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Research Article

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

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Abstract: This study investigates the effect of Calcium Carbonate and Zinc Oxide nanoparticles on thermal behavior of virgin and waste polypropylene. $CaCO_3$ 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 Infraredspectroscopy (FTIR) test used to check the structure of polypropylene. X-Ray Diffraction is used to check the crystallinity of nanocomposite. Thermal conductivity of the modified composite was studies 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 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 $CaCO_3$naoparticles. 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 $CaCO_3$ nanoparticles

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 and Calafut, 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. $CaCO_3$ is one of the most common and inexpensive inorganic fillers that have been used in the nanocomposite preparation process (Abdolmohammadi *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) (Özmihçi Ömürlü, 2009; Ong *et al*., 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 (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

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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 (Szczepanik *et al*., 2008).

In this study the effect of $CaCO_3$ and ZnO nanoparticles on thermal behavior of polypropylene and its waste was investigated. Different ratio of nano$CaCO_3$ 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 25 rpm. Thermal conductivity and thermal image is used as indicators for thermal behavior. Thermal conductivity is tested due to different nanoparticles percentage is tested. The magnitude and behavior of temperature distribution due to MFR test are examined.

MATERIALS AND METHODS

The materials used were polypropylene homo-polymer, 575-S (MFR = 8.3 g/10 min), was supplied by Subic company and ($CaCO_3$ and ZnO) nanoparticles were supplied by (Shijiazhuang Sun power Technology Co., Ltd, Chain) with particle size about 15.88 and 40 nm, respectively.

Preparation of the Nanocomposite: Virgin and waste PP pellets and $CaCO_3$ immersed in alcohol solution and mechanically mixed in twin screw extruder (SLJ). The screw speed rang (0-320) rpm and screw diameter is 30 mm, the power of main motor and heating (4 KW and 3 KW), respectively. The virgin PP/$CaCO_3$ nanoparticles and waste PP/$CaCO_3$ 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.

Characterization:

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 absoarption 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 allocated to the sample and starting the test.

The XRD experiments were performed using a Rigaku Diffract meter with Cu Kα radiation (30 mA and 40 kV) from 10 theta to 40 theta at scanning speed of 2°/min 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 $CaCO_3$).

Fig. 1: Thermal conductivity device

Fig. 2: FLIR thermal camera (T640)

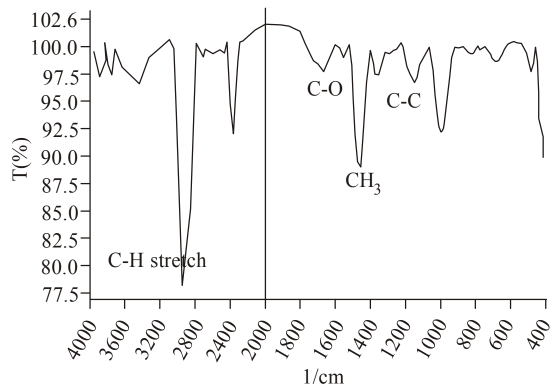


Fig. 3: FTIR for polypropyle

Thermal properties: Thermal coefficient meter model (YBF-3) as shown in Fig. 1 with upper and lower plate of copper material is used to determine the effect of nanoparticles ($CaCO_3$ 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 min are used for producing sample in dimensions of (65 mm radius and 2 mm 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 Fig. 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.

RESULTS AND DISCUSSION

Structure: FTIR is used to know the special function group and find the chemical structure of materials depended on IR spectrum (Fig. 3). FTIR chart of polypropylene, which show the main peak of

