Improving the Durability of Streak and Thermal Insulation of Petroleum Pipes by Using Polymeric Based Paint System

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Abstract:
This research deals with increasing the hardening and insulating the petroleum pipes against the conditions and erosion of different environments. So, basic material of epoxy has been mixed with Ceramic Nano Zirconia reinforcement material 35 nm with the percentages (0,1,2,3,4,5) %, whereas the paint basis of broken petroleum pipes was used to paint on it, then it was cut into dimensions (2 cm. × 2 cm.) and 0.3cm high. After the paint and percentages are completed, the samples were immersed into the paint. Then, the micro-hardness was checked according to Vickers method and thermal inspection of paint, which contained (Thermal conduction, thermal flux and Thermal diffusivity), the density of the painted samples was calculated., The results of the research indicate that the concentration (5%ZrO₂) gives the best results that the hardness of this concentration reached to (92 Hv). By contrast, the thermal conduction was continued at an insulation limit (2.4 W/m.K). The thermal diffusivity was (1.16 mm²/sec.), the thermal flux reached to (70.4 w.s⁻¹/m².K) and the density at the same percentage was (4.87 g/m³). This means that there is a linear proportionality and development with increasing in the percentage of Nano Zirconia additive to epoxy.

Key words: Ceramic Material, Petroleum Pipes, Polymer Matrix Material, Thermal Insulation.

Introduction:
Polymer Matrix Composites have several and wide applications, many researchers are interested in the field of composite materials because of its lightweight, high strength and ease of treatment with many available options in this system (1). Resin Epoxy is widely used in insulation such as electrical machines, electronic circuits, switches, batteries, transformers and even in making the heat resistant pipes, as well as in surface protection operations such as marine ship coatings and materials surface covering (2). So, the density of reinforcing material has a large effect on the characteristics of the resulting composite material (3,4). In spite of the large use of different reinforcing materials of fiber, bristles and others, there are many unknown properties of composite materials, whereas the composite materials during industrial are random or scattered, so there are properties that identify the characteristics of these composites, which is how to mix, an inter-phased and reinforcement material (5). One of the effecting factors of composite material is the thermal conduction whereas the material ability of thermal transfer is called the thermal conduction; however there is energy thermal in materials indicating that their electrons have kinetic energy that works on increasing the collisions in them (6). Insulations are considered very important applications in composite materials, which are based on Polymer (EP) and are propped by different ceramic materials (7). Labeed et.al; have studied the effect of adding alumina particles and graphite in order to improve the mechanical properties of composites based on epoxy. Alumina has been added by mass of (10%-40%) as reinforcing material, a set of mechanic tests have been made such as hardness, friction, compressive strength. They found out that the best reinforcing percentage of alumina is 20%, they also found out that the friction factor can be reduced in addition to other properties except hardness, which
is considered a superficial property (8). Bello SA et al. concluded that the reported decrease in the measured properties as %wt of coconut shell particle addition increased from 20 to 35 %wt.

However, the reversed behavior of these composites at higher %wt of coconut shell particle addition may be attributed to poor bridging effect between filler and matrix arising from the fact that matrix particle saturation level has been exceeded. Also, this review has exposed the possibility of using mechanical milling (9). Shiv RK et al. have studied the effect of adding different weight fraction of Nano zirconia on wear characteristics of resin-based dental composite. The dental composites were fabricated by adding (0–3 wt. %) of silane-modified Nano zirconia particles into a monomer system (50 wt.% biphenyl-A glycidyl methacrylate, 49 wt.% tri-ethylene glycol methacrylate, 0.2 wt.% Camphor Quinone, and 0.8 wt.% ethyl 4 dimethyl amino benzoate (10). Noor S M et al. have studied the effect of mixing TiO₂ nanoparticles with epoxy resin. The TiO₂ nanoparticles would be synthesized and characterized by scanning electron microscopy (SEM), XRD FTIR, for two particle sizes of 50 and 25 nm. The thermal conductivity is measured with and without composite epoxy resin; the results showed that the thermal conductivity was increased as nanoparticle concentration increased too. The thermal conductivity was increased as particle size decreased (11). Therefore, many of petroleum and gas pipes that extend for long distances through the soil suffering from cracks in the external surfaces as a result of different weather conditions of acidity and humidity, need to be treated by composites materials that included treatment as low cost and high durability (11). The aims of research is to study the possibility of applying the coating on oil pipes and the ability of resistance to titanium oxide to different conditions.

