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**Heat Transfer and Thermal Expansion of Coefficient
EP -(MWCNT/_x-TiO₂)Nanocomposites**

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ABSTRACT

The thermal properties (thermal transfer and thermal expansion coefficient) of the enhanced epoxy resin (MWCNT / x-TiO₂) were studied by weight ratios with the values (0%, 3%, 5%, 7% and 10%) and a constant ratio of 3% of MWCNT. The ultrasonic technology was used to prepare the neat and composites which were then poured into Teflon molds according to standard conditions. Thermo-analyzer sensor technology was used to measure thermal transfer (thermal conductivity, thermal flow, thermal diffusion, thermal energy and heat resistance). The thermal conductivity, flow, and thermal conductivity values were increased sequentially by increasing the weight ratio of the filler while the results of stored energy values and thermal resistance decreased by increasing the percentage of salts. The thermal mechanical analysis was used to measure thermal expansion and elasticity coefficient. The scanning electron microscopy was used to interpret the results of thermal analysis and distribution of the nanoparticle within the polymer matrix.

Keywords: Epoxy, MWCNT, Thermal Conductivity and Nanocomposites.

**خصائص الأيصالية ومعامل التمدد الحراري للمترابكات
EP - (MWCNT/_x-TiO₂) النانوية**

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الخلاصة

تم في هذا البحث دراسة المميزات الحرارية (الانتقال الحراري ومعامل التمدد الحراري لراتنج الايبوكسي المعزز MWCNT/ x-TiO₂ بالكاربون المتعدد الطبقات واوكسيد التيتانيوم النانوي بنسب وزنية لقيم (0%، 3%، 5%، 7% و 10%). مع ثبوت 3% من MWCNT. تم استخدام تقنية الموجات فوق الصوتية لتحضير المترابكات التانوية ومن بعدها تم صبها في قوالب من التفلون حسب الشروط القياسية. تم استخدام تقنية المتحسس الحراري لقياس الانتقال الحراري مثل الايصالية الحرارية والتدفق الحراري والانتشار الحراري والسعة الحرارية والمقاومة الحرارية). اظهرت قيم نتائج التوصيل الحراري والتدفق والانتشار الحراري زيادة تعاقبية بزيادة النسبة الوزنية للمادة المألثة بينما نتائج قيم الطاقة المخزونة والممانعة الحرارية انخفضت بزيادة النسبة المئوية للمالآت. تم استخدام تقنية التحليل الميكانيكي الحراري لقياس التمدد الحراري ومعامل المرونة. تم استخدام المجهر الالكتروني الماسح في تفسير النتائج التحليل الحراري والتوزيع للمسحوق النانوي ضمن مصفوفة البوليمر.

الكلمات الرئيسية: الايبوكسي، الانابيب الكربونية النانوية، التوصيلية الحرارية، المترابكات النانوية

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1. INTRODUCTION

Although all types of polymers (thermoplastics, elastomers, and thermosets) are of great importance, polymer nanocomposites have been used. A range of nano-strengthened with different shapes has been used in fabricated polymer nanocomposites. An important parameter for characterizing the effectiveness of strengthens is the ratio of surface area to volume. Nanocomposites are defined as the blending of two or more types of materials such as ceramic – polymer, metal-polymer where without chemical reaction. So, no covalent bonding occurs between materials, **Harper, 2004**. Nanocomposites are used to make configuration materials (polymer, ceramic and metal) with improved functional and physical characterizing **Laurent, 2000**. Polymer-based nanocomposites are the most important classifications of materials due to the extensive applications in various industrial and electronic applications, **Bhatnagar, 2004**. There are several types of polymers classified according to their molecular nature and weight, as well as the nature of its composition. If it is a synthetic industrial origin, it is heat resistant, including rubber and the third type plastic, which is softened by heat. There are different methods to form with additives to form nanocomposites, **Donald, et al., 2003**. In particular, polymer strengthened with inorganic additives (fillers) in the nanometer range less than 100 nm, known as nano-composites, have attracted great interest from researchers, due to unexpected syndrome properties derived from the two materials, **Frigioneand, 2008**. Many of the studies and research on nanoparticles focus on the thermosetting polymer class as a base material for the formation and composition of polymer-based nanoparticles. These polymers, which are non-enhanced by nanoparticles, have low thermal conductivity, with high thermal expansion coefficient of length, surface and volume, **Espositoand, 2009**. Epoxy resin (thermosetting class) has been extensively used in a different wide civil engineering applications, such as pipes coatings, surfaces adhesive, painting materials and electronic applications. Like other thermosetting materials, epoxy polymers are also very brittle, which restrict their application in products that require high shock or impact and fracture strength, **Suresha, et al., 2009**. For epoxy resins reinforced with different types of additives (fillers), this is even more important. Improved thermal conductivity and decreased thermal expansion in epoxy resins may be achieved either by molecular order of chain segments or by the addition of highly thermally conductive fillers from ceramics or metals (TiO_3 , Al_2O_3 , ZnO , SiO_2 , CNT, MWCNT, Al, Cu...) **Tekce, et al., 2007**. Temperature rate, applied pressure, densification of the polymer, the orientation of chain segments, crystal structure, the degree of crystalline and many other factors may affect the heat transfer of epoxy polymers **Yang, 2007**. MWCNT- shows the best performance additives (fillers), have a high thermal conductivity and it is lightweight. Ceramic titanium oxide is the most extensively studied material, which makes TiO_2 one of the most investigated ceramics in materials science. Titanium oxide is known to be a very hard material, corrosion-resistant material: it is frequently used in paint, white pigments, and sun-blockers **Poulomi, et al., 2011**. The effects of nanopowders of load weight fraction, dispersion agent, a curing agent with a different percentage on the heat transfer and thermal expansion properties in MWCNT/ x - TiO_2 reinforced epoxy has been investigated **Ahnkim and Kwon, 2013**.