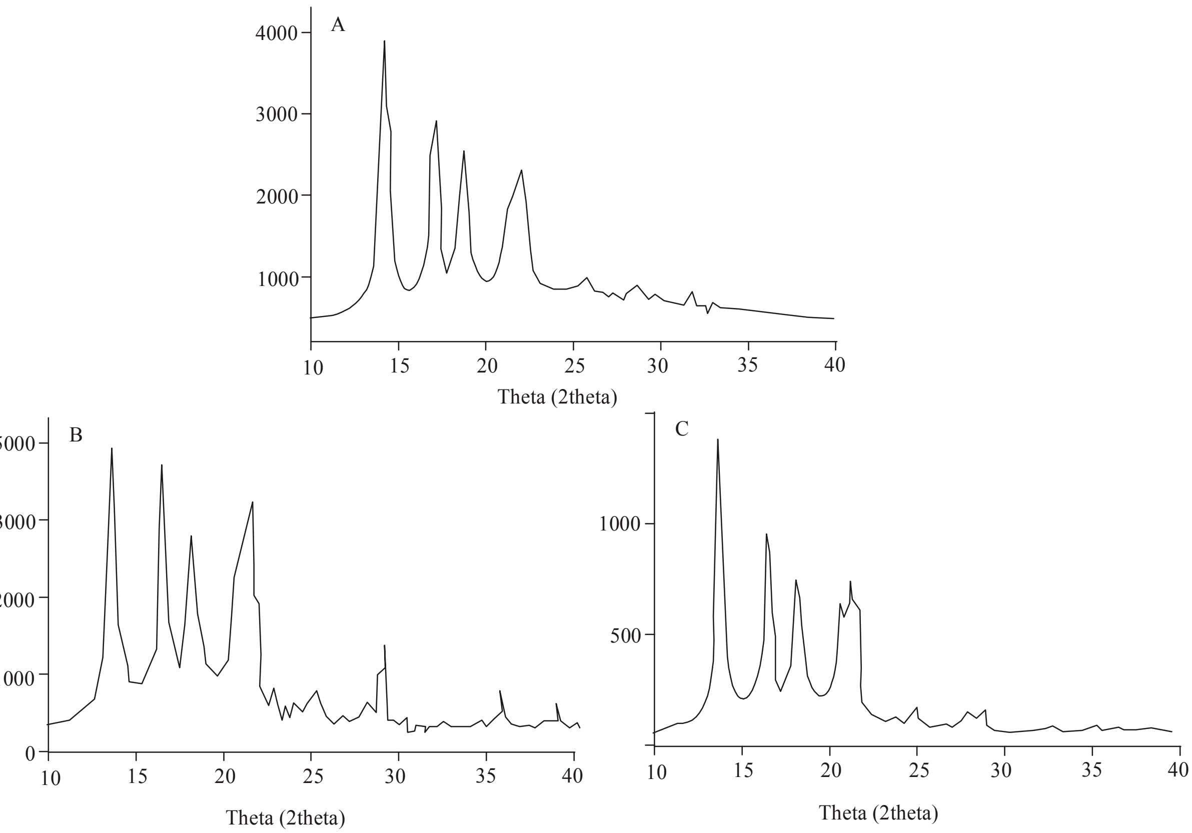


Fig. 4: XRD for; (A): neat PP; (B): 5%$CaCO_3$; (C): 10%$CaCO_3$ nanocomposite at 25 rpm