Material and Methods:
The Primary Materials Used in the Research
Zirconium dioxide (ZrO₂)

Zirconia is considered as one of the most important oxides used in the field of thermal insulation because it has a very weak thermal conductivity, shock resistance and weather-resistant materials. So, zirconia that is made in China was used as a reinforcing material of epoxy in this study with different weight percentages, Nano-sized 35 nm, density Zirconia is 5.68 g/cm³, with a melting point of up to 2700°C, which has white colour.

Epoxy

Epoxy Resin 105 is characterized by the pale yellow colour with medium viscosity heated on 65 °C in order to release its viscosity. Epoxy is also characterized by typical physical properties with high resistance to humidity, and has a density of 1.19 g/cm³.

Specimens Preparation

In this research, paint bases were prepared from damaged and decommissioned petroleum pipes. So, the samples of pipes were divided by a machine CNC with dimensions (2cm×2cm) and high 0.3cm, and then they have been cleaned and painted with a plain dye of an ordinary colour of brown antioxidant whose types are coral with a density of 1.2 g/cm³. After that, the based epoxy was mixed with Zirconium oxide Nano-particles (ZrO₂) at weight percentage 0, 1, 2, 3, 4, 5%. The mixing of the two materials was carried out together using magnetic star, which is equipped with a thermal and regulated heat and speed of rotation, then ultrasonography machine was used in order to disperse Nano powder by using epoxy, after that the hardener with density 1 g/cm³ has been added by a ratio 2:3, and then the bases to be painted were covered during the paint at different proportions as shown in Fig. 1. The models were hardened and left outside for five days in order to complete the treatment.

Tests and Measurements

Physical Density Test

The ratio between mass and apparent magnitude (the material grain size + sealed pores size) contains the material and sealed pores, the composite density increases or decreases depending on several factors such as the density of the materials involved in its composition and chemical composition, the size and forms of the particles of each of the constituent materials. There are several test methods to calculate the density by comparing its density with common materials such as (water and mercury) according to the United States Standards (ASTM (C373 – 71)) (12).

Vickers Micro-Hardness Test

Hardness has been measured according to Vickers, METKON kind, which is made in France, of the models that have been painted after making polish, the effect used is a pyramid-shaped ceramic girden with an angle of 136 ° between the two faces
with a load of 100 gm, with time 10 Sec, it is automatically raised after the indicator light is illuminated by the end of the specified period of time. Thus, the effect dimensions are calculated in the two axes and in two orthogonal directions and taking five analyses and calculating their mean X, to obtain the hardness value from the digital screen installed directly on the machine. The following equation represents Vickers Hardness: (13)

\[ HV = 1 \cdot 854 \cdot \frac{P}{(dav)^2} \]

Where:
- HV: Hardness Vickers
- P: Applied Load (gm.)
- dav: Diameter Average Affect

**Thermal Tests**

The thermal conductivity of a material is a measure of its ability to conduct heat. It is commonly denoted by w / m.k. In the last few years, a great deal of attention has been given to thermal conductivity, especially in composite materials with thermal insulation, as well as in metal-reinforced insulation composites whereas the adding of minerals significantly improves the thermal, electrical and mechanical properties of composites (14, 15). The large difference in the values of thermal conductivity by the classification of objects into two types: the first one is poor thermal conductivity, while the second one is of good thermal conductivity. The good one such as minerals are used in making walls (EIFS system) which lets heat go through it, such as radiators and heat exchanger, while the poor thermal conductivity are different and more, which are used to improve the thermal conductivity, as it really there is no a completely insulating material for heat.

