

Klamer et al. [3] investigated the temperature effect on the strengthened concrete beams with CFRP. The test results showed that, the mode of failure where the failure load for the beams which have been tested at 50°C have not significantly been affected compared to the test results at room temperature.

Blanksvärd [4] utilized adhesives resin consists of FRP mortar which comprises mortar, Polymer, sp and fibers rather than epoxies. It was reported that the matrix was more efficient for use with CFRP. This material was also expensive and difficult to be used due to the complexity of mixing and the presents of many components which made it difficult to be utilized as crack sealant in elements of prefabricated concrete [5] [6].

Cabral Fonseca , Nunes , Rodrigues, and Eusebio [7] observed the environmental conditions effects on three different epoxy types used to strengthen or rehabilitation concrete structures. Test specimens were immersed in sea water with alkaline solutions up to eighteen months at temperature ranges between 40 to 60oC. The mechanical properties and the samples loss weight were measured. So, the results showed that epoxy was greatly impacted by seawater or alkaline solutions exposure.

AlSaafy et al. [8] observed the thermal and the mechanical properties for the adhesives with nanoclay-modified to be used in constructions applications. Glass transition temperature (Tg), which was measured by DSC, has been found to decrease with nanoclay addition. XRD and TEM results identified an intercalated/exfoliated structure of the nanoclay, and nanomer (I.30 E) within the epoxy matrix. At elevated temperatures, a decrease in the tensile strength of adhesive was reported with nanoclay addition. But, an enhancement in tensile modulus has been found with all nanoclay addition ratios. The bonding temperature for CFRP/concrete combined systems with the modified adhesive was noticed to be less than that in the control adhesive matrix (0% NC) using pull-off tests at different elevated temperatures. In addition the new proposed material did not show any cost effectiveness as it was very expensive to be used in civil engineering application.

A number of researchers have used environmentally friendly materials (like ground-granulated blast-furnace slag (GGBS), and high-calcium fly ash) and methods in concrete mixtures to reduce pollution, and the cost. These materials can be used with adhesive. (HCFA) [9-12].

Thus, the study aim is to investigate the physicochemical and some mechanical properties of sand-powder adhesive subjected to high temperature using thermal analysis. Three mixes with a weight ratio of fine sand to adhesive of 0:1, 1:1 and 1.5:1 are investigated. The observed mechanical behaviors are explained throughout these adhesive's physicochemical properties. Simultaneous Thermal Analyzers (STA); represent real-time measurement and sample weight change and heat flow analysis, are also investigated.

2. The experimental program
2.1 Materials properties
1-Epoxy adhesive under a commercial name of Sikadur -@330 obtained from Sika Company was used. The different properties of adhesive are listed in table 1.
2- Granular sand passes from 150um sieve and retaining on a 75 um sieve was used as a fine sand. The sand was washed well and oven dried before using it. The specific gravity, absorption, and the sulphates content after washing was 2.57, 2.26, and 0.04 respectively.
Table 1. Sikadur-330 Properties.

| Properties                             | Description                                                                 |
|----------------------------------------|-----------------------------------------------------------------------------|
| Mixing (Resin: Hardened)               | 1:4                                                                         |
| Pot life                               | +15°C is 90 minute.                                                        |
|                                        | +35°C is 35 minute.                                                        |
| Open time                              | +35°C :30 minute.                                                          |
| Temperature application                | +15°C up to +35°C                                                          |
| Tensile strength                       | (Curing for 7 days @ +23°C) = 30 N/mm²                                      |
|                                        | (at 7 days @ +23°C") = 3800 N/mm²                                         |
| Density                                | 1.31 Kg/L, mixture (A+B)"                                                 |

2.2 Mix design
Three epoxy mixtures were investigated experimentally during the course of this study. These mixtures have a varied sand to epoxy weight ratio of 0.0, 1.0, and 1.5 as presented in table 2. These adhesive mixes were proved mechanical properties and workability.

2.3 Mixing procedure and Casting
The used sand has been mixed with any part which either for the part A or the part B is prior mixing them together. So, the adding of fine sand to part A or B results reduces the reaction temperature [13][14]. Specimens were casted in 40 mm cube molds for compressive strength test and (40x40x160mm) prisms for flexural strength test.