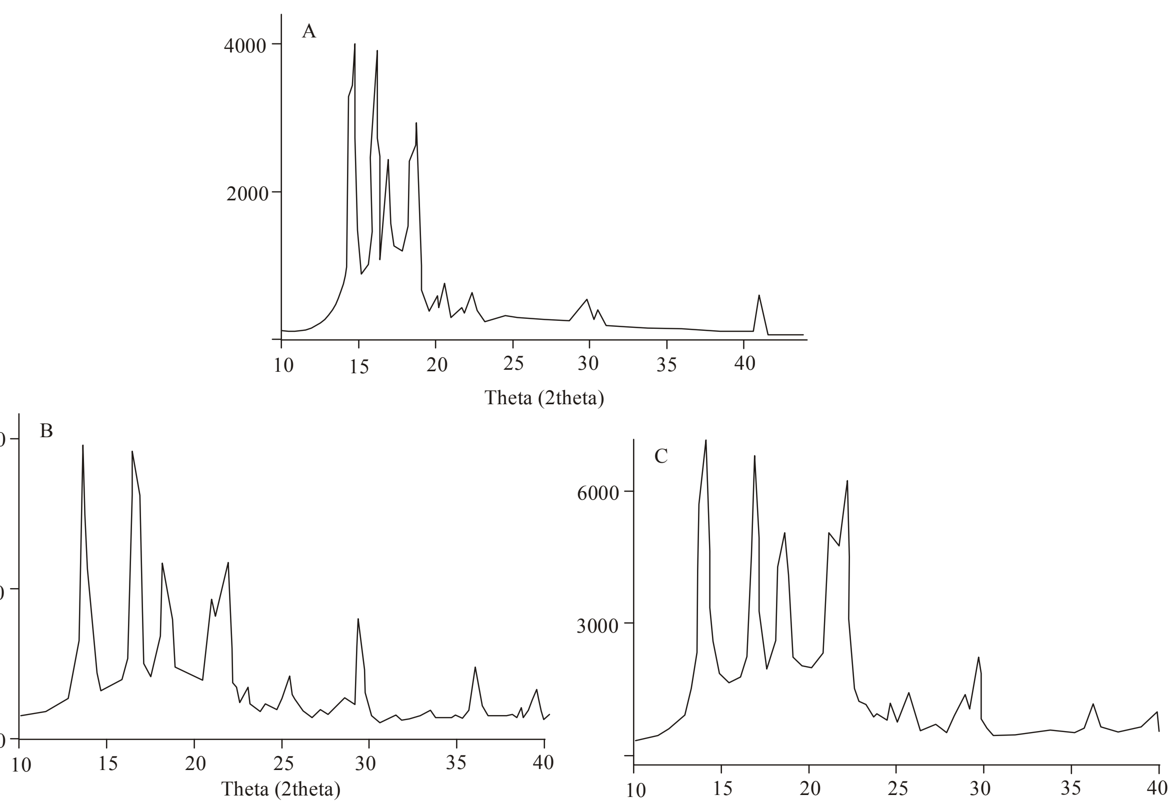


Fig. 5: XRD (A) waste PP, (B) 5%$CaCO_3$, (C) 10%$CaCO_3$ nanocomposite at 25 rpm

polypropylene, the main peak at (2800-3200) /cm wave number represented the stretch C-H group, while the peak at 1700/cm represented C-O which appear slightly due to exposed mixture to air and occur oxidation process. The third peak at (1000-1200) /cm wave number represented C-C bond this good agreement with the results of (Stuart, 2004).

Figure 4 shows the crystallinity level of neat PP and the nanocomposite with (5 and 10 wt. % $CaCO_3$) at 25 rpm. The nanocomposite shows sharp and highly intense peaks while neat PP shows less intense peaks. This may due to the development of crystallinity in the polymer. The crystallinity increase with $CaCO_3$ content increasing, this is due to $CaCO_3$ nanoparticals filled the hole and oriented the chain so the crystallinity increasing.

Figure 5 indicates the crystallinity levels of waste PP and its nanocomposite of 5 and 10 wt. % of $CaCO_3$ at 25 rpm. The crystallinity level for virgin PP is higher than for 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 the crystallinity level increases with nanoparticle percentage increasing and appear of new beaks at 2θ (30°-40°) which mean the exits of ZnO nanoparticles through the polypropylene matrix and acts as filler. The increasing of crystallinity level is strongly effect on the thermal conductivity behavior.

Thermal conductivity: The effect of nanoparticles ($CaCO_3$and ZnO) on thermal conductivity of VPP and its waste are shown in Fig. 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 $CaCO_3$/WPP nanocomposite due to the nature of nano-filler and crystallinity degree as shown in Fig. 4 to 6 and from fact that the intrinsic thermal conductivity of the ZnO nanoparticles is higher than that of $CaCO_3$ this results is compatible with the results of (Di Lorenzo *et al*., 2002; Vakili *et al*., 2011). The VPP and WPP show significant and clear difference for thermal conductivity up to 3% of $CaCO_3$ 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 point view. The K value increases to about 65% for ZnO polymer nanocomposite while about 60% for $CaCO_3$ 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