The thermal conductivity and its variables may be calculated by the following (16, 17):

\[ Q = \frac{dH}{dt} = -\frac{\lambda A dT}{dx} \]

Where:
- Q: Heat Quantity of Midst Unit (watt).
- H: Heat (J).
- t: Time (Sec.).
- \( \lambda \): Thermal Conductivity (w/m.k).
- T: Temperature (K).
- A: Cross Section Area of the Sample (m²).
- X: Increase the Sample of the Test (m).
- While, the thermal diffusivity \( \delta \) (s/ m²) is:

\[ \delta = \frac{\lambda}{C_p \cdot \rho} \]

Where:
- \( C_p \): Specific Heat Capacity (J/ g.k).
- \( \rho \): The sample Density (g/cm³).
- And the Thermal Flux \( \varepsilon \) (K. m² / Ws½), which is:

\[ \varepsilon = \sqrt{\lambda \cdot \rho \cdot C_p} \]

The system that is used to measure the thermal conductivity is Mathis TCI (MPTS) made in Canada, that measures the conductivity with 0-100 W/mk, also it’s used in a large field of temperatures (~5°C to 200°C).

**Discussion of Results:**

**The Results of Scanning Electron Microscopy Test (SEM) of Zirconium Oxide Nano-Particles (ZrO₂):**

Scanning Electron Microscopy has a great importance in Materials world, as it can be used to identify multiple surface structures for many basic and reinforcement materials, Fig. 2 explain the scanning electron microscopy (SEM) of zirconium oxide Nano-particles, which clearly shows the spherical structure of the powder.

**The Effect of Zirconia on Density**

Figure 3 shows the relationship between the Zirconium and density; it is clearly shown through the Figure that there is a change, whereas the density increases with the increase of Nano Zirconium, so this is an emphasized thing, because of the Zirconium spreading through Epoxy. Zirconium Nano-Oxide is characterized by high density comparing with the value of Epoxy density, which leads to increase the mixture density (18). It reached its highest value at the strengthening rate 5% and density rate was 4.87g/cm³.

**The Effect of Zirconium on Micro-Hardness**

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**Figure 2. SEM for epoxy resin reinforced with Zirconium Nano-Powder.**

**Figure 3. The Effect of Zirconia concentration on Density of paint.**
Figure 4 shows the relationship between the change in the weight ratios of zirconia nanoparticles and Vickers' hardness where, as is known, zirconia hardness is very high because it is an oxidization, when starting with the addition of zirconia, it was noted that the increase of hardness to 92Hv at the ratio 5%, the high hardness was due to the fact that the oxide is characterized by high hardness and low porosity, and the homogeneity of the distribution between the base material and the strengthening particles also has a significant role in increasing the hardness, and the rate of increasing of zirconia has reduced the liquid phase during the process propagation, which in turn helped to bind granules with epoxy (18,19).

![Figure 4](image.png)

**Figure 4. The Relationship between increasing Weight ratio of Zirconia and Vickers Hardness.**

**The Effect of Zirconia Ration on Thermal Conductivity**

Figure 5 explains the relationship of the effect of the reinforcement content (Nano Zirconia) on the thermal conductivity. So, we can notice the decrease of thermal conductivity from (0.24w/m.k) to (0.11w/ m. k) of the reinforcement ratio 0% to %5 respectively, i.e. the reverse proportionality between thermal conductivity (λ) and increased reinforcement ratio. The resins do not contain electrons in its internal structure, which help to transfer heat, depending on structural vibrations in order to transfer energy thermal (20), by adding Nano-Zirconia oxide, which works on inhibits these vibrations that bring heat, and the thermal conductivity is decreased. Thermal insulation is increased as well as oxides characterized by low connectivity, which helps to reduce the conductivity of the paint and increases the obstruction with increased reinforcement ratios of Zirconia (21, 22).