2.4 Adhesive Consistency
The adhesive flow was determined due to ASTM C1437 [15] and the details in ASTM C 230 [16] using flow table (figure1). The flow table has been used to compute the cement mortar consistency by determining the consistency of adhesive as new technique to evaluate the consistency of adhesive with additive [13, 14]. The measured flow considers the resulted increase in the adhesive mass average base diameter measured as the original diameter percentage. The authors measured the initial flow (after cone has been truncated and removed and before table dropping).
2.5 Mechanical properties tests
The mechanical properties were investigated for sand modified resin. For each set of specimens with different sand/epoxy ratio, both of the compressive strength and flexural strength were examined at age of 7, and 14 days. A reference specimen without any sand addition was examined and used for comparison.

2.6 Simultaneous Thermal Analysis (STA)
It represents the measurement of real-time and analysis for sample weight change as well as heat flow. STA tests combine differential temperature analysis which are DTA or DSC with proven thermogravimetric (TGA) technology, assure reliable results and simple data interpretation. TGA was used as a technique to characterize materials used in various applications. The Simultaneous Thermal Analysis STA has been carried out by using a PerkinElmer STA-6000 in INFRA Analysis Library/UM University/ Malaysia. Adhesive samples were taken from adhesive samples subjected to high temperature. Every specimen has been submitted to a heating by a rate of 10 °C/min up to 600 °C under argon atmosphere. The heat flow measure allows determining the temperature at phase changes happen. The main features of STA 6000 are the innovative SaTurnA Sensor for high quality, simultaneous DTA/DSC and TG measurements. This advanced sensor, designed with the standard ring directly below the holder of sample pan, is optimized to achieve flat differential thermal analysis baselines and good sensitivity, because both the sample and reference are measured simultaneously; so the analysis can be done with sure integrity. STA test involves continuous weighing of a polymer as it is subjected to a sustain temperature program. This technique can provide quantitative information about the kinetics of the thermal decay of polymer materials from which the thermal stability can be evaluated.

3. STA Thermal Curve
The abscissa (X-axis) have represented time or temperature and the ordinate (Y-axis) represented weight (mg) or weight percent (%) and represented the derivative of the weight loss by time. The descending STA thermal curve shows a weight loss occurred. The following parameters can calculate from STA curve using "Pyris software":

1- Carbonate points or extrapolated onset temperature (To): it gives the temperature for the weight loss beginning. Always, for resin there are two carbonate points. Extrapolated onset Temperature (To) has been specified to use it by ASTM and ISO.
2- The 1st derivative peak temperature (Tp): The peak calculation for the first derivative of the weight loss curve called (Tp).The first derivative peak indicates the point of greatest rate of change on the weight loss curve.

Figure 1. Epoxy flow test using flow table.
3- Glass transition temperature (Tg): it is the gradual and the reversible transition in amorphous materials, from a hard and relatively brittle "glassy" state into a viscous or rubbery state as the temperature is increased resulting in transition from glassy to rubbery deformation. Rubber elastomers such as polyisoprene and polyisobutylenes can be used above Tg, so in the rubbery state they have softness and flexibility characteristics. The convention is to report a single temperature, defined as the temperature range's midpoint, bounded by the tangents to the heat flow curve's two flat regions. Moisture absorption can significantly reduce the glass transition temperature (Tg) of epoxies, a factor that should be considered when designing for humidity. The adhesive mechanical properties dramatically reduce at this point, with the resin modulus, and thus the CFRP composite, decreases. At this point the polymer then starts to lose its ability to transfer stresses from the concrete to the fibers [8].

4- Specific heat Cp: it is energy required to raise the temperature for a material's unit quantity (e.g., 1 g or 1 mole) 1°C. The heat flow curve is generated from the Cp curve by using the following algorithm:

\[ \text{Heat Flow} = C_p \times \beta \times \text{sample weight} \]  

Where, Heat flow per (J/sec), 
\( \beta = \) is the heating rate for the heat flow calculation. The default value for all curves is: (Final Temp – Starting Temp) / time duration of curve 

sample weight is in grams. 
And \( C_p = \) specific heat (J/ g °C)