The aim of the study is a fabrication of MWCNT/ TiO_2 reinforced epoxy resin based nanocomposite. Heat transfer and thermal expansion of nanocomposite under variousthe operating conditions and the effect of filler content on thermal transfer with low thermal expansion are studied.



2. THEORETICAL APPROACH

The Thermal conductivity analyzer (Mathis TC i) technique was used. Heat is transported in materials by free electrons and phonons. Material conducting is inherent with both of these mechanisms, and the neat conducting is the sum of these. The heat potential energy inherent with lattice waves (phonons) is transported in the same direction of their motion. Lattice waves contribution in insulator materials results from each movement of phonons from high – to-low temperature zones of a cross section body, where a heat gradient exists, by conduction and it involves the transfer of work within an insulator material without any motion of the material as a whole. Heat transfer mechanisms calculation uses the heat energy equivalent of Fourier equation **Marcus and Blaine, 2013**. The thermodynamic conductivity of the insulating material is done either through the phonon, which is the vibration of the material or by some electrons that are not bound by the nucleus or the catalyst or through the two. Test samples can be a paste, solid, powder, liquid, or chips **E1952, 2013**.TC i- Mathis Sensor features provide direct, and indirect testing properties, including:[ρ , ϵ , D , k , C_p].The equation of conductivity coefficient is given by **Callister, 2003**.

$$\frac{dh}{dt} = -\frac{kAdT}{dL} \quad (1)$$

h = heat (J), t = Time (sec), K = conductivity ($WK^{-1} m^{-1}$), T = temperature (K), L = thickness of (m), A = cross-sectional area of test specimen (m^2)

The thermal diffusion equation (mm^2 / s):

$$\delta = \frac{k}{C_p \cdot \rho} \quad (2)$$

C_p = specific heat capacity (J/kg. k), ρ = density (kg / m^3), ϵ = effuisivity ($Ws^{1/2} m^{-2} k^{-1}$),where

$$\epsilon = \sqrt{k \cdot \rho \cdot C_p} \quad (3)$$

R = thermal resistance ($m^2 \cdot k / W$)

$$R = \frac{dL}{K} \quad (4)$$

The mechanical thermal analysis of plastic materials is important to know the effectiveness of the material to resist different temperatures. It is known that the thermal expansion coefficient of polymers is relatively high compared to the mineral and ceramic materials. Therefore, the properties of the polymer thermal expansion coefficient can be improved by strengthening its molecular bonds and supporting it with low temperatures thermal ceramic materials such as titanium oxide, zinc oxide, and aluminum oxide as well as adding carbon nanotubes. The other important characteristic is the thermal stress feature in the presence of pressure where it can predict the nature of the plastic material to resist any sudden thermal stress and to prevent the distortion of the material due to differences in temperatures applied to the material, as in Eq. (5) and (6), **Paul Gabbott, 2008**.

$$X_i - X_f / L_i = \alpha (T_f - T_i) \quad (5)$$

The thermal stress σ_t is (MPa) is given by:

$$\sigma_t = E \cdot \alpha_l (T_i - T_f) \quad (6)$$

where: X_i = initial length at T_i , X_f = final length at T_f , α_l = the linear coefficient of thermal expansion, E = Young's modulus **Paul Gabbott, 2008**.



3. EXPERIMENTAL WORK

In this work, the base material (epoxy) is used as a transparent liquid, consisting of resin. The other part is the hardener. It is mixed within a ratio of (2:1), thermosetting epoxy has a density of approximately 1.04 g / cm^3 . The reinforced material diameter was used in 30 nm multi-layer carbon nanotube powder with a length of 10 micrometers and with a specific surface area (SSA) greater than $110 \text{ m}^2/\text{g}$ and purity of 93% and a 3% fixed addition of multilayer carbon mixed with titanium oxide powder is done. Using an ultrasonic device with acetone as the solvent for one hour and then mixing with the resin for 10 minutes using ultrasound. Then the hardener was added to the mixture (resin and powder) for the purpose of polymerization, and formation of nanocomposite samples with dimensions of 10mm diameter and 25mm length. **Fig.1** shows the scanning electron microscopy with the X-ray spectrum of the titanium oxide powder.

