Characterization of thermo-physical and hardness properties of unsaturated polyester resin hybrid nano composites

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Abstract

In this work, two groups of nanocomposite material, was prepared from unsaturated polyester resin (UPE), they were prepared by hand-lay-up method. The first group was consisting of (UPE) reinforced with individually (ZrO₂) nanoparticles with particle size (47.23nm). The second group consists of (UPE) reinforced with hybrid nanoparticles consisting of zirconium oxide and yttrium oxide (70% ZrO₂ + 30% Y₂O₃) with particles size (83.98nm). This study includes the effect of selected volume fraction (0.5%, 1%, 1.5%, 2%, 2.5%, 3%) for both reinforcement nano materials. Experimental investigation was carried out by analyzing the thermo-physical properties like thermal conductivity, thermal diffusivity and specific heat for the polymeric composites samples, as well as the hardness test. The results showed that the values of (hardness, specific heat) increased as the nanoparticle content in composite samples increased for both groups’ nanocomposites, whereas the values of thermal conductivity and thermal diffusion decrease for both groups composites. And it was found that the properties of composite materials reinforced by hybrid nanoparticles have higher properties as compared with their counterparts of other nanocomposite reinforced by zirconia nanoparticle. The morphology of the fracture surface was showed homogeneous micro structure formation for both groups composites, indicating a good compatibility between the matrix material and the reinforcement nanoparticles.

Key words

Thermo-physical properties, unsaturated polyester, nanoparticles, hybrid composite.

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(Y2O3) ويتم خلال حجم حبيبي (83.98 nm) (0.5%, 1%, 1.5%). تضمنت الدراسة تأثير الكرس الحمي المختار (الحرارية، الانتشارية الحرارية، الحرارة الناعمة) للمواد المترافكة المحوره. أظهرت النتائج أن قيم كل من الحرارة الناعمة، الحرارة الحرارية، الانحراره نحثي، تزداد كلما ازداد محتوى دفاعات التاثير في المترافك وكلا المجموعتين. أما قيم التعادل بين الفيزيائية الحرارية، الانتشارية الحرارية، الانحراره نحثي، فتتكسر كلما ازداد محتوى دفاعات التأملي. وفقاً للنتائج التي أظهرتها، يمكن أن يكون للمادة الانتقائي الفيزيائي، المنشأ، التترابتي، نحثي، النموذج بالدقات النحائين الناحية يتضمن خصائص أعلى علامة بمقارنة مع نظيرتها من البيانات المدعومة بدقات الزركونيوم الناحية. كما أن البنية التشكيلية الدقيقة لسطح الكرس تظهر نشاطاً موجيداً لكل المجموعتين المترافك، مما يدل على التوافق الجيد بين المادة الانتقائي ودفاعات الناحية الناحية.

**Introduction**

Technology at present requires materials with a combination of properties that cannot be directly ingested by traditional materials such as metals, ceramics and polymers. As a result, engineers are forced to search for alternative materials to meet the complex service requirements of today’s applications. These materials should possess good process-ability together with excellent mechanical characteristics [1].

Polymer has become an important material in fabrication due to its ease of fabrication, low cost and great variety of functionalities. One of the reasons for the great popularity of polymer in wide variety of industrial application is due to the tremendous range of properties exhibited by plastics and their ease of processing [2]. Polymer resin is used as matrix which reinforces with different type of filler for different application [3]. Plastic properties can be tailored to meet specific needs. Through modification with an enormous rang of additives (filler, fibers, plasticizers and stabilizers) which make them efficacious in aerospace bodies, electronics/microelectronics basis, automotive parts, marine structures, and biomedical applications [4].

Polymer matrix composites are widely utilized in construction applications, including industrial and agricultural buildings [5]. The use of polymeric composites in agricultural and industrial buildings for structural and nonstructural elements is motivated by their main advantages among which can be mentioned: high specific strength, formability, fatigue resistance, controlled dimensional stability, corrosion resistance to various chemicals, wear resistance, convenient thermal and acoustical characteristics, light transmission and translucency, electromagnetic transparency, electrical non-conductivity, etc. [6].

