Effect of sulfuric acid solution on thermal conductivity and impact strength of epoxy resin reinforced by silicon dioxide powder

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Abstract
In this search, Ep/SiO$_2$ at (3, 6, 9, 12 %) composites is prepared by hand Lay-up method, to measure the change in the thermal conductivity and Impact Strength of epoxy resin before and after immersion in H$_2$SO$_4$ Solution with a 0.3N for 10 days. The results before immersion decreases with the increase of the weight ratios of the reinforcement material (SiO$_2$), It changed from (82.6×10$^{-2}$ to 38.7×10$^{-2}$ W/m.°C) with change weight ratios from (3 to 12) % respectively, but after immersion time in the chemical solution where it was (65.6×10$^{-2}$ W/m.°C) at the weight ratios (6 %) and became (46.6 × 10$^{-2}$ W/m.°C) after immersion in sulfuric acid. The results of the Impact strength decreased by increasing the percentage weight ratio, it changed from (1.48 to 0.87 kJ/m$^2$) with change weight ratios from (3 to 12) % respectively, but found an increase in the value of Impact Strength after immersion in the chemical solution Where it was (1.28 kJ/m$^2$) at the weight ratio of 6 % and became (1.82 kJ/m$^2$) at the same weight ratio after immersion in sulfuric acid at normality of 0.3 for 10 days.

Key words
H$_2$SO$_4$, epoxy resin, SiO$_2$, thermal conductivity, impact strength.
Introduction

There was an insistent need to find alternatives to the materials so that these alternatives are of a high quality in terms of weight, cost and properties in general to be adopted in the various manufacturing applications that called composite materials, which is known as the material resulting from the mixing of two or more material by a physical coherence without chemically interaction to obtain new materials that differ in their properties from the properties of their constituents [1]. Researchers are interested in studying polymer compositions reinforced by SiO$_2$ Particle in Special, characterized by poor thermal and electrical conductivity and resistance to oxidation and carry around to high temperatures [2].

In 2015, Maryam Zuhair studied the mechanical and thermal properties of epoxy resins reinforced by magnesium oxide and nano-silica oxide In different weight ratios, where the results showed that the thermal conductivity of all cases (the base material with the nano-magnesium oxide once and twice the silica oxide once and the mixture again) is higher than the value of the thermal conductivity of the base material as well as the value of the wear coefficient was higher for all cases than the values of wear coefficient of epoxy resin without reinforcement and the value of the elasticity coefficient is higher at the hybrid composite at the rate (0.2 %) [3].

In 2016, Hind W. Abd Allah studied the effect of granular particle size on the thermal conductivity. Magnesium oxide and silica particles were used in different granular sizes (125, 75, 37 (μm)) at 5 % volume fracture. Both types was prepared at the ratios 2.5 %. The results showed an increase in the thermal conductivity values with a decrease in the granular volume of the additives. The thermal conductivity showed an improvement of the mixtures compared with the base material of silica values and gave high values compared to the composite substance of magnesium and silica [4]. The aims of this research are to:
- Prepare composite material of epoxy resins supported by micro particle of SiO$_2$ at different weight ratios (3, 6, 9 and 12) wt%.
- Studying the thermal conductivity and Impact strength property of composite materials which are tested before and after immersion in sulfuric acid.

Thermal conductivity

Thermal conductivity is a very important physical characteristic, which represents the amount of heat transferred through the unit of area [5]. Which occur when the transfer of thermal energy from the areas of high temperature to areas with low temperatures, that is, when there is a difference in temperature called thermal gradient [6]. There are different mechanism of thermal conduction depending on the type of material and the nature of the movement particles. The thermal conductivity is different depending on the type of material and the nature of the movement of the molecules Solid conductive materials, in which free electrons are responsible for the transmission of heat energy as well as phonons, In heat-insulating polymers where there are no free electrons, the heat is transmitted by flexible waves, due to the oscillation of the particles, as a result of the proximity of the molecules and their association with the bonds, this oscillation will move to the neighboring molecules so The heat is then transferred and these flexible waves are called phonons [7].