4. RESULTS AND DISCUSSIONS

The heat transfer of the different samples was measured by TCi- Sensor method; four different conductive epoxy resins are investigated. The heat capacity of a thick sample is measured with C-Therm Sensor TCi. The heat transfer is calculated using equations (1, 2, 3 and 4) and the results are summarized in **Table 1**. Conductivity, effusivity and thermal diffusivity results increases by increasing MWCNT / TiO_2 content as on **Fig.3, Fig.4, and Fig.5**. This caused high conductivity of MWCNT as well as the homogeneous dispersion of nanocomposite and high density of the TiO_2 powder. This is explained in **Fig. 6**. While thermal resistance and heat capacity results in decreasing with the increase of MWCNT / TiO_2 content, **Fig. 7 and Fig. 8**. This is due to that the nano-powder MWCNT has a low heat capacity and high thermal diffusivity. Thermal mechanical analysis (thermal expansion, elastic modulus, and thermal stress) results are shown in **Tables 2 and 3**. The Thermal mechanical analysis TMA tests of thermal expansion at different temperature showed enhancement with increasing the weight percentage of MWCNT/ TiO_2 content, **Fig. 9**. While elastic modulus results showed a decrease by increasing weight percentage of MWCNT / TiO_2 content. Thermal stress results showed a decrease by increasing the weight percentage of MWCNT / TiO_2 . **Fig. 10** shows the E- Modulus and thermal stress by TMA measurement

5. CONCLUSIONS

In this research, the following conclusions were reached:

1. All the thermal properties affecting the thermal transfer process (eg, conductivity, flow, diffusion) have clearly improved and all the added percentages of the enhanced nano-powder mixture of the base material was compared to the epoxy.
2. In addition to improving the thermal properties of the nanocomposites, the stored heat energy and the heat dissipation rate decreased due to the reduction in the thermal capacity compared to the neat epoxy.
3. This type of the nanocomposites has a stability in the dimensions to a certain degree of temperature in the range (30-250) $^{\circ}\text{C}$ where the values of the coefficient of thermal expansion have been maintained for all the ratios of the environment compared to the dominant sample.



6. REFERENCES

- B. Ahn Kim and C.Kwon Moon, 2013, Study on the Mechanical and Thermal Properties of Tio2/Epoxy Resin Nanocomposites, Manuscript Received.
- B. Suresha; G. Chandramohan; M.A. Jawahar; S. Mohanraj, 2009, Journal of Reinforced Plastics and Composites, 28: 225.
- C. A. Harper, 2004, *Electronic Packaging and Interconnection Handbook*, McGraw Hill.
- D. Callister, 2003, *Material Science and Engineering, An Introduction*, Sixth Edition, Department of Metallurgical Eng., The University of Utah, John Wiley & Sons, Inc., USA.
- E1952, 2013, Method for Thermal Conductivity and Thermal Diffusivity by Modulated Temperature Differential Scanning Calorimetry, ASTM International, West Conshohocken, PA.
- Esposito Corcione, C.; Frigione, M., 2009, A novel procedure able to predict the rheological behavior of Trifunctional epoxy resin/hyperbranched aliphatic polyester moisture, *Polymer Test*, 28: 830–835.
- Frigione, M.; Calò, E., 2008, Influence of hyperbranched aliphatic polyester on the cure kinetics of a trifunctional epoxy resin, *J. Appl. Polym. Sci.*, 107: 1744–1758.
- H.S. Tekce; D. Kumlutas; I.H. Tavman, 2007, Effect of particle shape on thermal conductivity of copper reinforced polymer composites, *Journal of Reinforced Plastics and Composites*, 26: 113-121.
- M. S.Bhatangar, 2004, *Polymers Chemistry, Technology of Polymers, Processing and Applications*, Ch. 2, Chand S. Company LTD New Delhi.
- P. H. Laurent, 2000, *Robotics and radiation hardening in the nuclear industry*, Master's thesis, University of Florida, American.
- Paul Gabbott, 2008, *Principles and Applications of Thermal Analysis*, Editor, Blackwell Publishing, Oxford, UK.
- Poulomi Roy; Steffen Berger; and PatrikSchmuki*, 2011, TiO2 Nanotubes: Synthesis and Applications, *Journal of Angew. Chem. Int. Ed.*, 50: 2904 – 2939.
- R. Donald, W. Askelane, and P.P Phule, 2003, *The Science Engineering of Materials*, 4th ed., John Wiley: New York.
- S.M. Marcus and R.L. Blaine, 2013, *Thermal Conductivity of Polymers, Glasses, and Ceramics by Modulated DSC*, TA Instruments TA086.
- Y. Yang, 2007, Thermal conductivity, Ch. 10, *Physical Properties of Polymers Handbook*, edited by J.E. Mark, 2nd ed., Springer.