![Figure 5](image.png)

**Figure 5. The Relationship between Increasing of Wight ratio of zirconium and Thermal Conductivity.**

**The Effect of Zirconium ratio on the Thermal Flux**

The relationship of reinforcing content effect (Zirconium) on thermal flux is explained in Fig. 6, it is clear that there is increasing in the thermal flux, when the reinforcing ratio be a little, but with increasing the reinforcing Ratio from 1% to 5%, we can see there is a decrease of thermal flux because the structural vibrations of epoxy help to increase the streaming, such as thermal conductivity, but with the increasing the reinforcing ratio of the bad conductive ceramic material, it works as barriers to stop the heat spreading through the paint (23).

![Figure 6](image.png)

**Figure 6. the relationship between zirconium concentration and the thermal flux.**

**The Effect of Zirconium on the Thermal Diffusivity**

Figure 7 explains the effect relationship of reinforcing content (Zirconium) on the thermal diffusivity δ, so it is clearly that there is increase of thermal diffusivity of epoxy, whereas there is a large effect of structural vibrations on resins, which helps thermal diffusivity through painting. But by increasing the reinforcing ratio of the ceramic material, the structural vibrations will try to reduce the spreading and hang the thermal transfer, such as thermal flux and thermal diffusivity (20- 23).
Paint protection is used as the best way to protect oil pipelines heat and withstand high temperatures, which is one of the conditions that significantly lead to damage oil pipelines that extend for long distances and high economic feasibility as compared to the conventional methods. It should take into account that the application of working conditions accurately prevents any leakage of moisture and oxygen to the surface of the pipe to be protected.

Conclusions:
This research has come up with the following conclusions: a major increase in hardness and density because of the reinforcement of ceramic Nano Zirconia; increase the values of Thermal Insulation of paint because of the increased the percentage of Nanomaterial. Getting the best percentage of reinforcement 5% which gives a good hardness (92HV), density (4.87g/cm³), less thermal Conductivity (0.11w/m. k), thermal flux (15s1/2/m².k) and thermal diffusivity (0.05mm²/sec).

Authors' declaration:
- Conflicts of Interest: None.
- We hereby confirm that all the Figures and Tables in the manuscript are mine ours. Besides, the Figures and images, which are not mine ours, have been given the permission for republication attached with the manuscript.
- Ethical Clearance: The project was approved by the local ethical committee in University of Baghdad.

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تحسين متانة الخدش والعزل الحراري لانابيب النفط باستخدام نظام طلائي ذو أساس بوليمر
صالح يونس دروحی1
زهره ناجي مجيد2
اشواق طارق دحام3

الخلاصة:
البحث الحالي يتعامل مع زيادة صلادة وعزل الانابيب النفطية ضد ظروف تأكل البيئة المختلفة، حيث تم مزج المادة الأساسية الإيبوكسي مع مادة التدعيم السيراميكية الزركونيا النانوية (35nm) وبنسب تدعيج منوية 5% عن (10، 20، 30، 40، 50) مللي متر. حيث تم استخدام قواعد طلاء من انابيب نفط تالفة لغرض الطلاء عليها وتم تقطيعها بأبعاد (2cm×2cm) وبارتفاع 0.3cm، وبعد اتمام الطلاء ونسبة المئوية يتم تغطيس العينات خلال الطلاء. تم بعد ذلك إجراء فحص الصلادة المايكروية (Vickers)، وتم قياس التوصيلية الحرارية (watt/m.K) والانتشار الحراري (mm2/sec) والتدفق الحراري (w.s/m2.K). وتم حساب الكثافة للمخلوط عند نسبة التدعيج هو (4.87 g/m3). وتظهر النتائج أن تركيز ZrO2 (5%) يعطي افضل نتائج حيث بلغت الصادة عند هذا التركيز 92Hv، بينما كانت التوصيلية الحرارية نسبة العزل (2.4 w/mK) والانتشار الحراري (1.16 mm2/sec) وtedic الحراري (70.4 w.s/m2.K) عند هذه النسبة عن النوع البديع في الايبوكسي.

الكلمات مفتاحية: المواد السيراميكية، انابيب النفط، مادة ذات أساس بوليمر، العزل الحراري.