Study the relation between rheological, thermal and mechanical properties of waste polypropylene filled silica nanoparticles

Dr. Nizar Jawad Hadi [1,a]   **Dhey Jawad Mohamed** [2,b]

[a]**nizarjawad63@uobabylon.edu.iq**
[b] **dhey alhafagy@gmail.com**

[1, 2] Collage of Materials Engineering /Polymer and petrochemical industries department
Babylon University/Iraq

Abstract:-

This paper investigates the rheological, thermal and mechanical properties of waste polypropylene (WPP) reinforced with silica (SiO_2) nanoparticles (NPs). Recently the researches prove that the addition of NPs to the thermoplastic polymer produces significant change in its properties. SiO_2 NPs of 0.001, 0.003, 0.006, 0.009, 0.012 and 0.015wt% were mixed with the WPP using twin screw extruder. The mixing process performed at 10 rpm and 190°C. The crystallinity of nanocomposite was examined by X-ray diffraction. The melt flow rate (MFR) and melt volume rate (MVR)are tested due to SiO_2 NPs concentration at standard condition using melt flow index device also solid and melt density are examined. Differential Scanning Calomitry (DSC) is used to show the effect of SiO_2 NPs concentration on the thermal history of nanocomposite. Charpy impact strength and hardness are tested. The results show that the crystallinity level and the crystallinity temperature decreases with SiO_2 NPs concentration increasing while impact and hardness increasing. The MFR and MVR increases with NPs concentration increasing. Clear difference between solid and melt density

is observed. There is a compatible between the thermal, rheological and mechanical properties.

Keywords:- waste PP, SiO_2 NPs, twin screw extruder, rheological, thermal and mechanical properties.

Introduction:-

Polyolefin materials have grown to a crucial role in modern society, from daily life to high-performance engineering applications. The low cost of production, facile and inexpensive processability, and good properties of these materials have allowed them to replace some of the traditional more expensive and less adaptable materials. Moreover, the addition of organic and inorganic fillers has opened a wide field of research for new possible applications for these materials [1]. Because of its excellent properties, good chemical resistance, low density, and low cost, PP is one of the most widely used thermoplastics [2,3]. Plastics are considered extremely effective materials to recycle for two primary reasons. Firstly, there is a demand to use more and more plastics in our everyday life. Secondly, the recycling processes reduce the effect of waste on the environment and human health. The possibility of using recycled materials to manufacture relatively good article depends on the rheological and mechanical behavior of the recycled polymers [4, 5]. Recycling has been practiced for many years by industries without any great accuracy. Numerous academic research works have become more and more interested in the recycling of the widespread polyolefin as polyethylene and polypropylene [11].The addition of inorganic nanoparticles (such as silica, calcium carbonate, carbon nanotubes, layered silicates etc.) at limited filler amounts <5wt% has been proven to be extremely effective in increasing the physical properties, mechanical resistance and flame retardancy. Since, the first industrial application of

polymer nanocomposite, several efforts have been made to introduce novel nanocomposite systems through the combination of various polymeric matrices and nanofillers [6,7]. The main condition to achieve the desired performance of the nanocomposite is the best dispersion of the nanoparticles through matrix. This is a difficult problem due to the strong tendency of nanoparticles to agglomerate, which can be explained by their small particle diameter, (high surface energy) [8,9]. Polymer rheological data is used in determining whether or not a type of polymer can be extruded, molded or shaped into a practical and useable product. The polymer rheology would probably help in determining the optimal design of processing equipment such as extrusion die design, screw geometries of an extruder. This indicates that the understanding of polymer rheology is the key to efficient design, material and process selection, efficient fabrication and satisfactory service performance [10].

In the present work the waste polypropylene PP is mixing with SiO_2 NPs of 0.001, 0.003, 0.006, 0.009, 0.012 and 0.015 wt. using twin screw extruder at 10 rpm and 190°C. The effect of SiO_2 NPs concentration on the rheological, thermal and mechanical properties of WPP nanocomposite was investigated. The relationship between the rheological, thermal, and mechanical properties of waste PP nanocomposite was studying.

Material and method:-

Waste polypropylene used is collected from food container products. Silica nanoparticles supplied from (Shijiazhuang Sun power Technology Co., Ltd, Chain) with purity of 99.9%, particle size is about (55 nm) and density of $2.4 g/cm^3$.

Samples Preparation:-

Firstly the polypropylene food container is cutting to pellets. SiO_2 NPs are immersed in alcohol solution and mechanically mixed. The mixing process is performed using twin screw extruder (SLJ). The extruder dimensions are (1.8m*0.6m*1.5m), and the weight (450Kg). The mixing process is performed at 10 rpm and 190°C to produce waste PP nanocomposite sheet with thickness 13mm.

