

# Thermal Behavior of Calcium Carbonate and Zinc Oxide Nanoparticles Filled Polypropylene by Melt Compounding

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**Abstract:**-This paper investigates the effect of Calcium Carbonate (CaCO<sub>3</sub> and Zinc Oxide (ZnO) nanoparticles on thermal behavior of virgin and waste polypropylene. CaCO<sub>3</sub> nanoparticles at content of (3, 5, 7, and 10 wt. %) mixed with virgin and waste PP by using co-rotating twin screw extruder at 25 rpm and 190°C. Two techniques used to incorporate ZnO nanoparticles in waste PP in two steps: the first one ZnO nanoparticles mixed with acetone solvents by ultrasonic device and then using twin screw extruder to produce nanocomposite sheet.

Fourier transmitted infrared spectroscopy (FTIR) test used to check the structure of polypropylene. X-Ray Diffraction (XRD) is used to check the crystallinity level of nanocomposite. Thermal conductivity of the modified composite was studied by using thermal coefficient meter model (YBF-3). The qualitative and quantitative temperatures distribution of the extruding polymer nanocomposite is tested by using FLIR thermal camera due to different melt flow rate. Strong relation between crystallinity, thermal conductivity (K) and thermal gradient of nanocomposite is observed. The results show that an improvement in thermal conductivity for both virgin and waste PP with nanoparticles content increasing, thermal conductivity values of waste PP is higher than that of virgin PP and the effect of ZnO nanoparticles is higher than that of CaCO<sub>3</sub> nanoparticles. The results of thermal image indicate that the uniform and smooth surface associate with melt flow rate (MFR) at load 2.16 kg. The temperature gradient increases with MFR values decreasing for waste PP while decreasing for virgin PP.

**Keywords:** crystallinity, melt flow rate, thermography, thermal conductivity, virgin and waste polypropylene, ZnO and CaCO<sub>3</sub> nanoparticles.

## 1. Introduction:-

Polypropylene is a type of semi crystalline thermoplastic polymer; which is widely used in variety of applications including packaging and labeling, textiles (e.g., ropes, thermal underwear and carpets), reusable containers of various types, laboratory equipment, loudspeakers, automotive components, and polymer banknotes. Due to its high strength-to-weight ratio, it is more rigid than other polyolefin. It has the highest melting temperature (160–170°C). Reusing of plastic materials is strategically very important for the environmental policy of industry (Maier et al, 1998).

Nanocomposite is an attractive class of materials providing novel performance. Due to some of their remarkable properties at low filler loading (less than 10 wt. %), they are being increasingly adopted by industry in the displacing the use of conventional filler materials. A variety of nanoparticles, are capable of enhancing thermal properties of nanocomposite.  $\text{CaCO}_3$  is one of the most common and inexpensive inorganic fillers that have been used in the nanocomposite preparation process (Sanaz et al, 2010; Di Lorenzo et al, 2002). Zinc oxide (ZnO), is a new kind of material, and is rather common material which is used for a quite large variety of different applications and widely used in polymer material due to its ability in enhancement the thermal properties because of low thermal expansion and high melting temperature (1900°C) (Filiz Ozmihci Omurlu, 2009; Ong Hui, 2009).

Thermal conductivity of polymers is an important thermal property for both polymer applications and processing. Polymers typically have thermal conductivity much lower than those for metals or ceramic materials. In other applications which require higher thermal conductivity, such as in electronic packaging and encapsulations, satellite devices, and in areas where good heat dissipation, low thermal expansion and light weight are needed, polymers reinforced with fillers, organic or inorganic, are becoming more and more common in producing advance polymer composite for these applications (M. H. Vakili et al, 2011).

The term thermography and thermo-vision include testing methods based on registering infrared part of radiation spectrum produced by body which then converted by special camera into a color map of temperature. Thermal imaging technology has become one of the most valuable diagnostic tools for industrial applications (M. Szczepanik et al, 2008).

In this work the effect of CaCO<sub>3</sub> and ZnO nanoparticles on thermal behavior of polypropylene and its waste was investigated. Different ratio of nanoCaCO<sub>3</sub> mixed with virgin PP (VPP) and waste PP (WPP) by using twin screw extruder and the same ratio of ZnO nanoparticles mixed with WPP by using sonication process and the same twin screw extruder at 190°C and 25rpm. Thermal conductivity and thermal image is used as indicators for thermal behavior. Thermal conductivity is tested due to different nanoparticles percentage. The magnitude and behavior of temperature distribution due to MFR behavior are examined.

## **2. Materials and method:-**

The materials used were polypropylene homo-polymer, 575-S (MFR= 8.3 g/10 min), was supplied by Subic company, and (CaCO<sub>3</sub> and ZnO) nanoparticles were supplied by (Shijiazhuang Sun power Technology Co., Ltd, Chain) with particle size about 15.88 and 40 nm respectively.

### **2.1 Preparation of the Nanocomposite:-**

Virgin and waste PP pellets and CaCO<sub>3</sub> immersed in alcohol solution and mechanically mixed in twin screw extruder (SLJ). The screw speed rang (0-320) rpm and screw diameter is 30mm, the power of main motor and heating (4KW and 3KW) respectively. The virgin PP/CaCO<sub>3</sub> nanoparticles and waste PP/CaCO<sub>3</sub> nanoparticles are mixing in the twin screw extruder at 25 rpm and 190°C. While the nanocomposite of waste PP/ZnO prepared by mixing ZnO nanoparticles with acetone solvent by ultrasonic device and then blended with waste PP pellets by using twin screw extruder at 25 rpm and 190°C.

## **3. Characterization:-**

### **3.1 Structure Test:-**

FTIR device Japanese originator (Kyoto Japan) company (Shimatzu Corporation) types (IRAFFINITY-1) was used to perform the physical tests to find out the structure of polypropylene. This technique is based on the simple fact that a chemical substance shows selective absorption in the IR region giving rise to close-packed absorption bands called an IR absorption spectrum, over a wide wavelength range. Various bands present in the IR spectrum correspond to the characteristic functional groups and bonds present in a chemical substance. The powder of PP pellets was mixing with potassium bromide (KBr) material at percentage of 1:3, then compressed into a thin disk and starting the test.