Fig.1 shows the method of measurement of thermal conductivity
thermal conductivity can be calculated from the following relationship [8]:

\[
K \left( \frac{T_B - T_A}{d_S} \right) = e \left[ T_A + \frac{1}{4} d_S \int T_A + \frac{1}{2e} d_S T_B \right] \tag{1}
\]

whereas:

K: thermal conductivity (W / m.K).

(e): reflect the thermal energy passing through the unit area of the disk per second and its units (W / (m$^2$.K)) and can be calculated from the following relationship [9]:

\[
H = 4IV = 4\pi r^2 e (T_A + T_B) + 2\pi r e \left[ d_A T_A + d_S \frac{1}{2} (T_A + T_B) + d_B T_B + d_C T_C \right] \tag{2}
\]

\[H; \text{ The time-rate of energy applied to the heating coil.}
\]

(TC, TB, TA): represents the temperature of the disks (C, B, A) respectively.

(dA, dB, dC): represents the thickness of copper disks (mm).

dS: sample thickness (mm).

I: The current passing through the circuit (Ampere).

V: The voltages fitted to the circuit (Volt).

**Fig.1: Scheme thermal conductivity meter.**

**Impact strength**

Impact strength is a measure of the strength of polymer material and its resistance to refraction under the influence of stress and high speed and durability. The strength of the Impact strength depends on many variables, including type of material, stress resistance, manufacturing conditions, the environment, the geometric shape of the sample. Therefore impact strength can be defined as the amount of energy absorbed during the collision to the cross section of the sample. It is measured by kJ/m$^2$ and is calculated from the following relationship [10, 11].

\[
\text{Impact Strength (I.S)} = \frac{U_c}{A} \tag{3}
\]

As: - I.S: shock resistance (kJ / m$^2$)

Uc: Energy to break the sample (kJ).

A: Area of the cross section of the sample (m$^2$).
Experimental work
First: Materials used in research:
The following materials were used in this research:
1- Epoxy Resin: Which is in a liquid form type of (Epoxy Sikadur® 52 LP), which is manufactured by the US company Sky Spring, which solidifies after the addition of the hardener of the type (Bisphenol A (epichlorohydrin) Oxiraine) and manufactured by US company Sky Spring and the ratio of crucified to resin (2: 1).
2- Silicon dioxide (SiO₂): Silicon dioxide supplied from the US company (Sky Spring) was used in grain size (100 μm), density (2.6 g/cm³) and purity (99%).

Second: Preparation of thermal conductivity test models:
The amount of epoxy resins was mixed with the hardener material using a hand-Layup method. SiO₂ powder was then added to the mixture at different percentage (3, 6, 9 and 12) %.
Mix the mixture well and pour into the prepared mold with a thickness of (3 mm) and then leave in the mold to hard well for 48 h then the sample is extracted and placed in the oven at 50 °C for 2 hours as shown in Fig. 3 to complete the hardening process.
The samples are then cut according to the international standard of the thermal conductivity and Impact strength measuring device using a manual saw with very small teeth and sharp to ensure that the samples do not vibrate during the cutting process. Then the process of smoothing and polishing the edges of the samples using silicon carbide papers with different degrees of smoothness and the samples are then diluted with sulfuric acid diluted at 0.3 N for 10 days. Table 1 listed the standard dimensions of the thermal conductivity and Impact test. Fig.4 shows the photographic image of the thermal and Impact samples.
Table 1: Standard dimensions of thermal conductivity and Impact strength test.

| Standard System | Standard dimensions of samples | Test Type              |
|-----------------|-------------------------------|------------------------|
| Lee’s Disk      | ![Lee’s Disk Diagram](image)  | Thermal conductivity Test Sample |
| ISO -179        | ![ISO -179 Diagram](image)    | Impact Test Sample     |
Results and discussion