Characterization:-

The effect of SiO_2 NPs concentration on the crystallinity of waste PP are conducted by using X-ray diffraction (XRD 6000) manufacture by (SHIMADZU) Japan, the experiments are carried out using CuKα radiation at scanning speed of 2/minute on samples. Scans are performed over 2θ ranges from 10º-40º.

Melt indexer type (SHI JIA ZHUANG ZHONG SHI TESTING MACHINE CO., LTD) according to the Standard of (ISO1133:2005) was used to measure the MFR and MVR of WPP and its nanocomposite through capillary die with diameter of 2.095mm and the length of 8mm.

Solid density test is performed using (Matsu Haku HIGH Precision DENTESTER SITY GP-120S   D=0.0001 g/cm³) which contain water at room temperature based on ASTM D-792. At least three samples are tested; average and the standard deviation are calculated. In this method sheet, rod, tube and molded articles can be tested; the specimen is weighed in air and immersed in distilled water by applying Archimedes law. The melt density determined by dividing the melt flow rate and melt volume rate.

$$\rho' = \frac{MFR}{MVR} \qquad\qquad (1)$$

Differential scanning calorimetry DSC analyses were performed to show the effect of SiO_2 NPs on thermal history of waste PP. In the case of the isothermal crystallization, the samples of approximately 6 mg heated from 25 to 300 ℃ and maintained at this temperature for 5 minutes.

CEAST Resil impact instrument according to ASTM D-256, at ambient temperature is used to analyze the effect of adding SiO_2 NPs on impact strength of polymer nanocomposite. Also hardness test performed according to ASTM D-2240 standard at room temperature. For each compound, 4 samples were tested and the mean values were considered.

The **X-ray diffraction (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 2º/minute on samples which have been surface target using Cu, and the preset time is 0.24 second to show the crystallinity levels of the WPP nanocomposite at different of SiO_2 NPs.

Results and Discussion

Rheological properties:-

It is known that the melt rheology of thermoplastic materials is strongly influenced by the molecular weight and viscosity. Fig. 1 shows the effect of SiO_2 NPs on the MFR of WPP. The results show that the MFR value increases with the nanoparticles content increasing. The SiO_2 NPs increase the free volume and the Brownian motion of the chains. This produces decreasing in shear viscosity and increasing in the flow rate. The flexible and ductile structure of the polymer chains are obtained due to the reduction in shear viscosity. The viscosity is proportional to the density and molecular weight of polymer. The results of viscosity show that the viscosity decreases with the MFR increasing, due to the scission of the chains during the melting processes. The magnitude of viscosity

can be predicted according to the formula below A.V. Shenoy and Saini (1996) as shown in Table (1):

$$\eta= 4.98*10^4 \, \rho \, L/MFR \tag{2}$$

Fig.2 Shows MVR value for WPP nanocomposite due to SiO_2 nanoparticles content at constant time and distances of 6 mm. It can be seen that the MVR increasing with SiO_2 NPs percentage increasing because the chains motion increases and viscosity decreasing. The MFR and MVR inversely change with viscosity. The main rheological properties are shown in the table (2). In this table the flow rate (Q), shear rate at the wall of capillary and the true shear rate are increased with MFR and MVR. The viscosity decreased with the MFR and shear rate increasing. This behavior called shear thinning effect which characterize the rheological behavior of polymer chain.

Fig.3. the density gradually increases with nanoparticle concentration increasing, due to the SiO_2 NPs fills the spaces between polypropylene chains. Also the density of the SiO_2 NPs is higher than that of polypropylene. The calculation melt density is less than the solid density due to the change in volume between solid and melt state. The melt density is a very important data for numerical simulation study of rheological and flow behaviour of polymer melts. The polymer process strongly depends on melt density which effects on the manufacturing operation. The use of melt density instead of solid density produce accurate results in numerical study and reduces the cost of the manufacturing process.

Mechanical Properties:

The impact strength of WPP nanocomposite at different SiO_2 NPs content are shown in **Fig. 4**. The impact resistance of nanocomposite increases up to 0.012 of SiO_2 NPs. The viscosity is proportional with the

molecular weight, density, storage modulus and the crystallinity. The decreasing in the storage modulus increases the ductility and improves the impact resistance; this means that the interfacial regions are able to resist crack propagation more effectively than the polymer matrix. The increasing of the impact resistance with SiO_2 NPs concentration increases due to the decrease in the intermolecular force. This increases the resistance to the fracture of polymer. The impact resistance behavior simulates the MFR behavior up to 0.012 SiO_2 NPs. this result have a good agreement with (Yongri Liang) [12].