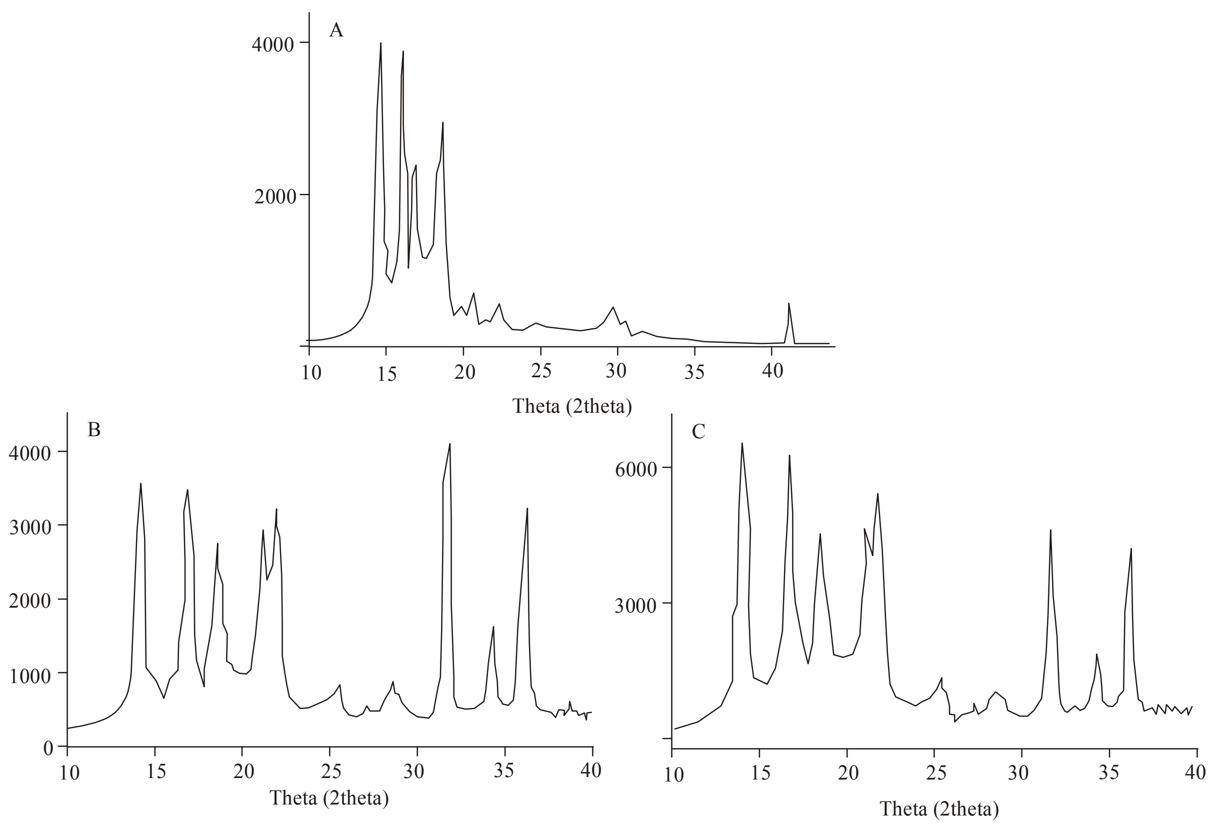


Fig. 6: The crystallinity level of nanocomposite; (A): neat waste PP; (B): 5% ZnO; (C): 10%ZnO nanoparticles

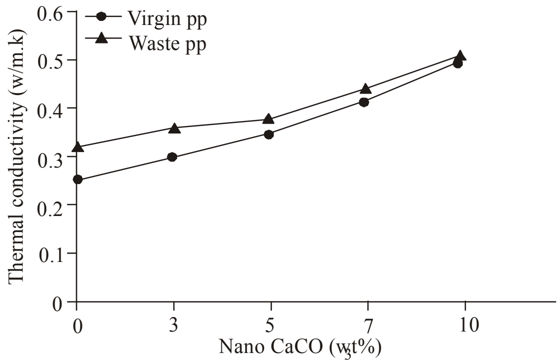


Fig. 7: Thermal conductivity behavior for virgin and waste PP with different $CaCO_3$ nanoparticles concentration at 100°C