The **XRD** experiments were performed using a Rigaku Diffract meter with Cu  $K\alpha$  radiation (30 mA and 40 kV) from 10 theta to 40 theta at scanning speed of 2°/minute on samples which have been surface target using Cu, and the preset time is 0.24(sec) to show the crystallinity levels of the nanocomposite waste PP with different nanoparticles (ZnO and CaCO<sub>3</sub>).

## **2-Thermal Properties:-**

Thermal coefficient meter model (YBF-3) as shown in (Figure1)with upper and lower plate of Copper material is used to determine the effect of nanoparticles (CaCO<sub>3</sub> and ZnO) on thermal properties of polypropylene and its waste at 100°C. The samples were prepared using thermal hydraulic pressing type (XLB-plate vulcanizer). The hydraulic pressure hot pressing machine at 200°C, 7Mpa and 15 minute are used for preparation samples in dimensions of (65mm radius and 2mm thickness).

The temperatures distribution and thermal behavior on surface of polymer nanocomposite melts through the capillary of melt mixer is examined using **thermal camera** type FLIR T6xx series as shown in (Figure 2). Quantitative and qualitative temperatures distribution can be obtained; during the extruding process of each polymer nanocomposite in melt flow index device the melt flow rate (MFR) value and thermal image were taken. The relation between MFR and thermal behavior was investigated.

## **4. Results and Discussion:-**

### **Structure:-**

FTIR is used to know the special function group and find the chemical structure of materials depended on IR spectrum. (Figure 3): FTIR chart of polypropylene, which show the main peak of polypropylene, the main peak at (2800-3200) cm<sup>-1</sup> wave number represented the stretch C-H group, while the peak at 1700 cm<sup>-1</sup> represented C=O which appear slightly due to exposed the mixture to air and then oxidation process. The third peak at (1000-1200) cm<sup>-1</sup> wave number represented C-C bond this is a good agreement with the results of (Barbara, 2004).

Figure 4: shows the crystallinity level of neat PP and the nanocomposite with (5 and 10 wt. % CaCO<sub>3</sub>) at 25 rpm. The nanocomposite shows sharp and highly intense peaks while neat PP shows less intense peaks. This may be due to the development of crystallinity in the polymer. The crystallinity increases with CaCO<sub>3</sub> content increasing, this is due to CaCO<sub>3</sub> nanoparticles filling the holes and orienting the chains so the crystallinity increases.

Figure 5: indicates the crystallinity levels of waste PP and its nanocomposite of 5 and 10wt. % of  $\text{CaCO}_3$  at 25 rpm. The crystallinity level for virgin PP is higher than that of its waste at 25 rpm because nanoparticles may be not filling the hole completely in addition to contamination effect.

Figure 6: shows the crystallinity levels of WPP and its nanocomposite with different weight percentage of ZnO nanoparticles (5 and 10). It's very clear that the crystallinity level increases with the nanoparticle percentage increasing and appears as a new peaks at  $2\theta$  ( $30^\circ$ - $40^\circ$ ) which mean the exists of ZnO nanoparticles through the polypropylene matrix and acts as filler. The increasing of crystallinity level is strongly effect on the thermal conductivity behavior.

### 4.3 Thermal Conductivity:-

The effect of nanoparticles ( $\text{CaCO}_3$  and ZnO) on thermal conductivity of VPP and its waste are shown in (Figures 7 and 8). The values of thermal conductivity increased with the nanoparticle concentration and crystallinity level increasing. The thermal conductivity values of ZnO/WPP nanocomposite is more than that of  $\text{CaCO}_3$ /WPP nanocomposite due to the nature of nano-filler and crystallinity degree as shown in Fig (4, 5, 6) and from fact that the intrinsic thermal conductivity of the ZnO nanoparticles is higher than that of  $\text{CaCO}_3$  this results is compatible with the results of (Di Lorenzo et al, 2002, M. H. Vakili et al, 2011).The VPP and WPP show significant and clear difference for thermal conductivity up to 3% of  $\text{CaCO}_3$  after that the convergence occur gradually up to 10%wt. therefore ZnO nanoparticles is more suitable to improve thermal conductivity in addition to the environmental and cost benefits.

The K value increases to about 65% for ZnO polymer nanocomposite while about 60% for  $\text{CaCO}_3$  polymer nanocomposite, this fact can be attributed to the intrinsic thermal conductivity of both nanoparticles and their large surface area which even at lower loadings of nano-fillers they are still effective to transfer heat through the samples, at a higher volume fraction, this effect becomes stronger. Again the ZnO/WPP nanocomposite is approximately better than  $\text{CaCO}_3$ /WPP nanocomposite which supports the using of waste PP to reduce the cost of final product and the effect of waste PP on the environmental.

Figure 9: show thermal images of VPP granules at melt flow rate test at 230  $^\circ\text{C}$  and different loads (1.965, 2.16 and 3.80 kg). It can be seen that the temperatures

range increases with loads increasing and the surface at 2.16kg is more stable and smoother as compared with the other loads.

The temperature gradient at 1.965, 2.16 and 3.80 kg are 8, 7.5 and 9.3 °C respectively this gives an indicator that 2.16 kg is the best load to produce surface free of defects as shown in Figure 10.

Figure 11: shows the thermo-graphic image taken at the automatically cutting region of MFR test at 2.16 kg of virgin polypropylene nanocomposite. The results show that the temperatures difference  $\Delta T$  value increases with  $\text{CaCO}_3$  nanoparticles content increasing. All specimens produced the same color due to a good homogenous distribution of nanoparticles through polymer matrix.

Figure 12 presents a thermo-graphic image taken at the automatically cutting region of MFR test at 2.16 kg of waste PP due to  $\text{CaCO}_3$  nanoparticles percentage. The results show that the  $\Delta T$  values increases with MFR values decreasing as results of addition of  $\text{CaCO}_3$  nanoparticles.

Figure 13 shows that the thermal images of waste PP with different ZnO nanoparticles content. The results show that the  $\Delta T$  value increases with MFR decreasing at ZnO nanoparticles content of 3, 5,7and 10%wt., which is compatible with the 0.38, 0.41, 0.46 and 0.53 w/m.k thermal conductivity of these material respectively.