NOMENCLATURE

| | |
|-----------|---|
| H | Heat, J |
| t | Time, sec |
| λ | Thermal Conductivity, W/K. m |
| T | Temperature, K |
| x | The height of test specimen, m |
| A | Cross-Sectional Area of the test specimen, m ² |
| δ | thermal diffusion equation, m ² / s |
| Cp | the Specific heat capacity, J/km. k |
| ρ | Density, km / m ³ |



| | |
|------------|--|
| ϵ | The Effuisivity, $Ws^{1/2} / m^2 \cdot k$ |
| R | thermal Resistance, $km. k / J$ |
| Li | the initial length |
| Lf | the final length |
| α_l | the linear coefficient of thermal expansion, dimensionless |
| E | Young's modulus, dimensionless |

ABBREVIATIONS

| | |
|------------------|------------------------------|
| MWCNT | Multi-wall carbon nanotube |
| TiO ₂ | Titanium dioxide |
| TMA | Thermomechanical analysis |
| TD | Thermo Dilatometer |
| SEM | Scanning Electron Microscopy |

Table 1. Thermal analyzer by C-Therm Sensor TC- i Values.

| Sample Code | Density ρ Kg/ m ³ | λ (w / m. k) | ϵ ws ^{1/2} /m2.k | δ mm ² / s | Cp (J/kg.k) | R m ² .K /W |
|------------------------|--------------------------------------|-------------------------|---------------------------------------|---------------------------------|----------------|---------------------------|
| Neat Epoxy | 1140 | 0.266 | 630 | 0.18 | 1275.23 | 0.0130 |
| 3wt% TiO ₂ | 1180 | 0.417 | 791.7 | 0.28 | 1270.75 | 0.0083 |
| 5wt% TiO ₂ | 1300 | 0.687 | 1057.3 | 0.42 | 1251.83 | 0.0052 |
| 7wt% TiO ₂ | 1380 | 0.852 | 1206.2 | 0.52 | 1237.72 | 0.0041 |
| 10wt% TiO ₂ | 1500 | 1.20 | 1405.6 | 0.73 | 1097.62 | 0.0023 |

Table 2. Thermal expansion for TMA.

| Sample code | Thermal Expansion $10^{60}C^{-1}$ at 30 ⁰ C | Thermal Expansion $10^{60}C^{-1}$ at 100 ⁰ C | Thermal Expansion $10^{60}C^{-1}$ at 150 ⁰ C | Thermal Expansion $10^{60}C^{-1}$ at 250 ⁰ C |
|------------------------|---|--|--|--|
| Epoxy | 94.72 | 175.55 | 188.74 | 114.74 |
| 3wt% TiO ₂ | 70.53 | 143.87 | 149.2 | 86.94 |
| 5wt% TiO ₂ | 35.86 | 129.03 | 135.36 | 97.16 |
| 7wt% TiO ₂ | 60.97 | 143.11 | 130.20 | 59.62 |
| 10wt% TiO ₂ | 98.87 | 165.45 | 133.78 | 67.45 |



Table 3.E- Modulus and thermal stress by TMA measurement.

| Sample code | E – MPa Modulus 30 °C | E- MPa Modulus 100 °C | E- MPa Modulus 150 °C | E- MPa Modulus 250 °C | $\sigma_{\text{therm. stress}}$ Pa $\Delta T=[30 -250]$ °C | Result Of $\sigma_{\text{th. stress}}$ |
|------------------------|-----------------------------|-----------------------------|-----------------------------|-----------------------------|---|--|
| Epoxy | 144.56 | 18.96 | 23.66 | 51.81 | -2.24 | Expansion |
| 3wt% TiO ₂ | 771.75 | 96.84 | 119.48 | 189.83 | -10.20 | Expansion |
| 5wt% TiO ₂ | 541.86 | 71.13 | 89.50 | 102.46 | -1.23 | Expansion |
| 7wt% TiO ₂ | 173.99 | 52.79 | 58.05 | 107.20 | - 0.32 | Expansion |
| 10wt% TiO ₂ | 210.65 | 66.87 | 78.98 | 112.87 | - 0.12 | Expansion |

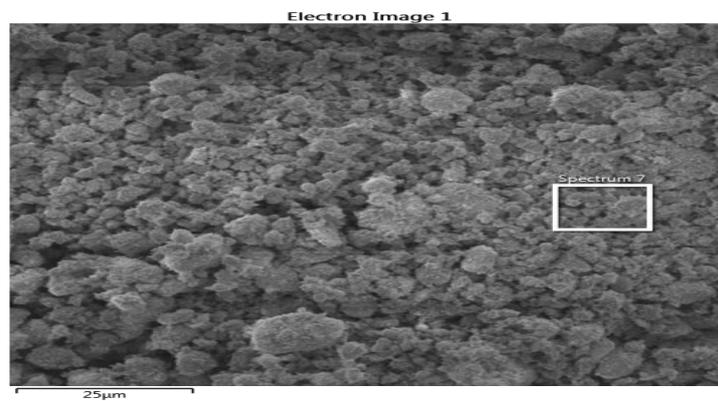
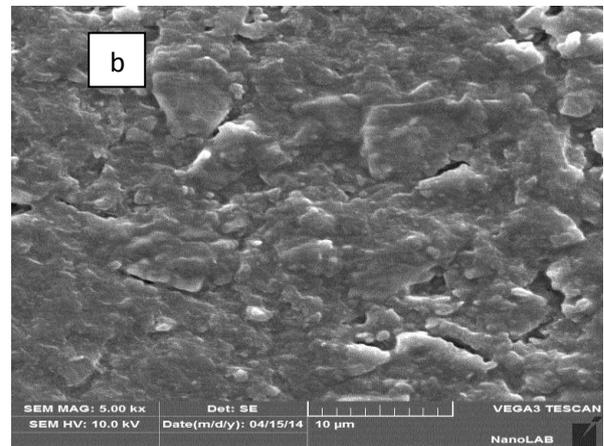
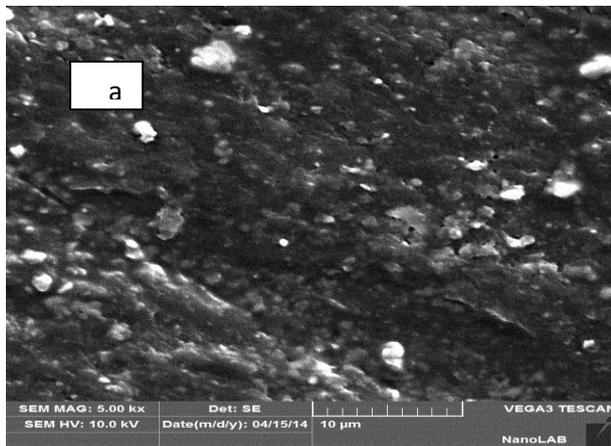