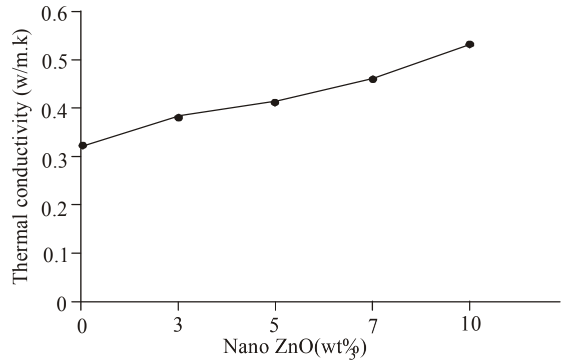


Fig. 8: Thermal conductivity behavior for waste PP with different ZnO nanoparticles concentration at 100ºC

effect becomes stronger. Again the ZnO/WPP nanocomposite is approximately better than $CaCO_3$/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 pure VPP granules at melt flow rate test at 230°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 2.16 kg 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 Fig. 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 ΔT value increases with $CaCO_3$ nanoparticles content increasing. All specimen surfaces were uniformly painted with the same color to assure a good homogenous distribution of nanoparticles through polymer matrix.

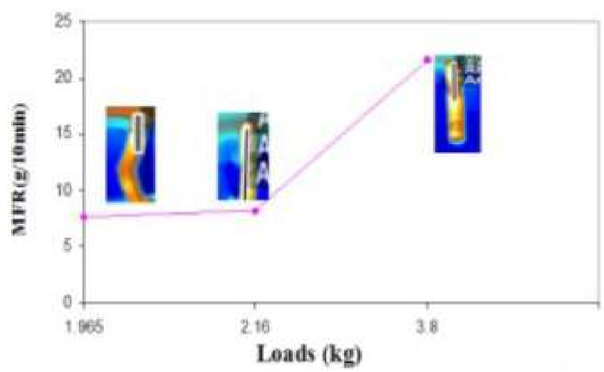
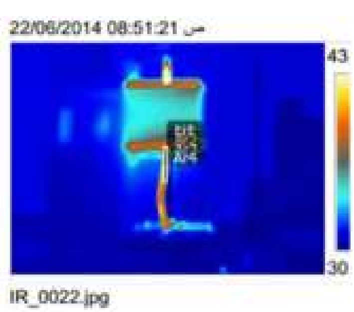


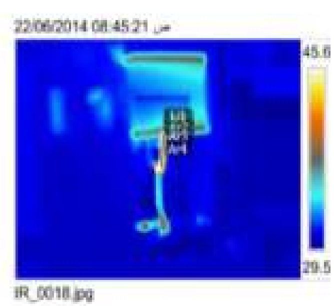
Fig. 9: The relation between melt flow rate and thermal images at different three loads

Measurements	°C
Max	49.6
Min	48.8
Average	49.3
Max	44.0
Min	43.4
Average	43.6
Max	44.2
Min	43.3
Average	43.8
Max	41.8
Min	40.1
Average	40.9
Max	52.7
Min	38.9
Average	44.0



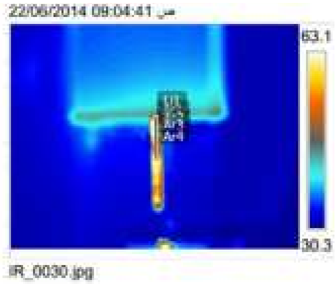
(a)

Measurements		°C
Ar1	Max	56.5
	Min	55.0
	Average	55.8
Ar2	Max	50.7
	Min	49.2
	Average	50.0
Ar3	Max	49.6
	Min	47.8
	Average	48.7
Ar4	Max	49.0
	Min	44.9
	Average	46.8
Li1	Max	63.3
	Min	44.9
	Average	50.2