Composites are materials consisting of two or more chemically distinct constituents on a macro-scale, having a distinct interface separating them. Composites offer superior properties which cannot be obtained by any constituent working individually. In practice, the composite materials are generally planned to develop one or more of the following features: mechanical properties (yield strength, tensile strength, modulus of elasticity, and compressive strength, hardness and impact resistance, fracture toughness) [7-9], wear resistance [10], fatigue resistance [11], high temperature resistance, corrosion resistance, thermal conductivity, electrical conductivity, acoustic conductivity, sound conservatism or sound absorption, weight, appearance and some other properties [12-13]. Composites also have lower density. In addition, these properties indirectly reduce unit cost of the material [14]. Today, large number of studies are carried out on the production of natural fibers from green plants, using in many areas and especially in the production of bio-composite materials [15-17].
The use of nanoparticle for the reinforcement of the composites has received increasing attention both by the academic sector and the industry, because of their advantages over other established material. Organic–inorganic nanocomposites are an emerging field of intensive investigation [18]. Through nanoscale engineering one can combine the flexibility of polymers with the high modulus and flame resistance of the inorganic component to produce a new class of lightweight materials [19]. Most of the effort thus far has been focused on the use of organo-silicate clays as the inorganic component in melts of a single polymer component [20].

The current work aims to prepare samples of low density and cost and with high durability, used in structural applications. Two sets of nanoparticles composites have been prepared as a function of nanoparticle content in composites, these nanoparticles are form the individual zirconium oxide, and hybrid nanoparticle consisting of a mixture of (Zirconium Oxide with yttrium oxide) (70% ZrO₂ + 30% Y₂O₃) added to (UPE) material and study their hardness and thermophysical properties.

**Materials and experimental work**

**Materials used**

Unsaturated polyester resin (UPE) manufactured by (Bonyan Kala Chemie) was used as matrix material with Ethyl Keton peroxide as a hardener. The weight ratio between hardener and resin was 2 gm of hardener per 100 gm of the resin. And the strengthening materials are nanoparticles, have been used two types of reinforced materials in this research the (ZrO₂) nanoparticles have particle size (47.23 nm). Fig.1, with purity (99.9%) provided from China (Hongwu international group Ltd.). And hybrid nanoparticles consisting of a mixture of zirconium oxide and yttrium oxide (70% ZrO₂ + 30% Y₂O₃) with particles size (83.98nm) fig .2 and purity (99.9%) supplied by China (Hongwu international group Ltd.). The Atomic force microscope AFM was used to determine the average diameter of nanoparticle and distribution of nanoparticle. Figs. 1 and 2 show the size and distribution for nanoparticles (ZrO₂) and (70% ZrO₂ + 30% Y₂O₃) hybrid nanoparticles respectively.

![Fig. 1: Particle size and distribution for zirconium oxide nanoparticles (ZrO₂) nanoparticles through Atomic Force Microscope (AFM).](image-url)
Fig. 2: Particle size and distribution of hybrid nanoparticles (70% ZrO$_2$ + 30% Y$_2$O$_3$) through Atomic Force Microscope (AFM).

**Preparation of samples**

Hand lay-out technique was used to prepare the neat unsaturated polyester resin (UPE) and nanocomposite materials. Nanoparticle powders were thoroughly mixed with unsaturated polyester resin with different loading (0.5%, 1%, 1.5%, 2%, 2.5%, 3%). In terms of volume fraction by using ultrasonic mixing device for this purpose, for at least half an hour to insurance riddance of pores. All the mixtures were prepared at laboratory temperature. Two sets of nanocomposites samples were prepared. The first group was consisting of (UPE) reinforced by individual (ZrO$_2$) nanoparticles have particle size (47.23 nm). The second group consists of (UPE) reinforced with hybrid nanoparticles consisting of a mixture of zirconium oxide and yttrium oxide (70% ZrO$_2$ + 30% Y$_2$O$_3$) with particle size (83.98 nm) nm. Mixing the constituents of the composite materials continuously until the mixture must be in homogeneity state with no bubbles in the mixing process, as well as with no conglomeration of nanoparticles is obtained in mixture. The liquid mixture was poured into the metal molds (have dimensions conforming to the international specifications of the material testing) continuously and slowly until the mold is filled to its desired level, and allowed to cure in mold for 48 hours at room temperature. All the specimens were then post cured in an electrical oven at 55°C for 2h, according to the instructions of the company producing (UPE) composite in order to complete the solidification process and to remove the stresses generated during the manufacturing process. Then the samples machined according to standard specifications to produce samples conforming for required tests for all the prepared samples.