## **5. Conclusion**

There is a clear relationship between the flow and crystallinity of polymers in the extrusion process and the thermal behavior and polymer structure. Conducting all these properties can be controlled on the conditions of the polymers manufacturing processes and reduce the defects that could appear in the final products moreover to improve the surface quality and dimensional stability. The increasing of thermal conductivity and crystallinity with the increase of nanoparticles concentrations is interesting results. The relation between the flow and thermal behavior of polymer melts nanocomposite can be used to explain the effect of temperatures gradient on the surface quality. Also of linkage between the flow of the molten polymer nanocomposite and thermal behavior can notice that the difference in the form of surface and the temperature gradient depending on the added nanoparticles type and their concentration.

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### **Figure Captions:**

Figure 1. Thermal conductivity device

Figure 2. FLIR thermal camera (T640)

Figure 3. FTIR for polypropylene

Figure 4. XRD for: (A) neat PP, (B) 5%CaCO<sub>3</sub>, (C) 10% CaCO<sub>3</sub> nanocomposite at 25 rpm.

Figure 5. XRD (A) waste PP, (B) 5%CaCO<sub>3</sub>, (C) 10% CaCO<sub>3</sub> nanocomposite at 25 rpm.

Figure 6. The crystallinity level of nanocomposite: (A) neat waste PP (B) 5% ZnO (C) 10%ZnO nanoparticles.

Figure 7. Thermal conductivity behavior for virgin and waste PP with different CaCO<sub>3</sub> nanoparticles concentration at 100°C

Figure 8. Thermal conductivity behavior for waste PP with different ZnO nanoparticles concentration at 100°C

Figure 9. The relation between melt flow rate and thermal images at different three loads

Figure 10. Thermal Images of pure virgin PP at different loads: - (A) 1.695kg, (B) 2.16kg and (C) 3.80 kg at line (Li1).

Figure 11. Thermal image of virgin PP nanocomposite :-( A) 3%, (B) 5%, (C) 7% and (D) 10wt% of CaCO<sub>3</sub> Nanoparticles

Figure 12. Thermal image of waste PP nanocomposite:- ( A) 3%, (B) 5%, (C) 7% and (D)10 wt.% of CaCO<sub>3</sub> nanoparticles

Figure 13. Thermal image of waste PP nanocomposite:- ( A) 3%, (B) 5%, (C) 7% (D)10wt% of ZnO nanoparticles