(b)

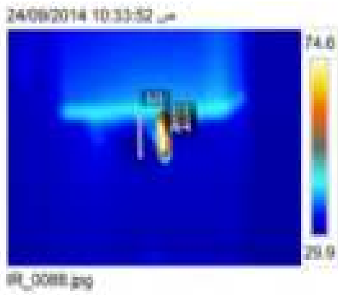
Measurements		°C
Ar1	Max	69.0
	Min	67.3
	Average	68.1
Ar2	Max	68.9
	Min	67.2
	Average	68.0
Ar3	Max	59.9
	Min	59.1
	Average	59.5
Ar4	Max	59.7
	Min	59.1
	Average	59.5
Li1	Max	71.2
	Min	53.7
	Average	62.5



(c)

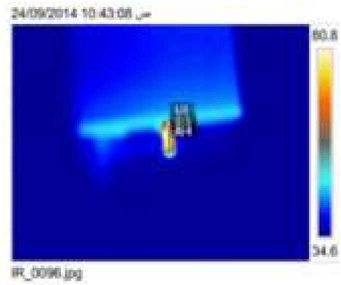
Fig. 10: Thermal Images of pure virgin PP at different loads: - (A): 1.695kg; (B): 2.16kg and; (C): 3.80 kg at line (Li1)

Measurements		°C
Ar1	Max	75.1
	Min	74.9
	Average	75.0
Ar2	Max	74.9
	Min	74.4
	Average	74.7
Ar3	Max	73.9
	Min	73.2
	Average	73.5
Ar4	Max	71.4
	Min	70.5
	Average	71.0
Li1	Max	39.6
	Min	30.2
	Average	33.1



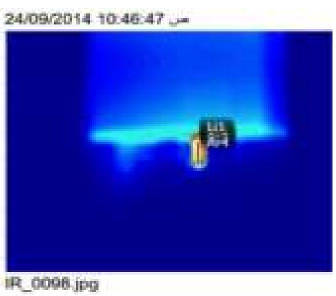
(a)

Measurements		°C
Ar1	Max	81.9
	Min	80.2
	Average	81.0
Ar2	Max	80.2
	Min	79.7
	Average	79.9
Ar3	Max	78.8
	Min	78.5
	Average	78.6
Ar4	Max	78.5
	Min	78.7
	Average	75.6
Li1	Max	80.6
	Min	52.3
	Average	72.2



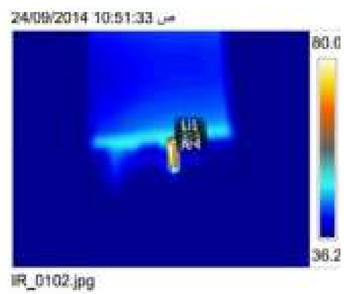
(b)

Measurements		°C
Ar1	Max	77.2
	Min	75.3
	Average	76.3
Ar2	Max	75.2
	Min	73.3
	Average	74.3
Ar3	Max	73.5
	Min	71.7
	Average	72.6
Ar4	Max	68.8
	Min	66.0
	Average	67.3
Li1	Max	75.9
	Min	50.9
	Average	69.5



(c)

Measurements		°C
Ar1	Max	78.5
	Min	76.7
	Average	77.6
Ar2	Max	77.0
	Min	75.8
	Average	76.4
Ar3	Max	74.9
	Min	73.6
	Average	74.2
Ar4	Max	73.8
	Min	72.1
	Average	72.9
Li1	Max	76.1
	Min	57.2
	Average	71.7



(d)

Fig. 11: Thermal image of virgin PP nanocomposite: - (A): 3%; (B): 5%; (C): 7% and; (D): 10wt% of $CaCO_3$ nanoparticles

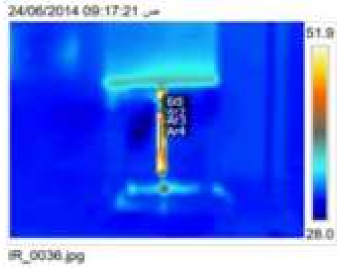
Figure 12 presents a thermo-graphic image taken at the automatically cutting region of MFR test at 2.16 kg of WPP due to $CaCO_3$ nanoparticles percentage, the results show that the ΔT values increases with MFR values decreasing as results of addition of $CaCO_3$ nanoparticles.