Figure 1. SEM Image of TiO₂ Nano – Powder.



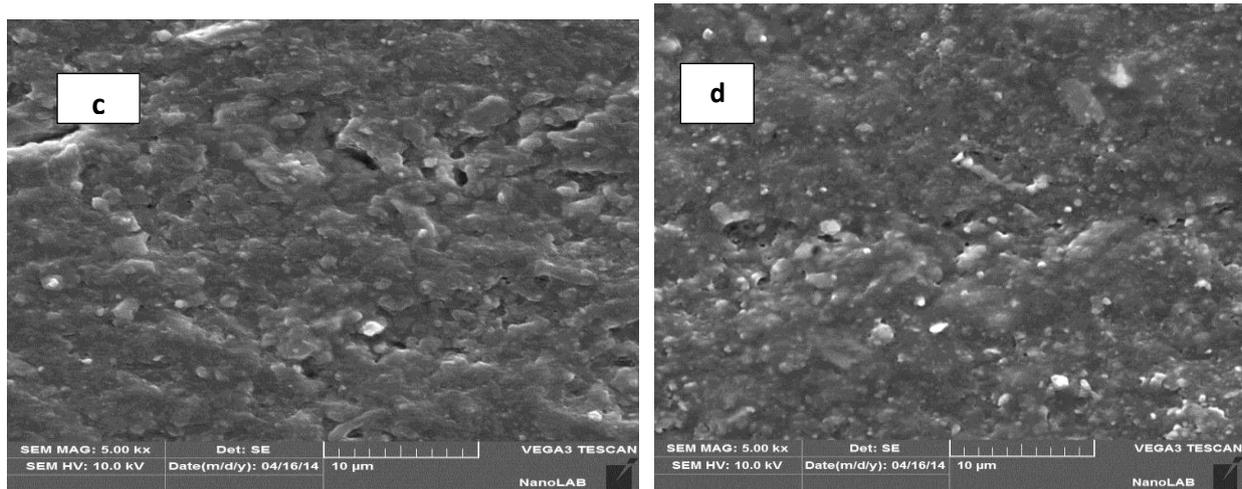


Figure 2. SEM images for Nanocomposites (a) :3wt% TiO₂, (b):5wt% TiO₂ , (c): 7wt% TiO₂ and (d): 10wt% TiO₂.

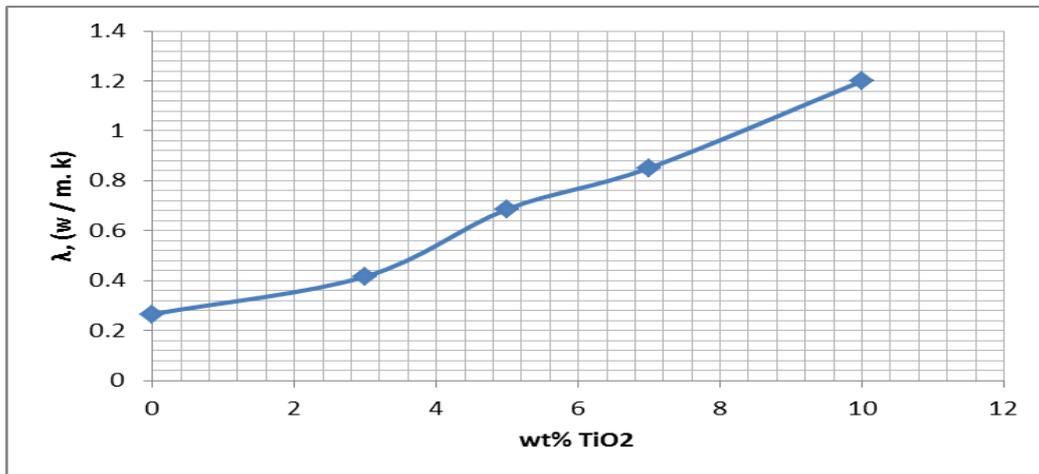


Figure 3. The thermal conductivity against filler content.

