Study of Mechanical Properties and Thermal Conductivity of Polymeric Blend [Epoxy and polysulfide rubber (EP + PSR)] Reinforced by Nano Ceramic Powder ZrO₂

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Abstract: A polymeric blend nanocomposites were prepared using mixer of Epoxy and polysulfide rubber [EP+PSR] as a matrix material and the Zirconium Oxide Nano-powder ZrO₂ as a reinforcement material, in different particle sizes and same adding ratio of 2% wt. Hand Lay-up molding method was used to prepare the samples. Impact strength, compression resistance and thermal conductivity tests, were carried out for the polymeric blend and composites samples before and after immersion in tap water. The results showed that adding Nano zirconia powder to the polymer blend improved the mechanical properties, while the thermal conductivity of the polymer blend was higher than that of the composites. Also, it was observed that water immersion caused a decrease in impact strength, compression resistance, modulus of elasticity and thermal conductivity in a manner proportional to the immersion time.

Keywords: Polymeric blend, Epoxy, Polysulfide, Nano Zirconia, Impact, Compression, Thermal conductivity.

1. Introduction

The polymeric composite materials meet the requirements of scientific and technological development due to their characteristics such as; light weight, high strength, thermal and electrical insulation, in addition to its low economic cost, that make it suitable for civilian, military and medical industrial uses instead of metal or ceramic based composite materials [1]. To obtain polymeric materials with unique specifications that are unavailable in a single polymer, polymeric mixtures have been used with the desired unique specifications. The polymeric blend can be either, Binary or Ternary or Quaternary depending on the number of polymeric components they contain [2]. The composite material consists of the matrix material which represents the continuous phase; reinforcement material (reinforcement phase) which stands most of the applied stress on the matter and leads to improve its mechanical properties; and the third phase is the interface region that is located between the matrix and reinforcement materials. The final properties of the composite material are affected by several factors, some of which relate to the matrix material, and others relate to the reinforcement material, such as the type, shape and size of the particles, and the adhesion between the particles and the matrix material and the adding ratio of the particles [3].
Impact test signifies the ability of material to absorb energy during plastic deformation and resistance to fracture under the influence of stress at a high speed. Some of polymeric materials become ductile under the impact of static tension but they look brittle under the impact of quick tensions. Absorbed energy depends on the components that are used in manufacturing the composite and their ability to resist the external stress, and surrounding circumstances [4].

The compression strength of composite materials is defined as the maximum stress that a solid can withstand under vertical pressure. It is an important design factor when preparing the polymeric mixture for the composite materials, because these materials are subjected to bending stresses and then failure may occur as a result of compression [5].

Study of thermal properties of polymers and their composites is important to know the suitability of these materials for practical applications when used as a thermal insulators or any other thermal applications. One of the most important properties is the thermal conductivity coefficient (K). Polymers and its composites are considered a poor materials for thermal conduction because they do not have free carriers of electrons, so heat transfer depends on vibration/rotation of the chain molecules. The heat is transmitted by elastic waves called phonons [6]. Thermal conductivity follows Fourier’s Low as in Eq.1. Coefficient of thermal conductivity can be determined using Lee’s disc instrument.

\[ Q = -KA \frac{dT}{dx} \ldots \ldots \ldots \ldots (1) \]

\( Q \): quantity of passing heat (w), \( K \): coefficient of thermal conductivity (w/m.°k)

\( A \): section area of heat flow (m²), \( dT/dx \): thermal gradient (°k/m)

2. Experimental Procedures

2.1. Materials and methods:

2.1.1. Used Materials: A polymeric blend of epoxy resin and polysulfide rubber [EP70% + SPR 30%] was used as a matrix material. The epoxy is poly prime –EP made by Henkel polybit Co. (UAE), it is a thermoset polymer, its density \( \approx 1.03 \) g/cm³. The poly sulfide is a rubber polymer with a density of 1.35 g/cm³ poly seal PSGG manufactured by Henkel polybit Co. (UAE). A nano Zirconia ceramics powder ZrO₂ (Chinese made) with particle size [(20 – 40) nm, 99% ZrO₂ content and density 6.10 g/cm³] & [(40 – 50) nm, 99.9% ZrO₂ content and density 6.27 g/cm³], was used as a reinforcement material with the same addition ratio of 2% wt.

2.1.2. Samples preparation. A Hand Lay-up molding method was used to prepare: - 1- Polymeric Blend Samples (EP 70% + PSR 30%) ; 2- Polymeric Blend Composite Samples supported by ZrO₂ with particle size (20 - 40) nm, and , 3- (40 -50) nm. After the completion of the casting process and heat treatment required for the completion of the polymerization process, the samples were cut to forms and dimensions for each test according to standard specifications (ASTM) for impact and compression tests and Lee’s disk for the thermal conductivity test.