Figure 13 shows the thermal image of WPP with different ZnO nanoparticles content. The results show that the ΔT value increases with MFR decreasing at ZnO nanoparticles content of 3, 5, 7 and 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.

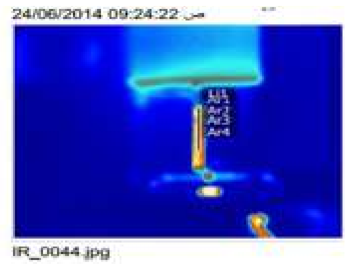
CONCLUSION

There is a clear relationship between the flow of polymers in the extrusion process and the thermal specifications on the one hand and between the material

Measurements		°C
Ar1	Max	52.7
	Min	51.6
	Average	52.2
Ar2	Max	52.5
	Min	51.8
	Average	52.2
Ar3	Max	52.2
	Min	50.4
	Average	51.3
Ar4	Max	51.7
	Min	50.8
	Average	51.2
Li1	Max	53.1
	Min	47.7
	Average	51.5



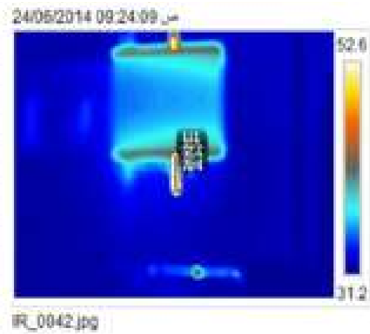
Measurements		°C
Ar1	Max	52.7
	Min	51.6
	Average	52.2
Ar2	Max	52.5
	Min	51.8
	Average	52.2
Ar3	Max	52.2
	Min	50.4
	Average	51.3
Ar4	Max	51.7
	Min	50.8
	Average	51.2
Li1	Max	53.1
	Min	47.7
	Average	51.5



(a) (b)

Measurements		°C
Ar1	Max	60.5
	Min	58.0
	Average	59.3
Ar2	Max	60.5
	Min	60.3
	Average	60.4
Ar3	Max	58.4
	Min	58.2
	Average	58.3
Ar4	Max	57.0
	Min	54.2
	Average	55.6
Li1	Max	63.6
	Min	51.6
	Average	59.3

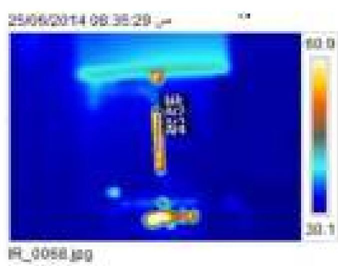
Measurements		°C
Ar1	Max	60.8
	Min	59.3
	Average	60.0
Ar2	Max	63.4
	Min	62.7
	Average	63.1
Ar3	Max	56.1
	Min	55.2
	Average	55.7
Ar4	Max	57.4
	Min	55.9
	Average	56.7
Li1	Max	63.7
	Min	41.0
	Average	56.0



(c) (d)

Fig. 12: Thermal image of waste PP nanocomposite: - (A) 3%; (B): 5%; (C): 7% and; (D): 10 wt.% of $CaCO_3$ nanoparticle

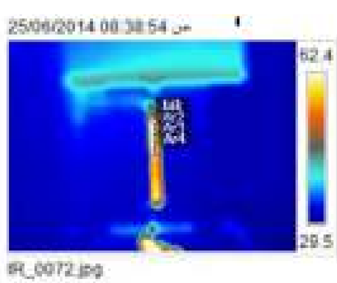
Measurements		°C
Ar1	Max	60.4
	Min	58.4
	Average	59.4
Ar2	Max	59.0
	Min	57.6
	Average	58.3
Ar3	Max	58.1
	Min	57.0
	Average	57.5
Ar4	Max	56.5
	Min	55.2
	Average	55.8
Li1	Max	60.4
	Min	53.9
	Average	56.7