**Hardness tests**

Hardness test carried out on a Durometer Shore D scale according to ASTM D2240 [821]. This method is suitable for thermoplastic polymers and thermosets polymers, the hardness test was carried out at room temperature by utilizing the Durometer hardness instrument 3120, kind (Shore
D), manufactured in USA. The hardness test was performed for all the samples which had dimensions 4mm thickness and 42mm diameter at five different sites for each sample and the average values were taken, this test was done in laboratories of the Materials Engineering Department, University of Technology.

**Thermo-physical tests**

Thermal properties test was carried out using thermal properties test device, manufactured by (Keltlvey), type (Transient Plane Source (TPS) - 500). The (TPS-500) technique is one of the most generally methods utilized for investigating in thermal transmission properties such as thermal diffusivity (Cv), volumetric specific heat (Cp) and thermal conductivity (K) which were determined by utilizing (Thermal Constants test by Hot Disk) [22]. The Hot Disk sensor (Fig.3a) consists of an electrically conducting pattern in the shape of a double spiral, which has been etched out of a thin metal (Nickel) foil. The plane Hot Disk sensor is placed between two pieces of the sample material (Fig .3b) and is then heated by an electrical current for a short period of time. The dissipated heat generates temperature rise of both the sensor and the surrounding sample material. In order to avoid influence from outside boundaries of the sample, the sample should be larger than the sensor diameter to ensure stable values of both thermal conductivity and diffusivity. In the Basic Method the sensor is placed between two sample pieces, which are a least as thick as the radius of the sensor. The values of thermal conductivity, thermal diffusivity and specific heat are read from the computerize gauge, this test was done in laboratories of the Materials Engineering Department, University of Technology.

![Fig. 3(a): Hot Disk sensor.](image1)

![Fig. 3(b): Hot Disk sensor operation.](image2)

**Morphology**

To analytical the morphology of the fracture surface samples, Scanning Electron Microscope (SEM) model (TESCNVGA.SB) made in Belgium, is used to examine the morphology for all prepared samples. To achieve good electric conductivity, all samples are first sputtered with gold from the surface along the edge.
**Results and discussion**

**Hardness test results**

It is noted from Fig. 4 that the value of hardness increases with the increase of the volume fraction of the nanoparticles powders in the (UPE) matrix. This is due to the shape and size of the nanoparticles and their hardness and the ease of penetration between the cleavages between the polymer chains, and this may be leads to increased close-packed of polymer chains and will restrict the movement of polymer chains and increase the hardness of the material prepared. Furthermore, may be due to the strong bonding at the interfacial region between the unsaturated polyester matrix and nanoparticles powders is because of the formation of strong physical cross-links (supra molecular) bonding leads to transferring the pressure through this strong interface, also the resistance of unsaturated polyester matrix to the plastic deformation mode by restrained motion of the unsaturated polyester chains along the direction of stress by the nanoparticles (formation of harder surface) as mentioned in literature [23]. Moreover, it is noted from Fig. 4 that the hardness values of nanocomposites materials reinforced with the zirconium oxide nanoparticles were slightly higher values than the hardness values of the samples reinforced by hybrids (70% ZrO$_2$ + 30% Y$_2$O$_3$) nanoparticles. Such a behavior may be related to the high hardness that the zirconium oxide has as compared with hybrids (70% ZrO$_2$ + 30% Y$_2$O$_3$) nanoparticles, and good compatibility between constituent (ZrO$_2$) and (UPE) matrix. Therefore, the maximum values of hardness increased from (79.2) for neat unsaturated polyester to (86.4) for nanocomposite material (UP:3% nZrO$_2$), and this it may be caused by the different in fusible viscosity of a polymeric composite reinforced by nanoparticles and neat unsaturated polyester, which depend on the homogeneity of the matrix material and the type of reinforcement nanoparticle. Which in turn will reduce the permeability of the liquid substrate into the interstellar pores and the interstitial space within the overlapping material, thereby increasing the hardness of the composite material prepared [24].