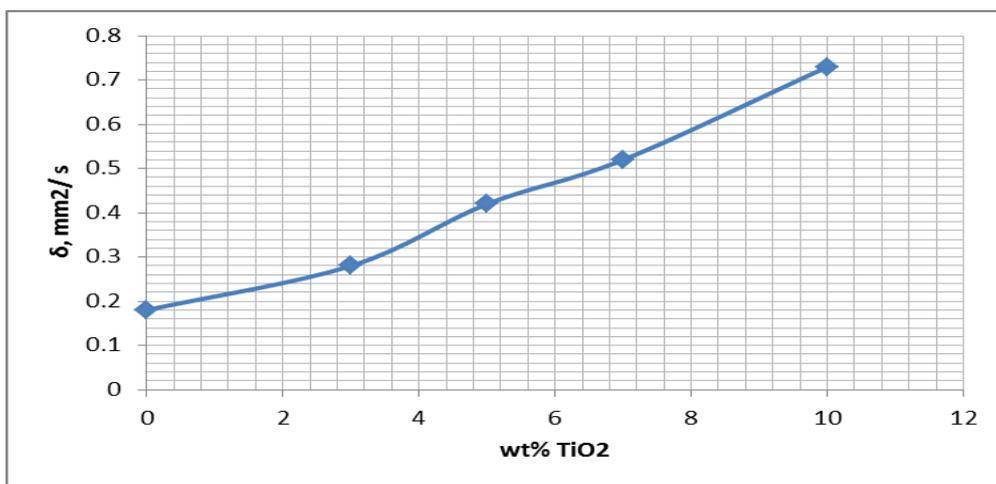


Figure 4. The thermal diffusivity against filler content.

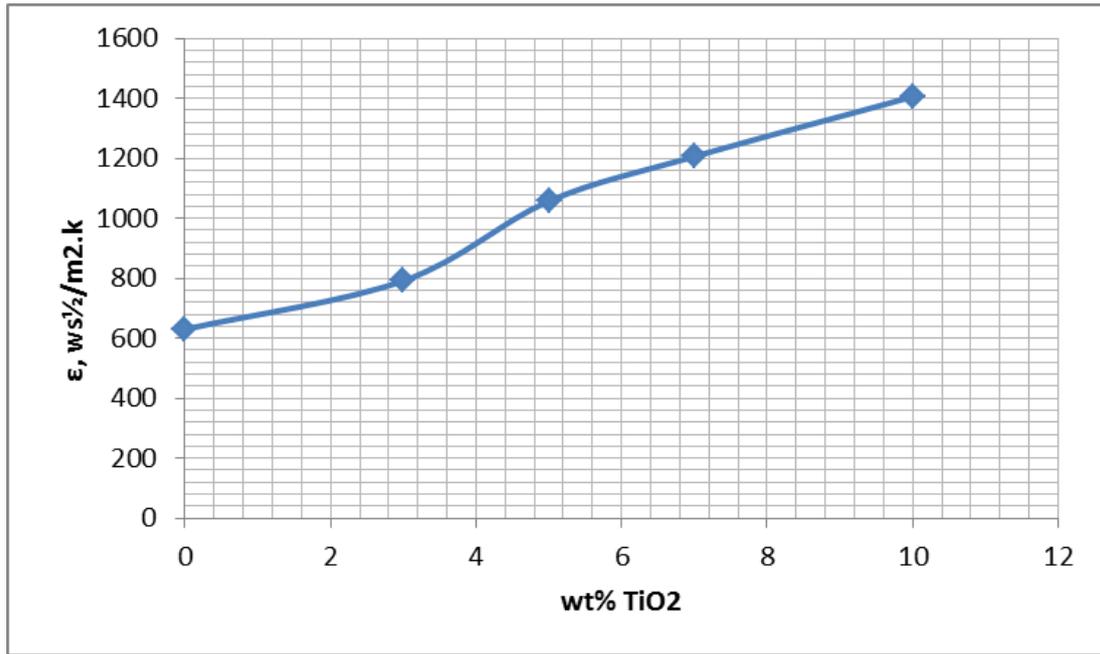


Figure 5. Effusivity against filler content.