Shore D hardness for WPP nanocomposite is shown in **Fig.5.** The hardness of waste PP slightly increases with SiO_2 NPs due to the SiO_2 NPs holes filling and chains orientation. The behavior of hardness and MFR of WPP nanocomposite approximately the same, the increasing in MFR and decreasing in viscosity enhance the alignment and arrangement of polymer chains. The alignment of chains increases the smoothness of the surface. The modification in surface reduces the defect and crack and gives additional justification for the impact resistance improvement.

Thermal History:-

It is well known that thermal degradation could significantly affect thermal properties of polyolefin, and the inorganic nanofillers can affect both the melting and the crystallization behavior of the PP matrix. The effects of SiO_2NPs on thermal history of the waste PP are shown in **Fig 6.** It can be seen that the crystallinity temperature increasing at 0.003 and 0.009 wt. of SiO_2NPs and then decreasing as compared with the pure polypropylene, also the small peak at approximately 125 ℃ represented the β phases this good agreement with (M. Garc) [13], the crystallinity temperature of WPP nanocomposite are shown in table (2). The appearance of β type hexagonal crystals obviously improves the impact

strength of PP because the β -type hexagonal crystals have higher ductility and strength than that of α type monoclinic crystals this result compatible with (Wei-Zhi Wang and Tianxi Liu) [14].

The crystallinity level associated with the changing in the melting temperature, the reduction in the melting point decreases the crystallinity state and vice versa. The crystallinity is proportional with the intermolecular forces which are decreasing with SiO_2 NPs content.

The crystallinity of Nanocomposite:-

Fig. 7: shows the crystallinity levels of WPP and its nanocomposite with different weight percentage of SiO_2 NPs. It's very clear that the crystallinity level decreases with the nanoparticle percentage increasing, the crystallinity increases so that the impact strength increases this result confirmed with impact and DSC results.

Conclusions:

The rheology and MFR strongly effect on the viscosity and structure of polymer chains. The shear rate and flow rate preoperational with MFE and MVR. The viscosity inversely changes with the MFR and MVR values. The shear rate increasing with viscosity decreasing, characterize the rheological behavior of polymer melts. The arrangement and orientation of chains depends on the viscosity behavior. SiO_2 NPs increases the MFR, MVR, impact resistance and hardness of WPP nanocomposite. The increasing in MFR decreases the viscosity and intermolecular forces between SiO_2 NPs and polymer chains. The reduction in intermolecular forces decreases the storage modulus and increases the impact resistance. The alignments of polymer chains due to reduction in viscosity may be improve the hardness. The solid and melt density increases with nanoparticles percentage increasing; the melt density is lower than that of solid density.

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Table (1): The Viscosity value for WPP at 2.16 Kg at 190 ºC
and different concentration of SiO_2 NPs

SiO_2 NPs Wt%	Viscosity of WPN. (pa.s)
0	1345.2
0.001	1255.36
0.003	1094
0.006	998.25
0.009	903.56
0.12	864.3
0.15	723.6

Table (2): The main rheological properties of waste PP nanocomposite
according to SiO_2 NPs concentrations

SiO_2 NPs	MFR g/10min	MVR cm^3/10min	Flow rate	Shear rate at the wall	True shear rate(1/S)
0	10.1	11.4	0.19	19.751	0.0362
0.001	12.3	13.8	0.23	23.789	0.0439
0.003	15.6	17.5	0.29	29.941	0.137
0.006	17.01	19	0.31	32.521	0.250
0.009	20.32	22.32	0.37	38.413	0.283
0.012	24.5	26.8	0.44	45.872	0.321
0.015	26	29	0.48	48.270	0.354

Table 3: The crystallinity Temperature of WPP
nanocomposite at different SiO_2 NPs concentration

SiO_2%	Tc (ºC)
0	117
0.003	119
0.009	118
0.015	114

Table 4: The overall behaviors of waste PP as
a function of SiO_2 NPs concentration