1. Thermal conductivity before and after immersion in H\textsubscript{2}SO\textsubscript{4}:

From Table 2 and Fig. 5 shows the vibration of the thermal conductivity values with the added weight ratios of SiO\textsubscript{2} before and after immersion of the samples with H\textsubscript{2}SO\textsubscript{4} solution at 0.3N for 10 days. We note that the thermal conductivity begins to decrease with increasing the weight ratios of SiO\textsubscript{2} powder and the reason for this is because the base material and the reinforcing material are considered heat insulation materials [12]. Vibrations in the internal structure of the resin are low. And a further reduction in the increase of the strengthening material, which will work to prevent vibrations. Thus causing a decrease in the value of thermal conductivity [13, 14]. We note in Fig. 5 The thermal conductivity starts to decrease with increasing immersion time this is because the process of immersion in chemical acid may cause, break down the chemical bonds and slip because this acid solution attacks the polymer strongly due to positive ions (H \textsuperscript{+}) works to form a bond With the ends of the polymer chains and negative ions (SO\textsubscript{4}\textsuperscript{-}) attack and weakness the interstitial area and therefore this acid has caused a disruption of the transfer of the phonons, which are responsible for the transfer of heat [15, 16].
Table 2: Scientific results of the thermal conductivity of SiO$_2$ samples before and after immersion with H$_2$SO$_4$ at 0.3N and for 10 days.

| Group                | Weight Fraction (%g) | Thermal Conductivity (W/m. °C) $\times 10^{-2}$ Before | After immersion with H$_2$SO$_4$ for 10 day |
|----------------------|-----------------------|--------------------------------------------------------|---------------------------------------------|
| EP + SiO$_2$         |                       |                                                        |                                             |
| 3                    | 82.6                  | 54.0                                                   |                                             |
| 6                    | 65.6                  | 46.6                                                   |                                             |
| 9                    | 50.9                  | 36.5                                                   |                                             |
| 12                   | 38.7                  | 25.1                                                   |                                             |

Fig.5: Thermal conductivity values with the weight fraction of SiO$_2$ compositions before and after immersion with H$_2$SO$_4$ at 0.3 N and for 10 days.

2. Impact strength before and after immersion in H$_2$SO$_4$:

Table 3 shows the practical results of the Impact strength values for samples reinforced by silicon dioxide before and after immersion in sulfuric acid. Fig. 6 shows that the Impact strength decreases by increasing the percentage weight of the reinforcement materials for all samples. For example, it was (1.48 kJ/m$^2$) at the percentage of 3 % and became (0.87 kJ/m$^2$) at the percentage of 12 %. This is due to the fact that the silicon dioxide added to the base material is a glass material with low resistance to Impact. The reinforcement particles form points to concentrate the stresses and centers of the dot defects which will increase the probability of spreading the cracks quickly as they are within the main polymer bonds and thus reduce the durability of the composite material and thus reduce the Impact [17, 18]. Showing from Fig.6 we found that the amount of Impact strength it increase after immersion in sulfuric acid, The reason for increasing Impact strength after acid immersion is due to reduce the elasticity of the composites because of increasing the crosslinking by interaction of acid with polymer back bounds this prevent cracks propagation and increase of the value of Impact strength.
Table 3: Shows the results of the Impact strength values of SiO₂ samples before and after immersion in sulfuric acid at normality of 0.3N for 10 days.

| Group                  | Sample Weight Fraction (%g) | Impact Strength (kJ/m²) before | Impact Strength (kJ/m²) after immersion with H₂SO₄ for 10 day |
|------------------------|-----------------------------|--------------------------------|-------------------------------------------------------------|
| EP + Particles SiO₂    |                             |                                |                                                             |
| 3                      |                             | 1.480                          | 2.235                                                       |
| 6                      |                             | 1.283                          | 1.830                                                       |
| 9                      |                             | 1.054                          | 1.450                                                       |
| 12                     |                             | 0.870                          | 1.210                                                       |

Fig.6: Shows the comparison of the Impact strength values of SiO₂ samples before and after immersion with H₂SO₄ at 0.3 N for 10 days.

Conclusion
1. The thermal conductivity of the epoxy resins decreases with the increase of the SiO₂ reinforcement material. The low thermal conductivity of the composite material prepared after immersion of the samples in the H₂SO₄ solution is higher than in normal conditions.
2. The impact strength is reduced by increasing the weight ratios of all samples in normal conditions. After the submerged sulfuric acid is immersed at a 0.3 N, the Impact strength value is higher than higher than in normal conditions and for all samples.

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