Fig. 1



Fig. 2

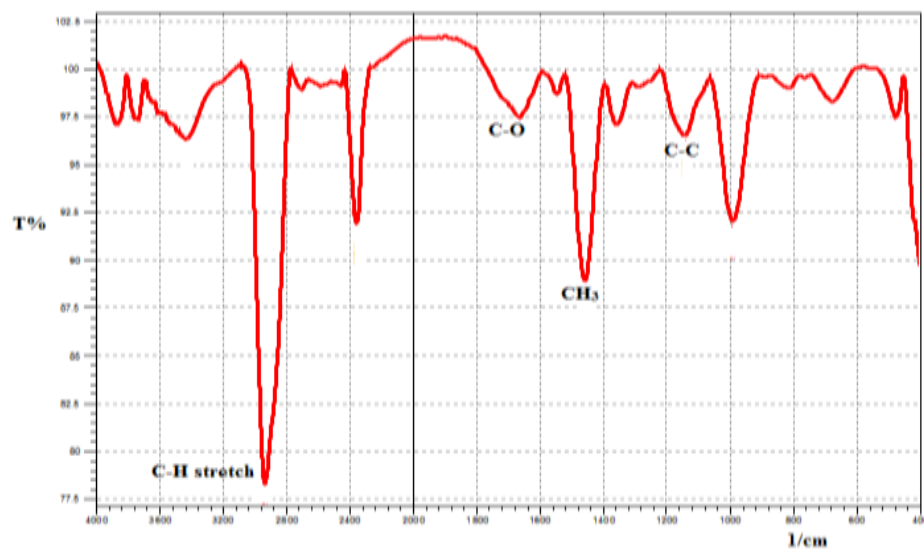


Fig. 3

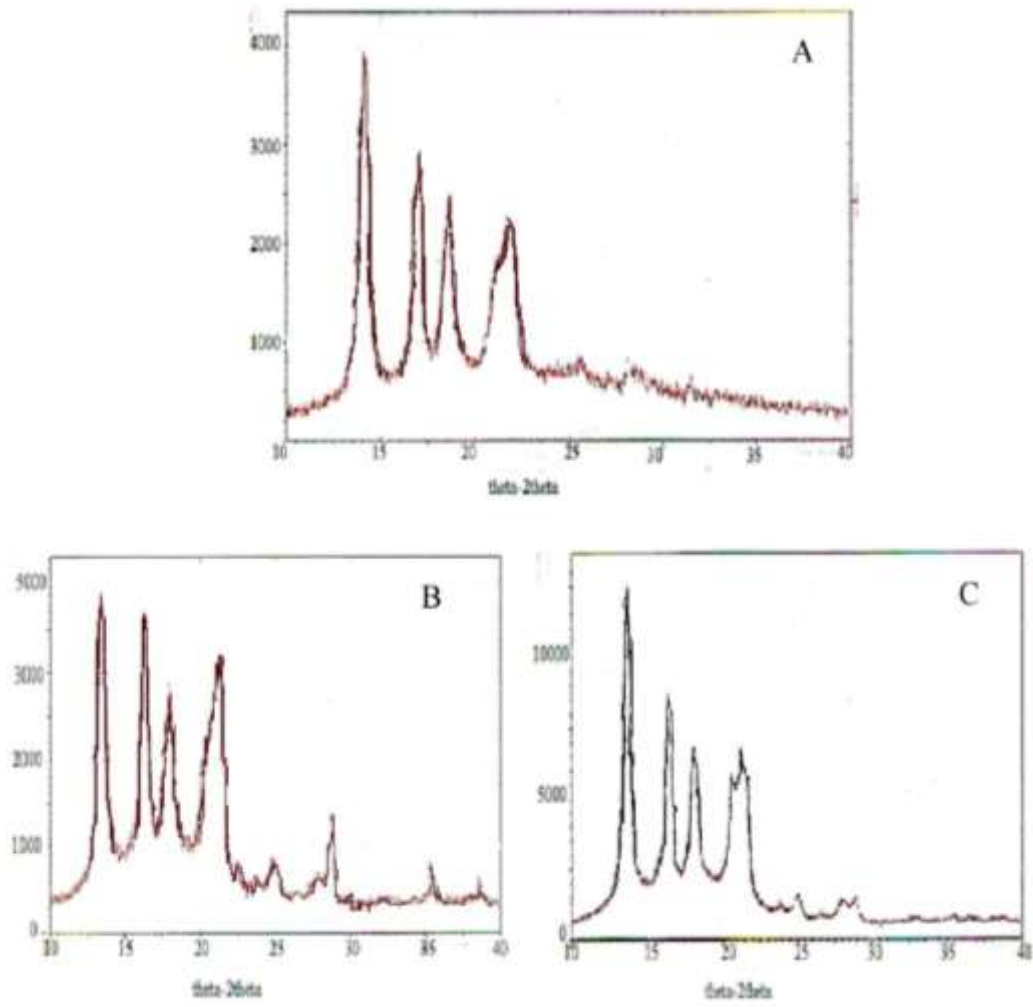


Fig. 4

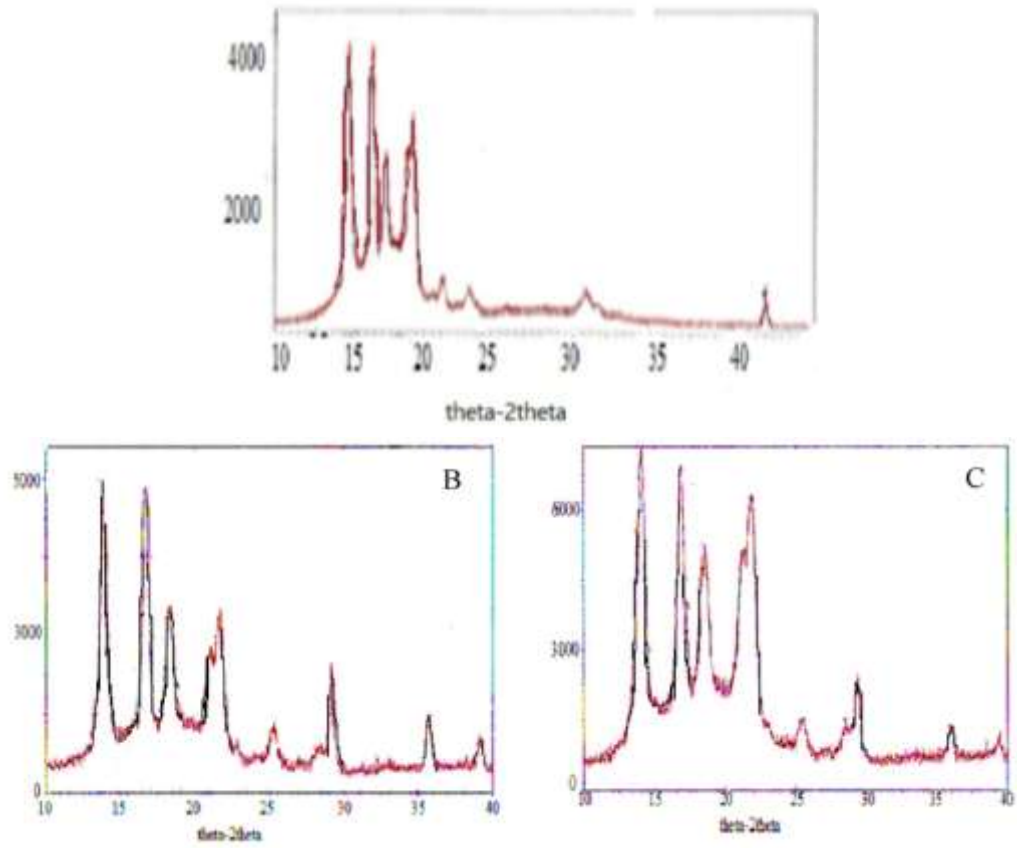


Fig. 5

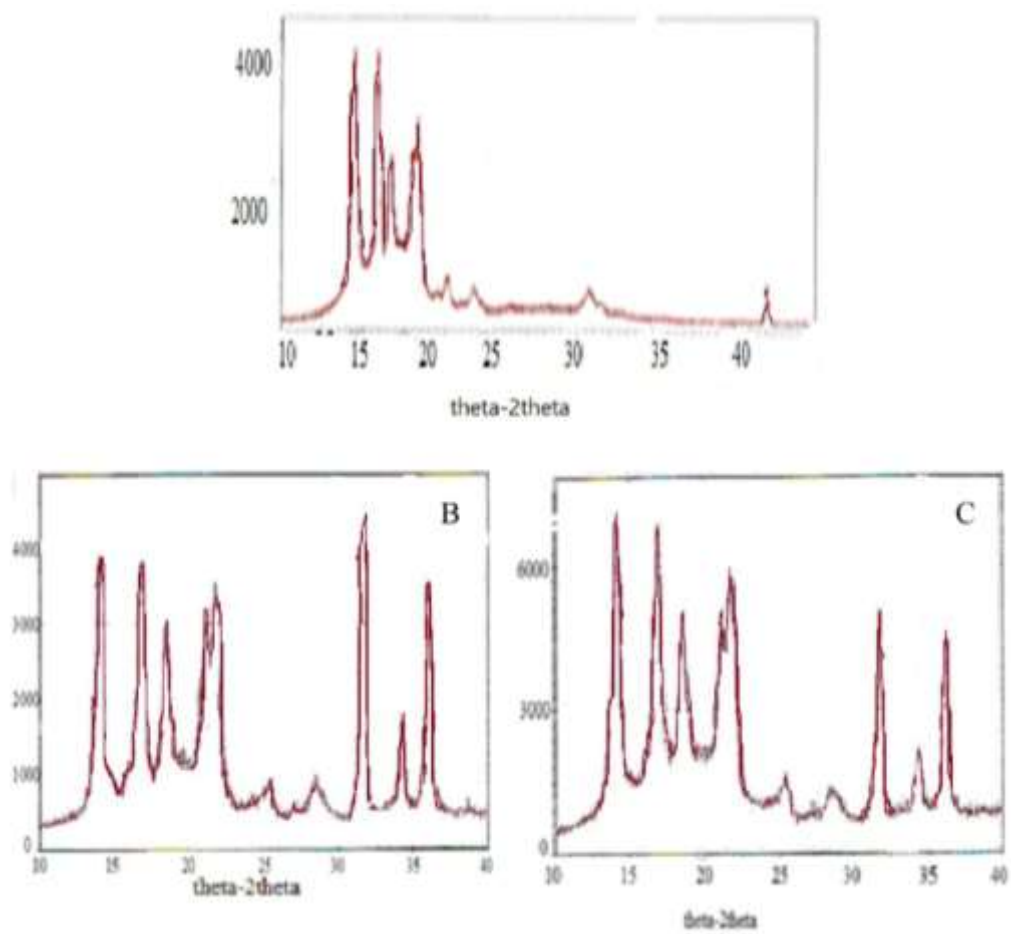


