Thermal conductivity and diffusion coefficient of polymer blend
80% EP/20% UPE reinforced with sand particles

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Abstract
New polymer blend with enhanced properties was prepared from (80%) epoxy resin (Ep), (20%) unsaturated polyester resin (UPE) as a matrix material. The as-obtained polymer blend was further reinforced by adding Sand particles of particle size (53 µm) with various weight fraction (5, 10, 15, 20%). Thermal conductivity and sorption measurements are performed in order to determine diffusion coefficient in different chemical solutions (NaOH, HCl) with concentration (0.3 N) after immersion for specific period of time (30 days). The obtained results demonstrate that the addition of sand powder to (80%EP/20%UPE) blend leads to an increase of thermal conductivity, with an optimum/minimum diffusion coefficient in (HCl)/(NaOH), respectively.

Key words
Polymer blend, sand particles, thermal conductivity, diffusion coefficient.

Introduction
Thermosets polymer such as epoxy (EP) and unsaturated polyester resins (UPE) are the most commonly used in a variety of applications due to their excellent properties, such as thermal stability, mechanical response, low density and electrical resistance [1].

Epoxy is a versatile and widely accepted matrix material for the fabrication of advanced composites, hardware components, electrical circuit board materials and missile equipment,
because of its excellent bonding, physicochemical, thermal, mechanical, dielectric and aging characteristics [2, 3].

The term polyester is analogous to the term steel in metals. Thereby, there is a multitude of polyesters with a significant range of properties. Unsaturated polyesters are sold in a liquid form that requires catalyzation in order to cure [4]. Particulate reinforced polymer composites are of great interest due to the advantage of low cost and ease of fabrication compared with fibrous and laminate composites [5, 6]. The particulate chosen as reinforcement are usually harder and stiffer than the polymer matrix, which improves the mechanical properties of the polymer composite [6]. Among the commonly used reinforcement particulate, silica particles have gained much attention in recent years due to availability, low cost and stiffness [7, 8].

Polymer blends and composites are considered a rapidly growing field in polymer science and have attracted a lot of attention, because new materials can be developed with enhanced and unique properties in relatively less time and with a minimum investment encouraging the blending of polymers [5].

Moreover, the study of transport of liquids through polymers is important for a variety of engineering applications. It has been found that it causes polymers to swell and that the extent of swelling depends on temperature, chemical nature, and degree of crosslinking of the polymer in addition to the molar mass of the polymer and of liquid molecules. Meanwhile, the diffusion of polymer membranes is classified into three types: (i) in Case I, the rate of diffusion can be much smaller than that of polymer relaxation due to physical changes in the polymer-solvent system, known as Fickian or; (ii) In Case II or non-Fickian type of diffusion, the rate of diffusion is much greater than that of polymer relaxation; (iii) in the anomalous type of diffusion, both the diffusion rate and the relaxation rate are nearly the same, as swelling increases, the free volume increases due to increased chain mobility which facilitates transport process [4].

The aim of this research work consists in the improvement of physical properties (thermal conductivity and absorption of chemical solutions) of blend (unsaturated polyester and epoxy) a new by the addition sand as reinforcement particulate at different loading levels. The optimization of the effect of sand loading level is investigation as an economic efficient approach for the development of low cost composite materials with enhanced properties.

**Experimental part**

1. Materials

1.1 Epoxy resin (EP)

The used epoxy resin (Quickmast 105) with a density (1.04 g/cm$^3$) has low viscosity in the form of transparent liquid (which transforms into solid state after adding the hardener to it in a percentage of (3:1), and supplied by Don Construction Products Ltd. UK.

1.2 Unsaturated polyester (UPE)

Unsaturated polyester (UPE) has two components, a base resin and curing agent (hardener). The medium viscosity polyester in the form of transparent liquid, transforms into solid after adding (2%) of hardener methylethylketone peroxide (MEKP) which is supplied by Saudi Industrial Resins (SIR) Company, Saudi Arabia. The properties of epoxy resin and unsaturated polyester (UPE) used in this work are shown in Table 1 as given by companies.
Table 1: Properties of epoxy resin and unsaturated polyester [5, 9].

| Test Methods          | Density (g/cm³) | Thermal conductivity (W/m.°C) | Tensile Strength (MPa) | Percent Elongation (%) |
|-----------------------|----------------|-------------------------------|------------------------|------------------------|
| Epoxy Resin           | 1.04           | 0.18-0.195                    | 25                     | <6                     |
| Unsaturated Polyester | 1.2            | 0.17                          | 41.4-89.7              | <2.6                   |

1.3 Silica sand
The sand is supplied by Don Construction Products Ltd. UK and have a density (2.65 g/cm³). Table 2 illustrates its chemical composition, as given by the company.