4. Results and discussion

4.1 Consistency of Adhesive (flow test)

As shown in table 2 the increase in sand ratio decreases initial and final flow rate. The flow ratio of mixing (initial and final) reduces when the fine sand ratio has been increased thus for E3 (sand to adhesive ratio equals to 1.5). Thus, the flow is not acceptable and the compressive strength decreases as will be interpreted in the next sections of mechanical properties. Thus, the sand to adhesive's optimum ratio is 1 (mix E2), where E2 has good thermal, workability as well as, mechanical properties.

| Mix ID | S/E* | Initial flow (%) | Final flow (%) |
|--------|------|-----------------|----------------|
| E1     | 0    | 131             | 125            |
| E2     | 1    | 111             | 173            |
| E3     | 1.5  | 101             | 111            |

S/E* = Ratio of sand to epoxy by weight basis

4-2 Compressive and flexural strength

Table 3 presented the compressive and flexural strength of the sand-adhesive mixtures. Results for compressive strength values clearly indicate that the sand proportion increase does increase the compressive strength. However, the best ratio between sand to the adhesive material equal to 1:1 (Mix E2) where the sand presents 50% from the total adhesive weight. This ratio (mix E2) gives the compressive strength increase that is equaled to 5.38%, and 6.288% for 7, and 14 days respectively, and a cost reduction for the adhesive to about half, where the sand-powder price is neglected
compared with the adhesive price. Related to the flexural modulus results. Table 2 reveals that the best sand/adhesive ratio is also 1:1, namely (Mix E2).

Table 3. Mechanical properties of different Epoxy mixing ratios (MPa).

| Sym | S/E | Compressive Strength | Flexural Strength |
|-----|-----|----------------------|------------------|
|     |     | 7-Days               | 14-Days          |
|     |     |                      |                  |
| E1  | 0   | 93                   | 43.3             |
| E2  | 1   | 98                   | 51.4             |
| E3  | 1.5 | 94.5                 | 43.7             |

4.3 Loss weigh and residual weight

From figure 2 and table 4 show residual weight for sand modified resin. Figure 2 shows the thermogravimetric analysis results (TGA) which performing the mass variations of the three mixes up to 550 °C. By the temperature elevation, the mass loss increased, then the residual weight is clearly reduced towards 550°C. Generally, for the mixes with sand (E2, and E3), the important mass losses is ranged between 300°C to 375°C, where for mix without sand (E1), the important mass losses is ranged between 100°C to 375°C.

However, it clearly that the addition of sand to the epoxy mixes will reduce the loss of weight and this reduce is larger with the higher sand ratio (i.e. Mix E3 with sand ratio equal to 1.5). It can be seen that the loss of weight for mix E1 (with no sand) at 300 °C reached to about 7% of the initial mass, and at temperature 375 °C it reached to 33%, while at temperature 550 °C the losses reached to about 52% from the initial mass. The additions of sand to the epoxy have a large effect to reduce the weight losses with temperature. Where at temperature 300°C, 375°C and 550°C, the weight losses are reached to 2%, 20% and 30% respectively for the mix E2 with sand ratio 1 and reached to 2%, 17% and 25% respectively for the mix to 1.5. These results show clearly significantly enhancing in thermal properties of adhesive causing by adding fine sand. Figure 2 shows also that at 500 °C the residual weights are 48%, 70%, and 75% from original sample weight for E1, E2 and E3 respectively.

Table 4. Physicochemical Properties of sand modified resin.

| Sym. | Residual Weight | To (Carbonate points) | Tp | Tg (Glass transition point) |
|------|-----------------|-----------------------|----|--------------------------|
|      | (T - % residual weight curve) | (T – Derivative weight curve) | (T – Heat flow curve) |
|      | To1 | To2 | t1  | t2  | T   | t   | T   | t   | Heat flow | Cp  |
| E1   | 47.78 | 100 | 297.42 | 8.34 | 27.742 | 340.67 | 32.067 | 348.67 | 30.208 | 31.2765 | 0.31 |
| E2   | 70.15 | 188.17 | 306.38 | 18 | 29.558 | 353.27 | 34.117 | 360.12 | 32.242 | 32.2273 | 0.33 |
| E3   | 75.46 | 188.38 | 294.05 | 18.01 | 28.358 | 348.37 | 33.633 | 351.13 | 31.208 | 31.0506 | 0.32 |

T: Temperature (°C), t: Time (min), Cp: Specific heat (J/g°C), Tp: 1st derivative peak temperature.
4.4 Carbonate point (To)
Figure 2 presents the relations between time and residual weight. The two points where weight loss begins (Carbonate points To1 and To2) can easily be reading. The adding of sand increase the time of To1 from 8.34 to 18 min for E2 and E3 when compare with E1.