Fig. 6

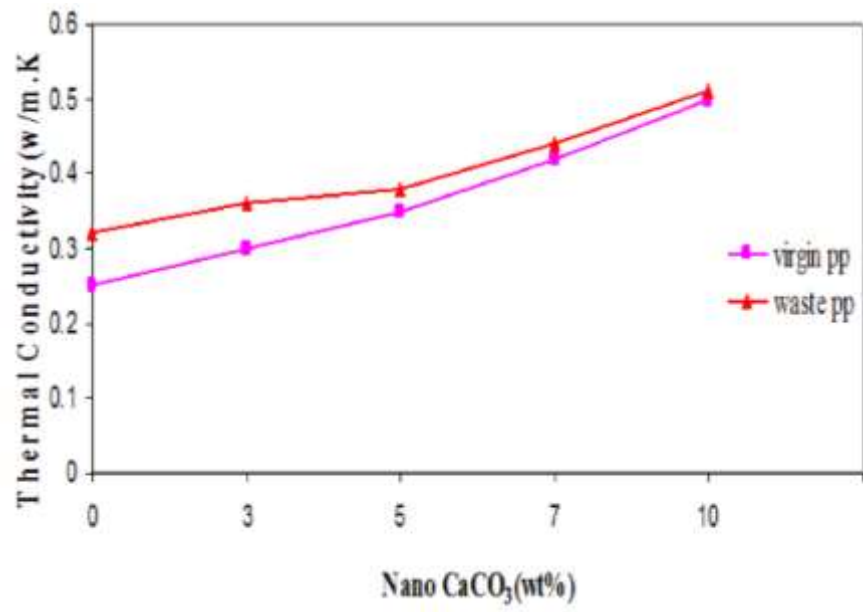


Fig. 7

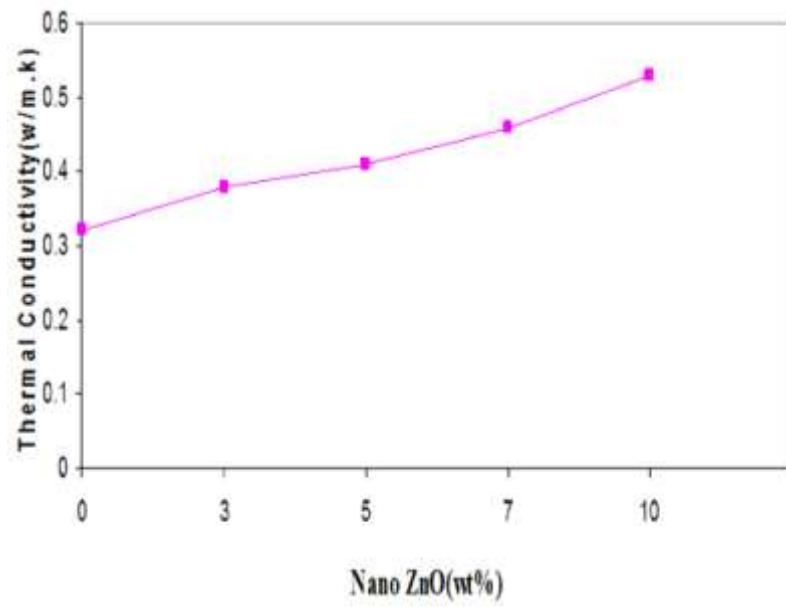


Fig. 8

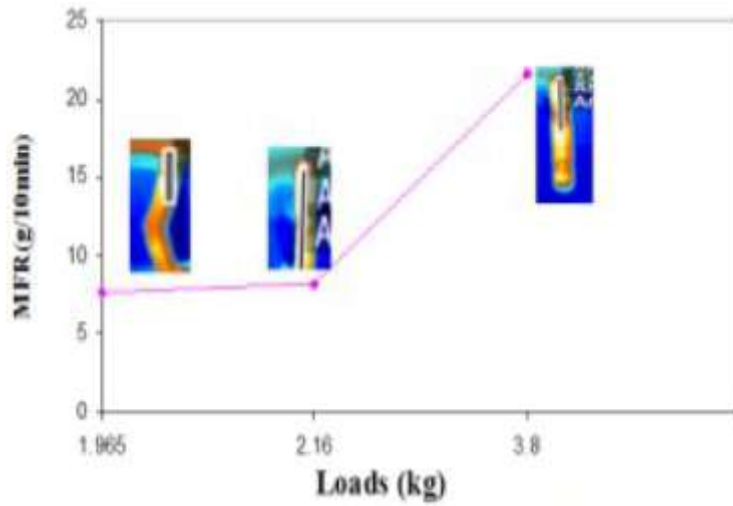


Fig. 9

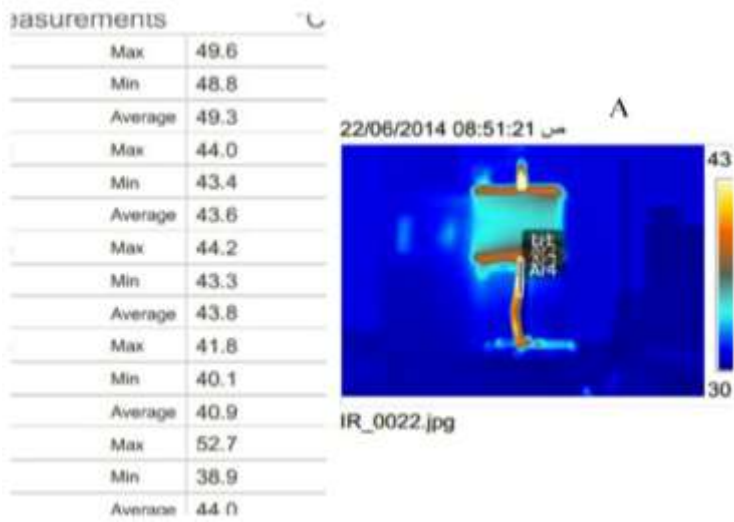


Fig. 10 (A)