Table 2: Chemical analysis of sand.

| Z | Symbol | Element | Concentration (%) |
|---|--------|---------|-------------------|
| 14 | Si     | Silicon | 6.558             |
| 11 | Na     | Sodium  | 0.327             |
| 13 | Al     | Aluminum| 0.5179            |
| 19 | K      | Potassium| 0.6870           |
| 20 | Ca     | Calcium | 0.2649            |
| 22 | Ti     | Titanium| 0.1122            |
| 26 | Fe     | Iron    | 0.1752            |
| 38 | Sr     | Strontium| 0.01689          |
| 56 | Ba     | Barium  | 0.0376            |

1.4 Preparation of silica sand particles
The collected silica sand was first screened to remove unwanted particles and was thereafter ball milled to achieve fine particle size. The as-obtained particles were separated into various particle size with the aid of sieve shaker. Silica particles that passes through the 53 μm mesh was used as reinforcement particulate.

1.5 Preparation of composite materials
Hand lay-up moulding was used adopted for the preparation of composites, and the according to the following procedure: (i) the epoxy resin is firstly mixed with hardener in the ratio (3:1); (ii) then the polyester resin is mixed with hardener in the weight ratio (98: 2); (iii) the as-obtained two mixtures are mixed together (EP 80% + UPE 20%) in order to prepare the polymer blend; (iv) after that, the polymer blend is reinforced with sand (53 μm); (v) and finally four composite materials were prepared: (EP 80%, UPE 20%) for sand-53 μm with different weight fractions (5, 10, 15, 20 %). The composites were poured into the mould according to the required test dimensions, as shown in Table 3.
Table 3: Samples dimensions and standard specifications for the testing specimens [6].

| Test                  | Sample dimensions | Standard Specifications |
|-----------------------|-------------------|-------------------------|
| Thermal Conductivity  | ![Image]          | Lee's Disk              |
| Diffusivity           | ![Image]          | ASTM-D570               |

2. Physical properties

2.1 Thermal conductivity test

Lee's disc instrument is used to calculate thermal conductivity of the samples under test. The instrument consists of three discs of brass and a heater. The heat transfers from the heater to the next two discs then to the third disc across the sample. The temperatures of the discs (TA, TB, TC) can be measured with thermometers. The surfaces of these discs should be clean and in good contact in order to obtain the optimum heat transfer through them.

After the supply power (6 V) was supplied to the heater, the current value through the electrical circuit was about found to be (0.25 A), and the temperatures of the discs were recorded after reaching the thermal equilibrium (nearly after 45 min). The values of thermal conductivity are calculated using the following equation:

\[ IV = \pi r^2 e (T_A + T_B) + 2\pi r e \left[ d_A T_A + d_S \left( \frac{1}{2} \right)(T_A + T_B) + d_B T_B + d_C T_C \right] \quad (1) \]

where \( I \) is the current value through the electrical circuit; \( V \) is the supplied voltage; \( r \) is the radius of disc; \( T_A, T_B \) and \( T_C \) are the temperature of the brass discs A, B and C respectively; \( d_A, d_B \) and \( d_C \) are the thickness of the brass discs A, B and C respectively; \( d_S \) is the thickness of the specimen.

From Eq. (1), the value of \( (e) \) is calculated which represents the quantity of heat that flows through the cross sectional area of the specimen per unit time (W/m\(^2\).\(^\circ\)C). The \( K \)-values can be calculated from the following equation [10]:

\[ K \left( \frac{T_B-T_A}{d_s} \right) = e \left[ T_A + \frac{2}{r} \left( d_A + \frac{1}{4} d_S \right) \right] T_A + \frac{1}{2r} d_S T_B \quad (2) \]

where \( K \) is the thermal conductivity coefficient (W/m.\(^\circ\)C). The samples that are used in diffusivity test as shown in Fig. 1.
2.2 Diffusion coefficient measurement

In order to calculate the diffusion coefficient in the polymeric blend and in hybrid composite material, two types of sensitive balances are utilized; two-digit electronic balance used to weigh the polymeric materials and the second four-digits electronic balance type AE 160 manufactured by (Metler/England). It is used to measure the weight of the samples that are used in diffusivity test as shown in Fig. 2.

The percentage weight (wt.%) change of the diffusivity samples after each period of immersion is calculated from the relationship (3).
Weight gain = \frac{W_2 - W_1}{W_1} \quad (3)

where \(W_2\) is the weight of immersed specimen and \(W_1\) the weight of dry specimen.

The diffusion coefficient (D) is calculated from second Fick’s law [6]:

\[ D = \pi \left( \frac{K b}{4 M_m} \right)^2 \quad (4) \]

where \(K\) is the slope of curves straight line representing the relationship between the weight gain (%) and square root of time (time)\(^{0.5}\); \(b\) is the thickness of the specimen; and \(M_m\) is the apparent maximum water content (the saturation level).

Samples Immersion in Chemical Solutions: Two types of chemical solution have been used in this work: Acid: HCl and Base: NaOH.

To use immersion solution is hydrochloric acid (HCl) was diluted with normality (0.3 N) according to the following equation:

\[ N_1 V_1 = N_2 V_2 \quad (5) \]

where to \(N_1\): normality of Concentrated acid; \(V_1\): size of acid Center; \(N_2\): normality of acid diluted; \(V_2\): size of acid diluted.