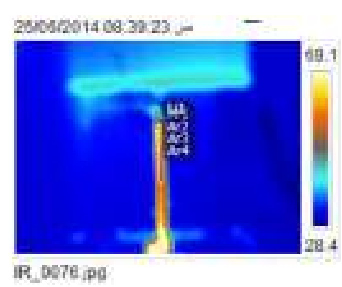
Measurements		°C
Ar1	Max	67.4
	Min	66.4
	Average	66.8
Ar2	Max	68.3
	Min	67.9
	Average	68.1
Ar3	Max	64.8
	Min	64.5
	Average	64.6
Ar4	Max	63.7
	Min	62.4
	Average	63.0
Li1	Max	96.0
	Min	63.4
	Average	66.0

(a) (b)

Measurements		°C
Ar1	Max	62.2
	Min	60.1
	Average	61.2
Ar2	Max	62.3
	Min	61.7
	Average	62.0
Ar3	Max	61.2
	Min	60.3
	Average	60.7
Ar4	Max	57.8
	Min	57.0
	Average	57.4
Li1	Max	63.2
	Min	56.7
	Average	66.3



Measurements		°C
Ar1	Max	67.4
	Min	64.5
	Average	66.0
Ar2	Max	64.5
	Min	64.1
	Average	64.3
Ar3	Max	62.5
	Min	61.8
	Average	62.2
Ar4	Max	61.0
	Min	60.7
	Average	60.9
Li1	Max	68.9
	Min	59.2
	Average	62.7



(c) (d)

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

structure and their crystallinity level on the other hand. Possible through the linkage between these operational Specifications can be controlled on the conditions of the polymers manufacturing processes and reduce the defects that could appear in the final product also to improve the surface quality and dimensional stability. The linkage between thermal conductivity and their increasing with the increase in the proportion of nanoparticles content and the increasing in the crystallinity as a result of the addition of these nanoparticles is important and clear. 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.

REFERENCES

Abdolmohammadi, S., S. Siyamak, N.A. Ibrahim, W.M.Z. Wan Yunus, M.Z. Ab Rahman, S. Azizi and A. Fatehi, 2010. Enhancement of mechanical and thermal properties of polycaprolactone/chitosan blend by calcium carbonate nanoparticles. Int. J. Mol. Sci., 13(4): 4508-4522.

Di Lorenzo, M.L., M.E. Errico and M. Avella, 2002. Thermal and morphological characterization of poly(ethylene terephthalate)/calcium carbonate nanocomposites. J. Mater. Sci., 37(11): 2351-2358.

Maier, C. and T. Calafut, 1998. Polypropylene: The Definitive User's Guide and Databook. William Andrew Publishing, Norwich, New York.

Ong, H.L., H. Md Akil and S. Mahmud, 2009. Effect of particle morphology on the properties of polypropylene/nanometric zinc oxide (PP/nanoZnO) composites. Adv. Compos. Lett., 18(3): 77-83.

Özmihçi Ömürlü, F., 2009. Enhancement of thermal, electrical and optical properties of zinc oxide filled polymer matrix nano composite. Ph.D. Thesis, Graduate School of Engineering and Sciences of İzmir Institute of Technology.

Stuart, B., 2004. Infrared Spectroscopy: Fundamentals and Applications. J. Wiley, Chichester, Eng.; Hoboken, N.J.

Szczepanik, M., J. Stabik, G. Wróbel and L. Wierzbicki, 2008. Detecting of defects in polymeric materials using pulsed infrared thermography. Arch. Mater. Sci. Eng., 30(1): 29-32.

Vakili, M.H., H. Ebadi-Dehaghani and M. Haghshenas-Fard, 2011. Crystallization and thermal conductivity of $CaCO_3$ nanoparticle filled polypropylene. J. Macromol. Sci. B, 50(8): 1637-1645.