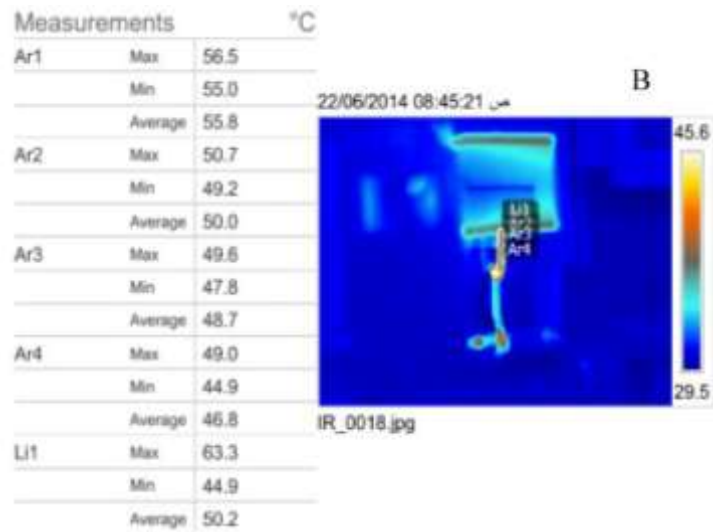


Fig. 10 (B)

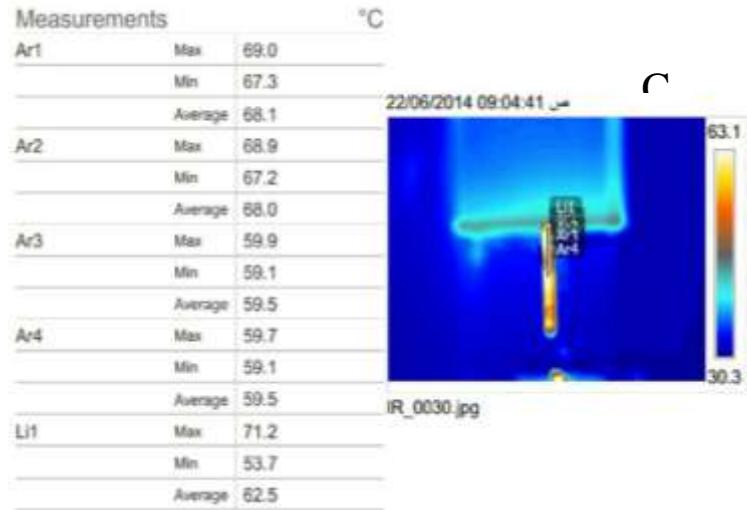


Fig. 10 (C)

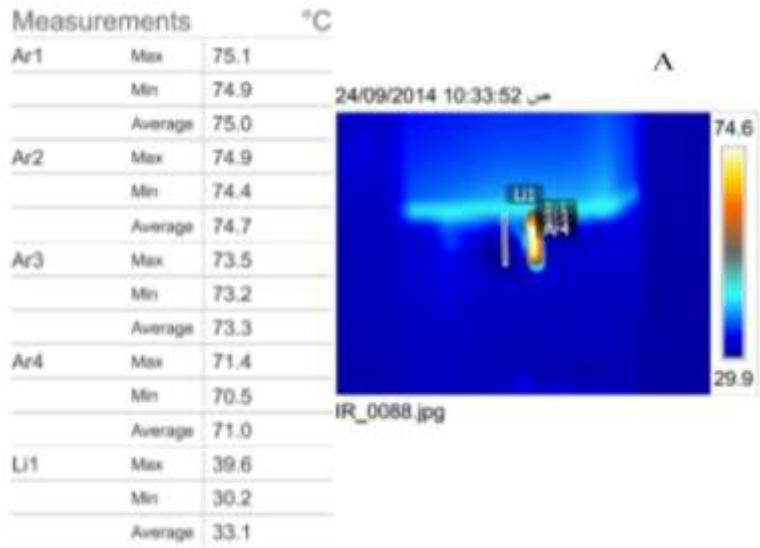


Fig. 11(A)

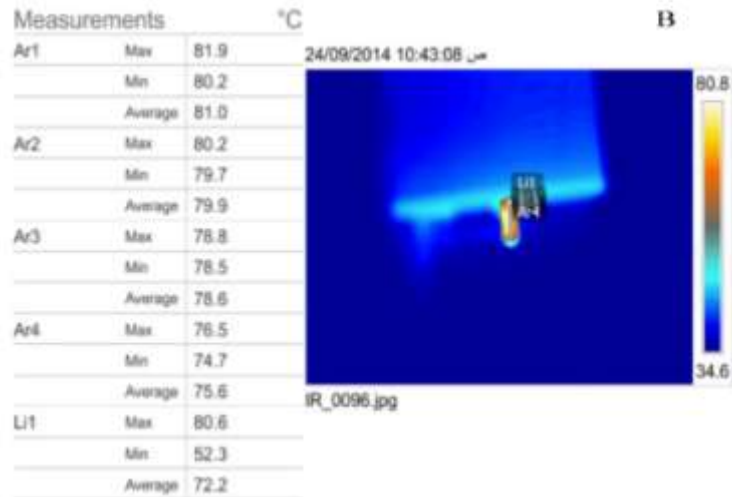


Fig. 11(B)