2.2. The Tests

2.2.1. Impact test. Charpy test, type shock monitor, was used to determine the impact strength of the material. Specimens were cut according to the standard specifications (ISO-179), impact strength was calculated using eq.2. [7]

\[ I.S = \frac{E_c}{A} \ldots \ldots \ldots \ldots (2) \]

I.S: impact strength (MPa), \( E_c \): energy of fracture (J), \( A \): cross section area (mm²)
2.2.2. Compression test. Compression test was performed to determine the compressive strength of the material using a hydraulic press. The maximum load that the sample can withstand represents the maximum compression strength of the material. Eq.3 was used to determine the compression strength [8]. From the graphical relationship between the applied stress and the resulting strain, a Young modulus of compression was determined.

\[ C.S = \frac{P}{A} \]  

(3)

C.S: Compression resistance (N/mm²), P: Max. applied load (N), A: cross section area (mm²)

2.2.3. Thermal conductivity test. To determine the thermal conductivity coefficient K of the polymeric blend and composite samples, Lee’s disk method was used, which is a suitable method for the materials with poor thermal conductivity. K was calculated using eq.4 [9].

\[ K \left( \frac{T_B - T_A}{d_5} \right) = \varepsilon \left[ T_A + \frac{2}{r} \left( d_A + \frac{1}{4} d_S \right) T_A + \frac{1}{2r} d_S T_B \right] \]  

(4)

\[ e \]: represents the thermal energy passing through unit area in unit time (w/m².ºC), and calculated using eq.5

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

(5)

H: thermal energy generated in the heater (J), I: current passed through the circuit (A) V: applied voltage (V), T_A, T_B, T_C: the temperature of the discs A, B, C, respectively (ºC) d_A, d_B, d_C: thicknesses of copper discs A, B & C respectively (mm) r: disc radius (mm), d_S: sample thickness (mm)

3. Results and Discussion

3.1. Impact Strength

The results showed that before immersion, the polymeric blend [EP + PSR] possessed the highest impact strength compared to the composites, this is due to the fact that the polysulfide is one of the elastomeric polymers that have a high ability to absorb a greater amount of energy, thus giving the polymer blend a high impact strength [10].

The composites possessed impact resistance less than its counterpart polymer blend because the particles of the ceramic powder give the polymer the brittleness characteristic. In addition, the particles themselves can form points for stress concentration, thus reducing the resistance of the composite material to high velocity shock [11]. The use of particles with a small size leads to a decrease in impact resistance, and this is what was observed in sample 2 [as the ZrO₂ particles size (20 – 40 nm)], so the impact resistance was (3.8 KJ/m²), whereas in sample 3 [ when the ZrO₂ particles size (40 – 50 nm) ], the impact resistance was (9.084 KJ ).

After immersing in the water, a decrease of impact strength was noticed for all samples. Diffusion of water and its penetration through the composite material, especially through the polymer and the voids created during the manufacturing process causes swelling and formation of stresses within the material, which leads to the material’s fold and failure. On the other hand, absorption of water causes plasticization of the polymer, as a result of the breakdown of the hydrogen bonds between the polymeric chains. As the
degradation due to moisture, the material loses its ductility and becomes brittle and thus its resistance to shock decreases [12].

Also, penetration of water molecules inside the composite material leads to a weakening of the bonds between the two phases of the mixture, or the interface region [13]. It was also noted that the decrease in impact strength was greatest in the large Zirconia particles reinforced composites. The large particles form large voids in the composite material, which facilitates the penetration of water and its negative effect on the polymer cohesion, thus reducing the impact strength.

Table 1. variation of impact strength vs immersion time in H\textsubscript{2}O.

| Sample No. | N. C | Immersion Time (week) |
|------------|------|-----------------------|
|            |      | 0 | 2 | 4 | 6 | 8 | 10 |
| 1          | 25.7 | 5.169 | 7.88 | 5.847 | 6.35 | 7.966 |
| 2          | 3.8 | 3.18 | 2.54 | 3.552 | 2.19 | 2.05 |
| 3          | 9.084 | 3.805 | 3.654 | 3.381 | 4.508 | 3.093 |

Figure 1. variation of impact strength vs immersion time in H\textsubscript{2}O.