![Fig 4: Hardness of the (UPE) nanocomposites as a function of the volume fraction of nanoparticles and hybrid nanoparticles content in the composite material.](image_url)
Thermo-physical properties

The thermo-physical properties (thermal conductivity, thermal diffusivity and volumetric specific heat) values of the neat (UPE), nanocomposite and hybrid nano composite materials for all samples that were obtained in the current work are illustrated in Figs. from 5 to 7. These figures illustrate the effect of the addition of ZrO$_2$ nanoparticles powders individually, and hybrid nanocomposite on the thermo-physical properties (thermal conductivity, thermal diffusivity and volumetric specific heat) for (UPE) nanocomposites respectively. It can be noted from these figures that the thermal conductivity and thermal diffusivity decreases, and volumetric specific heat increases with an increase in the ratio of volume fractions of zirconium oxide nanoparticles and hybrid (70% ZrO$_2$ + 30% Y$_2$O$_3$) nanocomposite content in the unsaturated polyester matrix, as compared with neat unsaturated polyester. Heat flows within a material by the transmission of phonons (thermal carrier) and free electrons (if present). Both of these carriers have a certain mean free path between collisions and an average velocity. The phonon velocity is high in light and in stiff materials. The mean free path of a phonon is structure sensitive and can be large in pure specimens of high perfection and large grain size. Polymers have no electrons and high stiffness (high phonon velocity), so that conductivities are high [25].

The decreasing in thermal conductivity of composites was caused by the presence of fillers. The conductivity of a composite is affected by the interface adhesion between fillers and matrix, since the conductivity may be impaired by the presence of an interfacial layer of some sort, or by voids or cracks in the vicinity of the interface. According to the results obtained these polymer nanocomposites can be classified as low thermal conductivity behavior as compared with neat polymer materials [13].

Since the reinforcement materials, are a thermal insulating ceramic material, they have a strong crystalline structure in which the atoms are arranged according to a crystalline three-dimensional grid. So that, the thermal conductivity and thermal diffusion values decrease when the volume fraction of the added nanoparticle is increased, due to the irregularity of the structural of the matrix material, because it is made of polymeric materials that are thermal insulating, have low thermal conductivity, and also have a random heterogeneous structure. This in turn leads to the random dispersal of thermal energy when transmitted through the random structural of polymeric composite materials, moreover, to the presence of nanoparticles powder a randomly dispersed within the structure of the matrix material, and this works to increase the dispersal of thermal energy. This in turn will lead to a decrease in thermal conductivity and thermal diffusion of the prepared nano composite material. And also, the thermal diffusion is dependent on the density of the material, when the density of the material is increased, conversely to that a thermal diffusivity of the material it will decreased also. Furthermore, it is also observed that the value of thermal conductivity and thermal diffusivity for unsaturated polyester composites reinforced by hybrid nanoparticle, is higher than that of their counterparts of composite materials reinforced by ZrO$_2$ individually. The nature of both the added nanoparticle powder of reinforcement material and their
association with the components of the composite materials as well as the nature of the interconnection between reinforcing materials and other components of composite materials. Fig. 6 shows that the value of the volumetric specific heat increases as the volume fractions content of nanoparticles content increases for both group of nanocomposite materials. That due to fact of the volumetric specific heat is inversely proportional to the thermal conductivity as well as thermal diffusion. And the volumetric specific heat depends on the type of material and its density. As well as the volumetric specific heat for unsaturated polyester composites reinforced by ZrO2 individually, is higher than that of the nanocomposite reinforced by hybrid nanoparticle [26].

![Graph showing thermal conductivity of (UPE) nanocomposites as a function of volume fraction of nanoparticles and hybrid nanoparticles content in the composite material.](image)

**Fig. 5:** Thermal conductivity of the (UPE) nanocomposites as a function of the volume fraction of nanoparticles and hybrid nanoparticles content in the composite material.