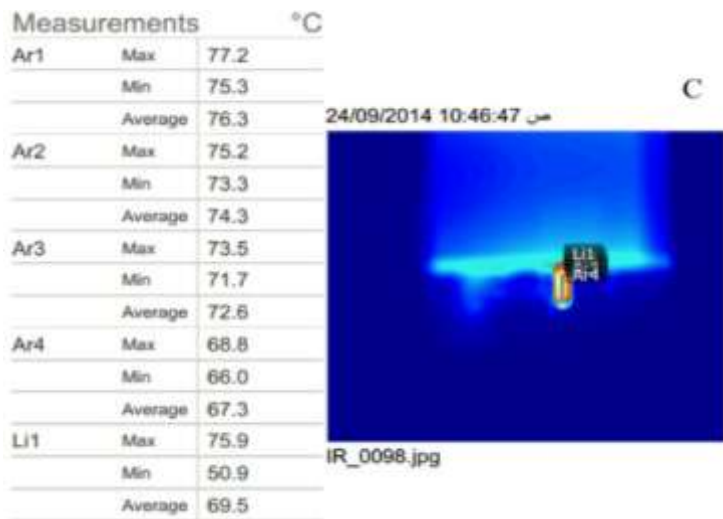


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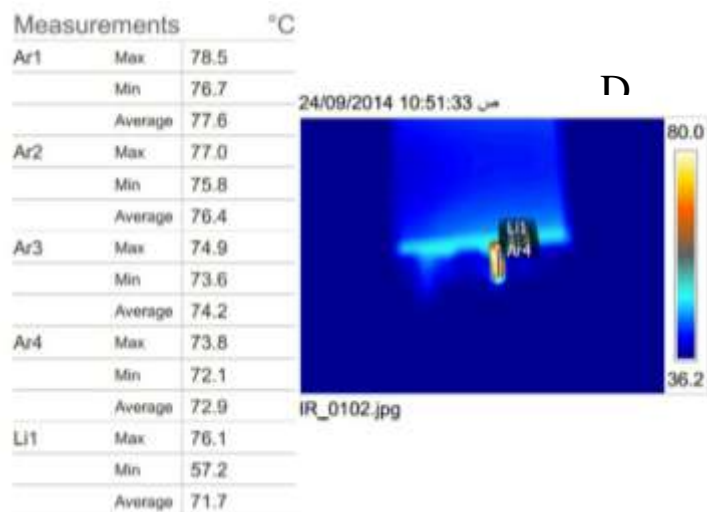


Fig. 11(D)



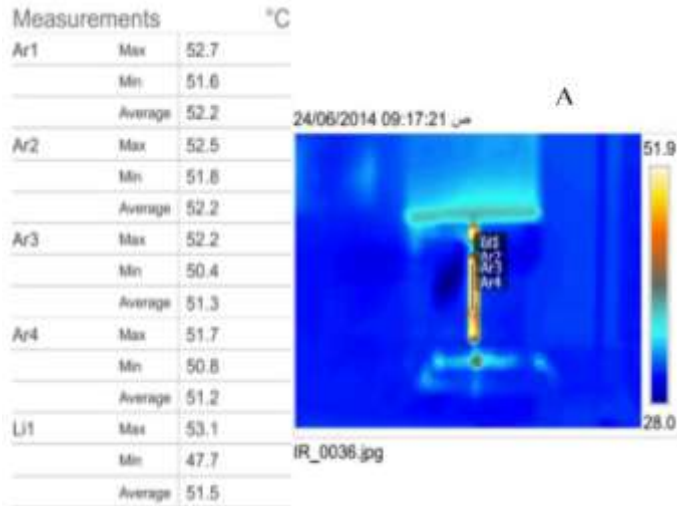


Fig. 12(A)

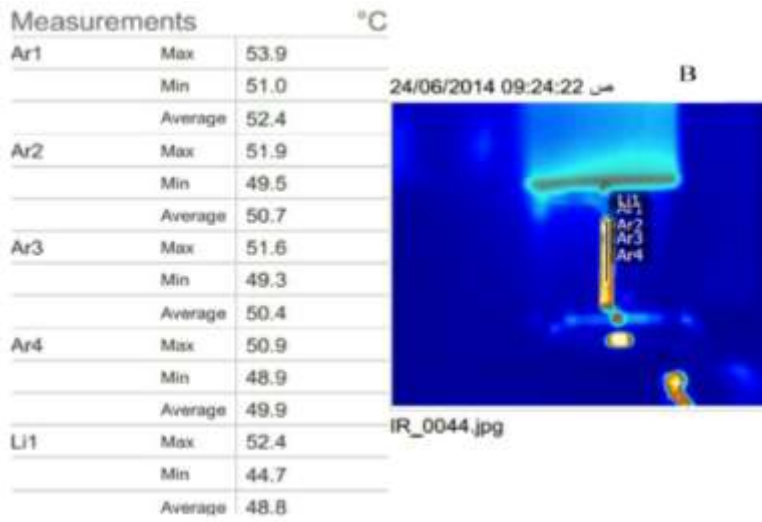


Fig. 12(B)