After getting the volume \(V_1\) from the Eq. (5), this amount is placed in a bottle of distilled water and pour the above orders and requests to obtain a homogeneous solution and normality (0.3N) and then placed in containers intended for immersion. Then immerse the hardness samples, thermal conductivity samples and samples for digital image processing in chemical solution (HCl) of (0.3N) and for a period of time (30 days) for tests the percentage of the change in mass for the samples placed in the solutions was calculated by applying the following Eq. (3). The curves of the absorption percentage with the square root of time were plotted for all prepared samples. Diffusion coefficient (D) was calculated by applying the following Eq. (4).

3. Results and discussion

The variation of thermal conductivity for EP/UPRE reinforced with sand-53µm is illustrated in Table 4 and Fig. 3. It is clearly noticed that the thermal conductivity increases with increasing weight fraction of sand particles in a nonlinear relationship. The presence of sand-53µm with the matrix of polymer blend improves its thermal conductivity, due to the greater thermal conductivity of sand-53µm compared to that of EP/UPRE: the recorded thermal conductivity for pure blend sample is 0.471 W/m.\(^{o}\)C whereas that for sand particle increases from 0.503 W/m.\(^{o}\)C at 0.05 wt% to 0.615 W/m.\(^{o}\)C at 0.20 wt%. It can be noticed that the thermal conductivity values for sand-53µm reinforced are higher than that of unreinforced blend the explanation of the above is as follows: apart from the volume effects of the components, a significant effect is played by the dispersed phase and the adhesion between the components. An increase in the adhesion between the components in the polymer blend or filled polymer produces a decrease in the heat resistance at the component boundaries and an increase in the coefficient of heat transfer of the material [11], as shown in Fig. 3.
Table 4: Values of thermal conductivity coefficient of EP/UPE reinforced with sand-particles with different weight fractions (5, 10, 15, 20 %).

| Type of Material                  | Thermal conductivity coefficient K (W/m.°C) |
|-----------------------------------|--------------------------------------------|
| Blend 80%EP/20%UPE               | 0.471                                      |
| 95%Blend+5% Sand                 | 0.503                                      |
| 90%Blend+10% Sand                | 0.589                                      |
| 85%Blend+15% Sand                | 0.593                                      |
| 80%Blend+20% Sand                | 0.615                                      |

Fig. 3: Thermal conductivity at different weight fraction of the blend reinforced with sand particles.

The diffusivity coefficients of HCl and NaOH in the blends (and their corresponding composites) are calculated, according to the second Fick's law. The results are reported in Table 5 and Figs. 4 and 5. It can be seen that the diffusivity coefficients of HCl and NaOH in the materials (under test) has increased compared with that of pure matrices: $2.047 \times 10^{-12}$ m$^2$/sec for HCl and $2.266 \times 10^{-12}$ m$^2$/sec for NaOH. This is enhancement due to the interface defects or in-homogeneity that exists in the blends and composites. The composite material formed from reinforced blend EP/UPE with sand-53 µm has the highest value of diffusivity in the acidic solution (0.3N) HCl; i.e. $4.01 \times 10^{-12}$ m$^2$/sec, while the lowest diffusivity value for the same acidic solution has been found for the composite material formed from the reinforced blend with sand-53µm; i.e. $3.39 \times 10^{-12}$ m$^2$/sec. Meanwhile, the highest value of diffusivity for the alkaline solution (0.3N) NaOH is found in the reinforced blend with sand-53µm; i.e. $4.40 \times 10^{-12}$ m$^2$/sec while the lowest value was for the pure blend; i.e. $3.82 \times 10^{-12}$ m$^2$/sec. It can be noticed also that the diffusivities of (0.3N) HCl in 80% Epoxy/20% Polyester blends and composites are lower than their identical in NaOH (0.3N), because epoxy in blend has high resistance to acids, in agreement with the results report by Caddock et al. [12].
Table 5: Values of diffusion coefficient of EP/UPE reinforced with sand particles with different weight fractions (5, 10, 15, 20%).

| Type of Material | Diffusion Coefficient D ($10^{-12}$ m$^2$/sec) |
|------------------|-----------------------------------------------|
|                  |浸没在NaOH | 浸没在HCl |
| Blend 80%EP/20%UPE | 2.266     | 2.047 |
| 95%Blend+5% Sand53μm | 3.82      | 3.39  |
| 90%Blend+10% Sand53μm | 3.87      | 3.41  |
| 85%Blend+15% Sand53μm | 3.94      | 3.41  |
| 80%Blend+20% Sand53μm | 4.40      | 4.01  |

**Fig. 4:** The relationship between the percentages of absorption of 80%EP/20%UPE reinforced with sand particles with square root of time after immersion in HCl.

**Fig. 5:** The relationship between the percentages of absorption of 80%EP/20%UPE reinforced with sand particles with square root of time after immersion in NaOH.

**Conclusions**

80%Epoxy/20% polyester blends reinforced with sand particles demonstrate superior properties with enhanced conductivity; the highest value of thermal conductivity is for the reinforced blend with sand. Meanwhile, diffusion measurements...
into HCl and NaOH solutions that limited effect is observed on EP/UPE blends and their composites reinforced with sand-53µm. The as-developed new composite materials can be used in humid, alkaline and acid environments.

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