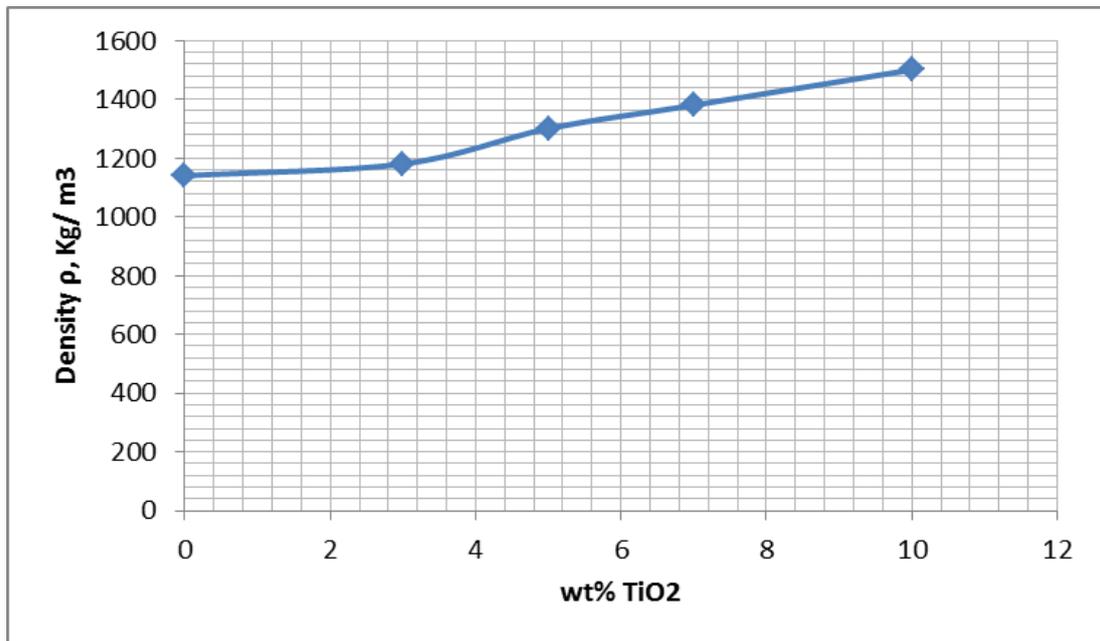


Figure 6. The density against filler content

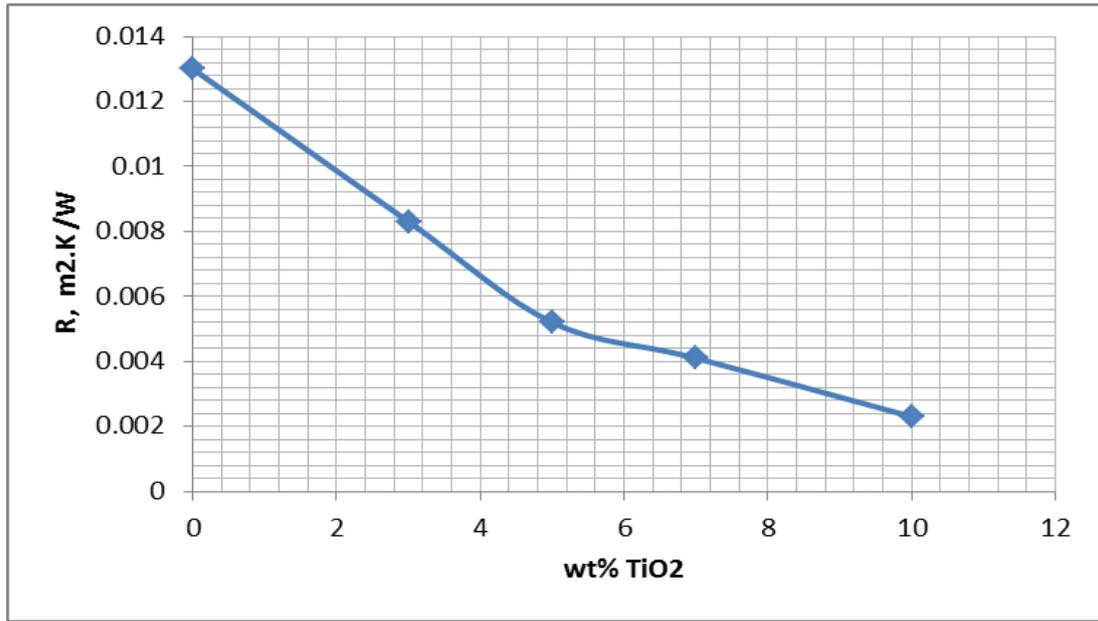


Figure 7. the thermal resistance against filler content.