3.2. Compression strength

Before immersion, it is noted that the polymer blends reinforced with nano zirconia had a higher compressive strength and elastic modulus than the non-reinforced polymer blend, this is due to the diffusion of hardened zirconia particles in the matrix material is isotropic in all directions, and the small size of the particles facilitates its diffusion process, so the inter-spacing becomes small and this impedes the generation of cracks and increases the strength of the interface connection between the zirconia particles and the polymer. [14]
After water immersion, the compression strength and elastic modulus of all samples decreased to varying degrees. Penetration of water in the composite material through defects, especially the voids, increases the amount of water absorbed, which leads to the occurrence of swelling [15]. On the other hand, the ceramic particles are characterized by their presence of pores and this facilitates the penetration and diffusion of liquids inside the composite material, and the longer the immersion period increases the diffusion process increases and works to break bonds and weakening of the bonding strength between molecular chains, accompanied by high rates of strain. [16]

Table 2. Compression strength before and after immersion in H$_2$O

| Surrounding Circumstances | Compression resistance (MPa) |
|---------------------------|-----------------------------|
|                          | Sample 1 | sample 2 | Sample 3 |
| before immersion         | 33.102   | 34       | 37.29    |
| 10 weeks immersion       | 32.447   | 25.086   | 30.329   |

Figure 2. variation of compression strength vs immersion in H$_2$O.

On the other hand, it is noticed that the highest elastic modulus before immersion was of sample 2 (83.334 MPa), the small size of the particles facilitates the process of their penetration into the interstitial space to a greater extent, which leads to an increase in the cohesion and strength of the composite material, as well as leads to restricting or limitation the elasticity of the added molecular structures, that is formed in the presence of the particles, makes the relaxation process more difficult and then leads to an increase in the elastic modulus.[17]
Table 3. Compression Young modulus before and after immersion in H$_2$O

| Surrounding Circumstances | Young Modulus (MPa) |
|---------------------------|---------------------|
|                           | Sample 3 | Sample2 | Sample1 |
| before immersion          | 61.539   | 83.334  | 71.875  |
| 10 weeks immersion        | 40.425   | 30.5    | 61.9    |

Figure 3. variation of young modulus after immersion in H$_2$O (compression test).

3.3. Thermal conductivity:
It is noted before immersion that the polymeric blend (sample1) possessed thermal conductivity coefficient higher than that of composites (samples 2&3). Mixing two polymers together leads to the formation of a crossed polymeric network, which means an increase in the density of the polymer due to the increased agglutination of the molecular chains, meaning that the molecules of the substance will touch one another, generating a higher thermal conductivity, and mixing the polysulfide rubber with epoxy leads to an increase in thermal conductivity [18]. On the other hand, zirconia powder is a ceramic material that is characterized by containing many air voids that represent insulating media for heat transfer, which led to a decrease in the thermal conductivity(K) of the composite [19].

After immersion in water, it was observed that the K values of all samples generally decreased. The entry of water and its diffusion in the composite material leads to restriction of the movement of phonons responsible for the transfer of heat to these materials, and also works to break the bonds between the polymeric chains, which leads to the failure of the material and its degradation and thus the dispersion of phonons and thus the decrease of k values [20]. It is noted that K values of composites in the last weeks of
immersion have become less than that of polymers and this makes them suitable for use as thermal insulators.

**Table 4.** values of thermal conductivity (K) vs immersion time in H$_2$O.

| Sample No. | Thermal Conductivity (K) (w/m .ºk) | Immersion Time (week) |
|------------|-----------------------------------|------------------------|
|            |                                   | 0          | 2          | 4          | 6          | 8          | 10         |
| 1          |                                   | 0.408839   | 0.323902   | 0.393944   | 0.344391   | 0.313093   | 0.323496   |
| 2          |                                   | 0.356854   | 0.349003   | 0.427408   | 0.35123    | 0.308332   | 0.335516   |
| 3          |                                   | 0.356379   | 0.491933   | 0.492584   | 0.416892   | 0.329382   | 0.330024   |

**Figure 4.** variation of thermal conductivity (K) vs immersion time in H$_2$O.

**4. Conclusions**

From the obtained results, we can conclude the following:- Adding of Nano ceramic powder ZrO$_2$ to the polymers improves their mechanical properties and increases the strength of the composite material but decreases its thermal conductivity ; Different crystal size of the ceramic particles has different effects on the composite materials properties ; Exposure of composite material to immersion in water and its diffusion in it causes the substance to degradation and its failure , which results in the restriction of phonons movement and their dispersion a decrease in thermal conductivity ,and this effect increases with the length of immersion time, which makes the composite materials suitable for usage as a thermal insulators.
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