![Graph showing thermal diffusivity of (UPE) nanocomposites as a function of volume fraction of nanoparticles and hybrid nanoparticles content in the composite material.](image)

**Fig. 6:** Thermal diffusivity of the (UPE) nanocomposites as a function of the volume fraction of nanoparticles and hybrid nanoparticles content in the composite material.
Fig. 7: Volumetric specific heat of the (UPE) nanocomposites as a function of the volume fraction of nanoparticles and hybrid nanoparticles content in the composite material.

Morphology

The SEM micrographs of fracture surfaces for polymeric composites depends on the class of polymeric material and their components and the ratios of the reinforcing materials, the wettability between their components, as well as depends on the conditions of fabrication and melting viscosity of the components, in order to link the mechanical properties of the unsaturated polyester composite with its microstructure, the scanning electron microscopy (SEM) was used to study the morphology of the fracture surface of (UPE) Fig. 8 and its composites which included the first group composites samples (UPE: X% ZrO₂), was reinforced by ZrO₂ nanoparticle individually, and the second group as hybrid composites (UP: X% (70% ZrO₂ + 30% Y₂O₃)), the SEM micrographs morphology includes the effect of selected volume fraction (0.5%, 1%, 1.5%, 2%, 2.5%, 3%) for both reinforcement materials at x30000 magnification, were recorded in Figs. 9 (a, b, c, d, e and f) and Fig. 10 (a, b, c, d, e and f) respectively. It was noted through microscopic imaging from these figures, that the morphology of the fracture surface of the polymer composites showed homogeneous micro structure formation for both groups composites, it was also observed that the microscopic structure of the fracture surface morphology for most of nanoparticles are embedded inside the matrix material as an integral part of the base material structure, indicating a good compatibility between the matrix material and the reinforcement nanoparticles especially at low ratio of nanoparticle content in composites, these photos seems to indicate better interfacial adhesion between constituents of composite [27], which enhances the hardness and thermophysical properties, moreover the structure of Fig. 8 shows that there are no phase separated dominant in the matrix structure of unsaturated polyester, as well as in the structure of the composite substances mentioned
above (Figs. 9 and 10). However, increasing the percentage of nanoparticles content in the composite would reduce the micro structure of the prepared composites materials, the morphology of the fracture surface also showed the occurrence of clusters of nanoparticles at the high ratios of the nanoparticle content, which distributed randomly within the structure of the matrix material. This can be observed by Figs. 9 and 10 (e, f) of both groups.

Fig. 8: SEM morphology of fracture surface for neat (UPE). at the magnification of (30000X).
Fig. 9: SEM fracture morphology as a function of volume fraction of ZrO$_2$ nanoparticles content in the composites, where: (a (x= 0.5%), (b (x = 1%), (c (x= 1.5%), (d (x=2%) (e=2.5%) and (f (x= 3%) at the magnification of (30000 X).
Fig. 10: SEM fracture surface morphology as a function of volume fraction of (70% ZrO$_2$ + 30% Y$_2$O$_3$) nanoparticles content in the composites, where: (a (x= 0.5%), (b (x = 1%), (c (x= 1.5%), (d (x=2%), (e (x =2.5%) and (f (x= 3%) at the magnification of (30000 X).

Conclusions

From this work, it was concluded that the addition of zirconium oxide nanoparticles individually, or hybrid nanoparticle (70% ZrO$_2$ + 30% Y$_2$O$_3$) it enhanced the thermo-physical properties and a hardness property, as well as, it was concluded that, the unsaturated polyester when reinforced with hybrid nanoparticle it will be have the higher values of thermal conductivity and thermal diffusion. Whereas when reinforced by zirconium oxide nanoparticles individually, it will be had the higher value of hardness and volumetric specific heat. These results, were supported by the electron microscopy, where the fracture surface morphology showed a homogeneous microstructure morphology for both groups of nanocomposites and especially at the low ratio of nanoparticles content, and this indicating a good compatibility between the unsaturated polyester and the reinforcement nanoparticles. So, it was concluded that the idea of adding these nanoparticles with limited
proportions to unsaturated polyester resin is expected to be successful in structural applications especially as insulator material.

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