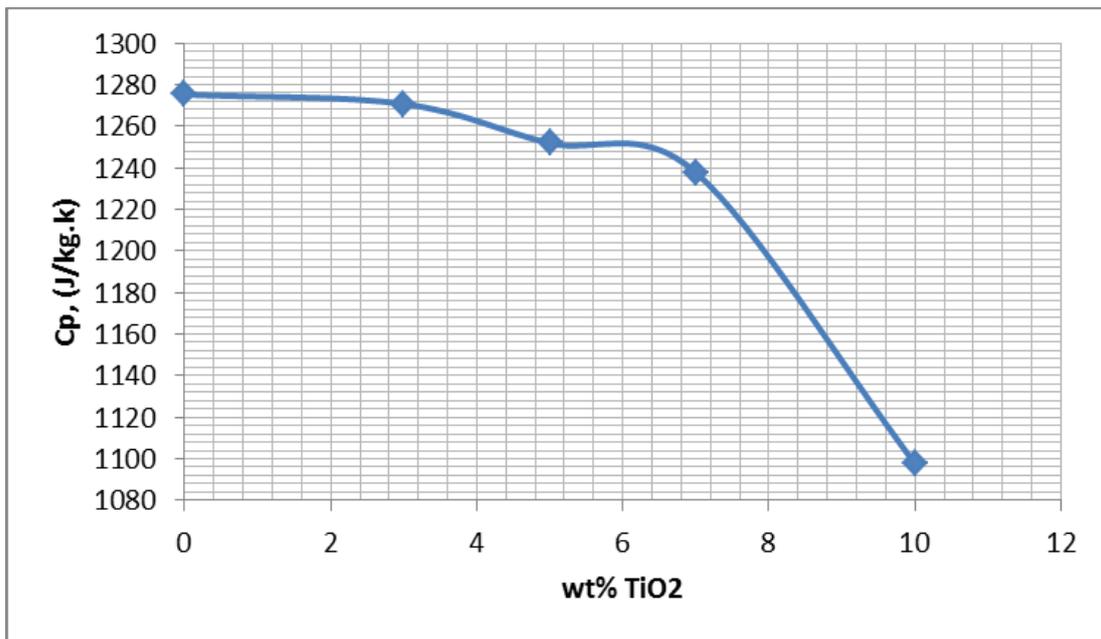


Figure 8. The heat capacities against filler content.

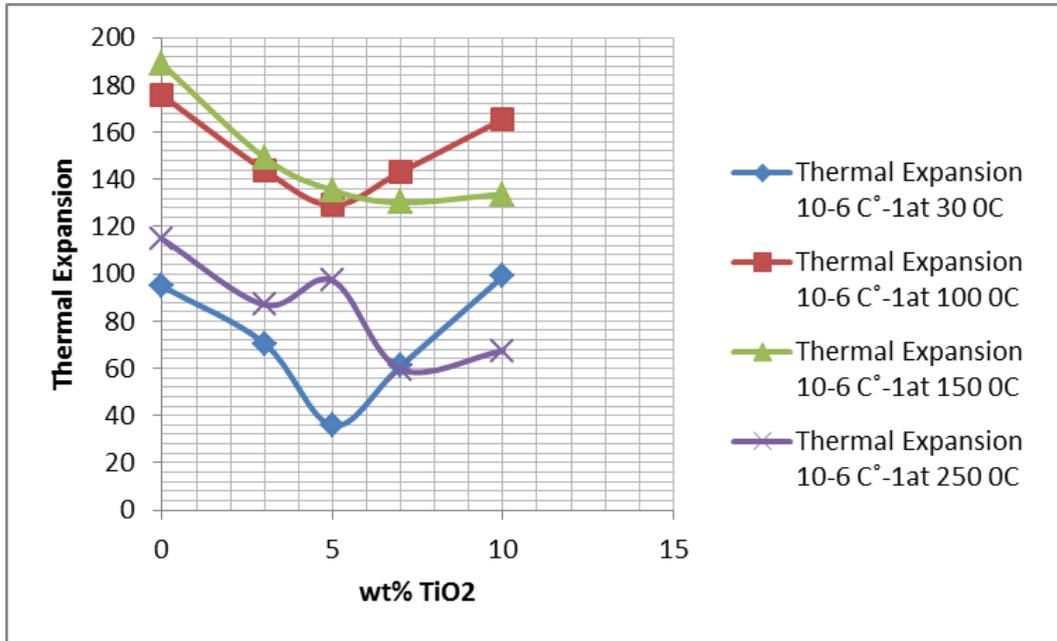


Figure 9. Thermal expansion for TMA.

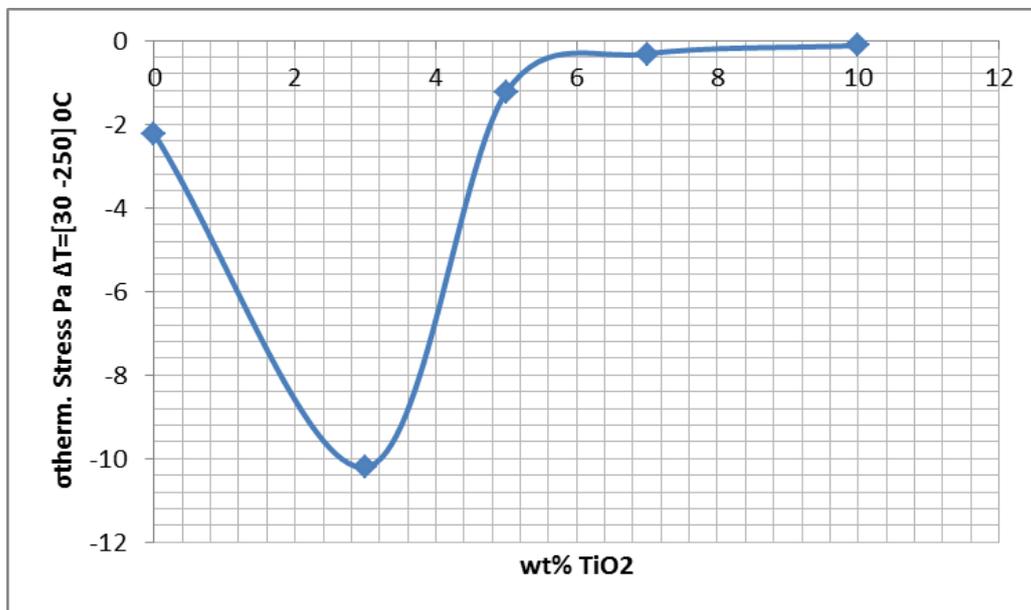


Figure 10. E- Modulus and thermal stress by TMA measurement.