The addition of sand to epoxy increases the time needed to reach the first degree of carbonation clearly and by a significant increase of 115%. There was also an increase in the time required to reach the second carbonation point, but by a small percentage which was 6.54% for E2 and 2.22% for E3. The temperature required to reach the first carbonation point is 88% for E2 and 88.38% for E3. It is a very large increase and at the same time it affects the increase of sand ratio to more than 1 as in the E3 mixture but it does not make much difference. As for the second carbonation point, the temperature required to reach this point was 3.01% and 1.1% for E2 and E3, respectively.

A good increase of the second mixture with a slight increase of the third mixture leads us to the same conclusion that the previous increase of the proportion of sand to more than 1% does not make a big difference.

4.5 The 1st derivative peak temperature (Tp)
Figure 2 also shows the relationship between time and loss of weight. In this way, the Tp rate can easily be calculated and represents the inversion point of this curve. It can be easily observed from this form that the sand addition increases the time required to reach the inversion point by 6.4% and 4.88% for the mixture E2 and E3, respectively. Adding sand to the epoxy increases the temperature needed to reach the point of reversal by 3.7% and 2.3% for the E2 and E3 mixtures, respectively.

The addition of sand by 1 as in the mixture E2 represents a good improvement at the point of the coup and increase the proportion of sand to more than 1 leads to a good enhancement in the properties of epoxy.

4.6 Glass transition temperature (Tg)
Ideally, Adhesives with the highest Tg have great thermal resistance and thus have the best tensile properties at high temperatures. It can be noticed from figure 3 and table 4 that the addition of sand to the epoxy will increase the Tg value for the sand/epoxy ratio equal to 1 and 1.5%. The Tg value for the reference mix E1, is about 348.67°C, while for the Mixes E2 and E3, the Tg value is about 360.12°C and 351.13 °C respectively.

The time required to reach the level of glazing is 6.7% when the sand ratio is increased from 0 to 1, but the decrease rate lessens when the sand ratio increases by 1.5% to 3.3%. It can be observed that the heat flow curve is for the non-container reference mixture on the oscillating sand before and after reaching the Tg glazing point, while the sand-containing mixtures are regular before and after the Tg glaze. This is due to the significant improvement in the thermal properties provided by the addition of sand.

4.7 Specific Heat (Cp)
From figure 3 and table 4, specific heat increases for sand-containing mixtures can be observed when compared with non-aerated epoxy on sand. This increase is 6.4% and 3.2% for mixtures E2 and E3, respectively. This increase indicates that the material is able to withstand a higher temperature before changing its temperature due to the addition of sand, which has a better temperature than epoxy. The results also indicate the conclusion of the earlier that the increase of the proportion of sand to more than 1 cause a good increase in heat quality, but less than the proportion of sand which is 1.
Figure 2. Physiochemical curve for sand modified resin.

Figure 3. Heat flow curve and weight derivative curve for sand modified curve.
5. Conclusions
The following conclusions can be drawn as a result of this research:

1. Addition of sand to enhance the mechanical properties of epoxy, whereas, the addition of sand to a clear increase in compression resistance and calibrated fractures.
2. The addition of sand resulted in increased epoxy resistance to high heat. When exposed to 550 °C, the weight loss of the epoxy was 52%, 30% and 25% for the non-sand mixture followed by the mixture containing sand 1% the mixture containing sand by 1.5. In other words, the epoxy containing a high proportion of sand retained 25% of its weight under the influence of a high temperature degree.
3. Adding sand increases the temperature and time necessary to reach the first and second carbonation point.
4. Adding sand to increase the temperature needed to reach the glazing point Tg and the point of reversal in the curve derived from loss of weight.
5. Adding sand to epoxy has increased the specific heat of epoxy.
6. The optimum ratio of adding sand to epoxy is 1, such ratio gives the best results and when the increase of sand for this ratio, the improvement in properties is good but at a lower rate.

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