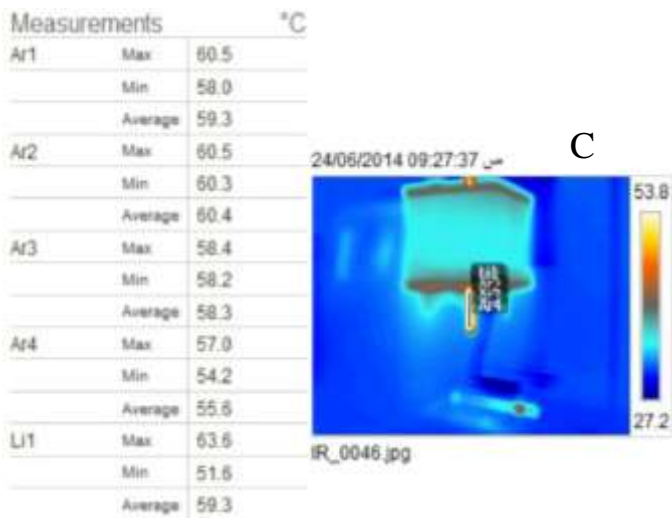


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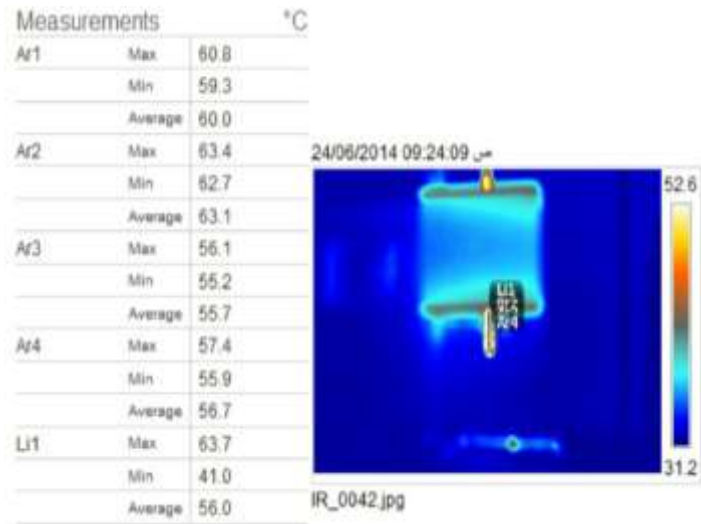


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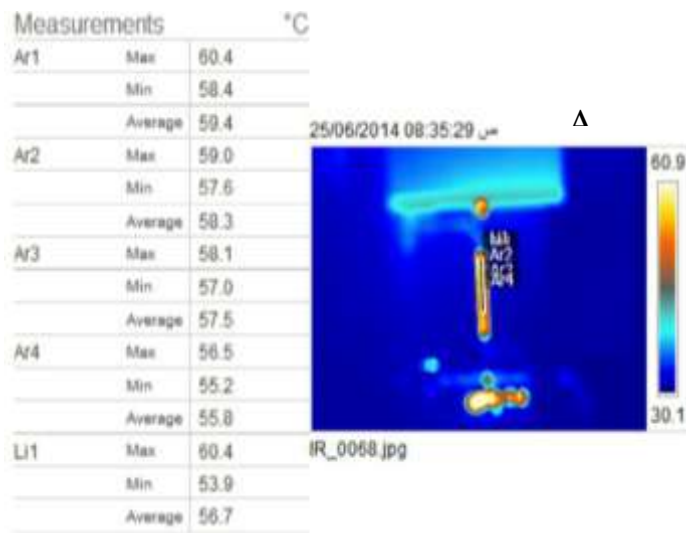


Fig. 13(A)

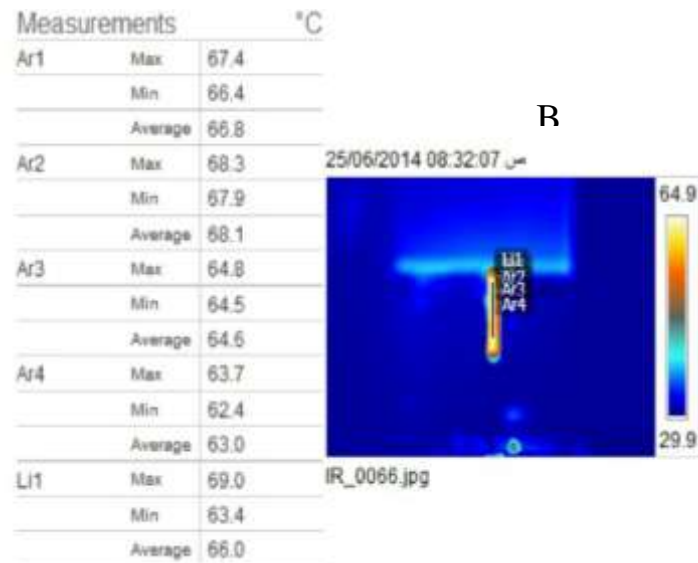


Fig. 13(B)

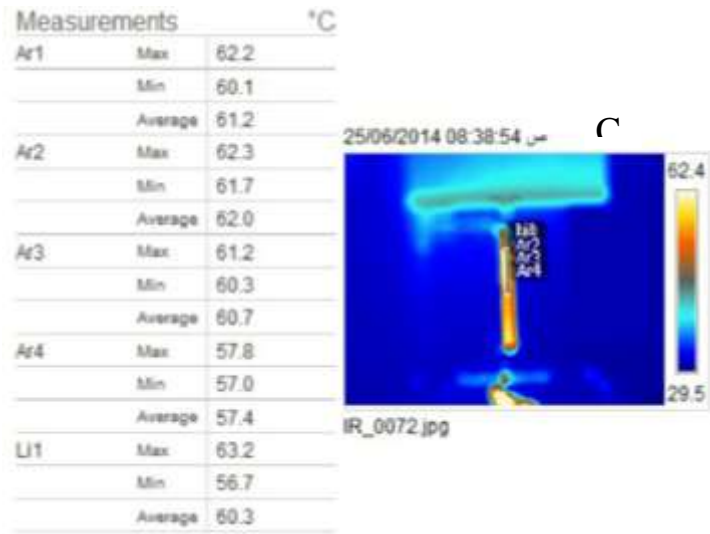


Fig. 13(C)

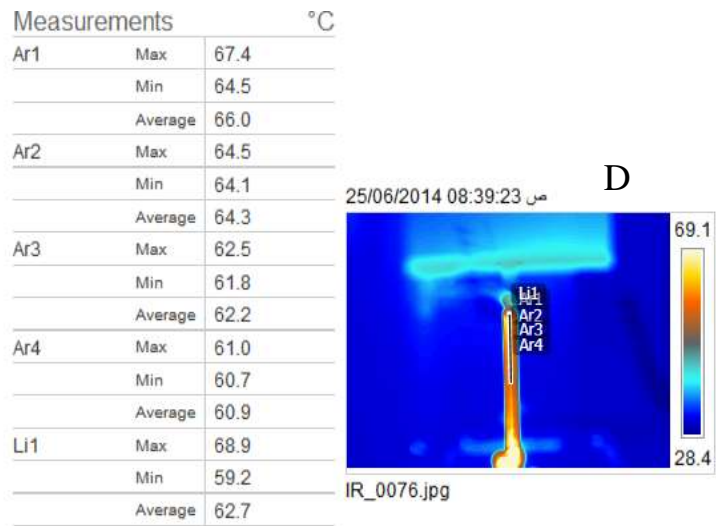


Fig. 13(D)