SiO_2 NPs concentration	Impact resistance	Hardness	Density	Melting point
0.003	↑	↑	↑	↓
0.009	↑	↑	↑	↓
0.015	↑	↑	↑	↑
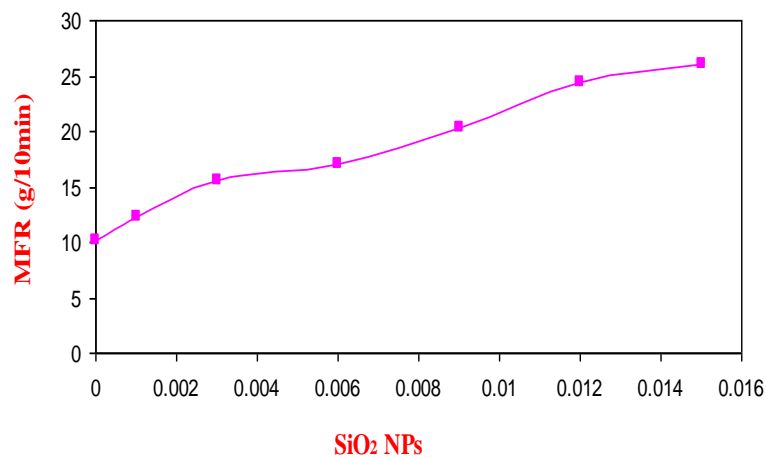
Fig.(1):- The MFR Behavior of WPP at Different SiO_2 NPs
concentration
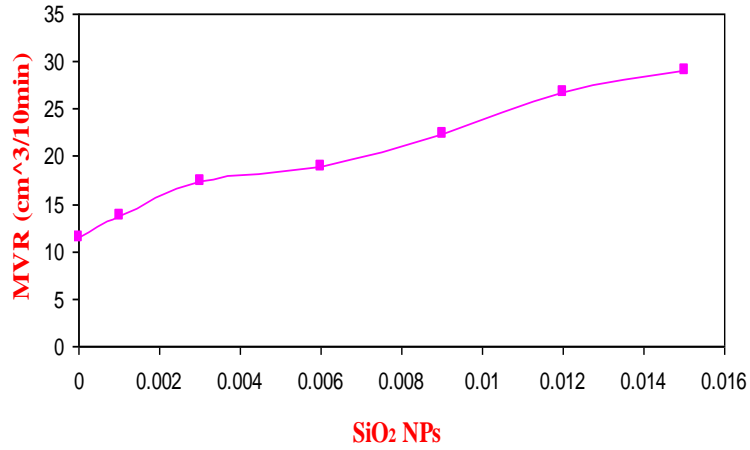
Fig.(2):- The MVR Behavior of WPP at Different SiO$_2$ NPs concentration
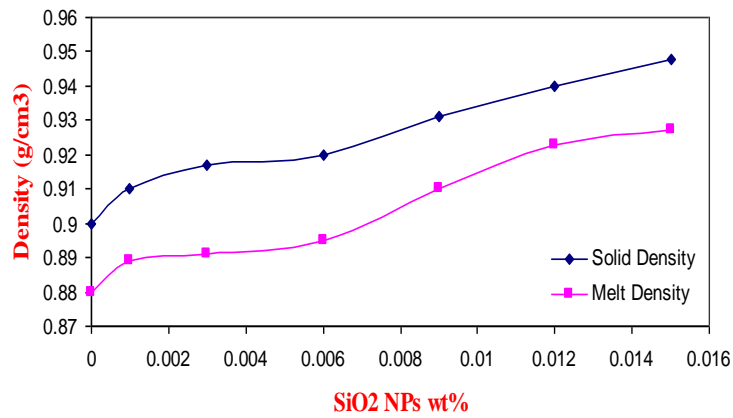
Fig.(3): The Density Behavior of WPP Nanocomposite with Different SiO$_2$ NPs Percentage
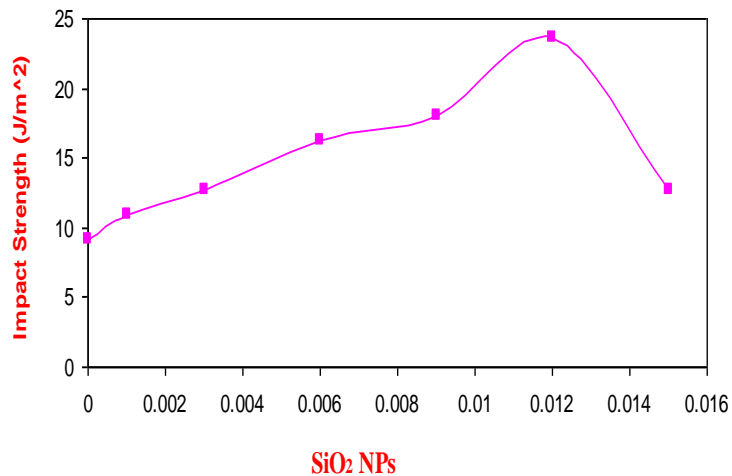
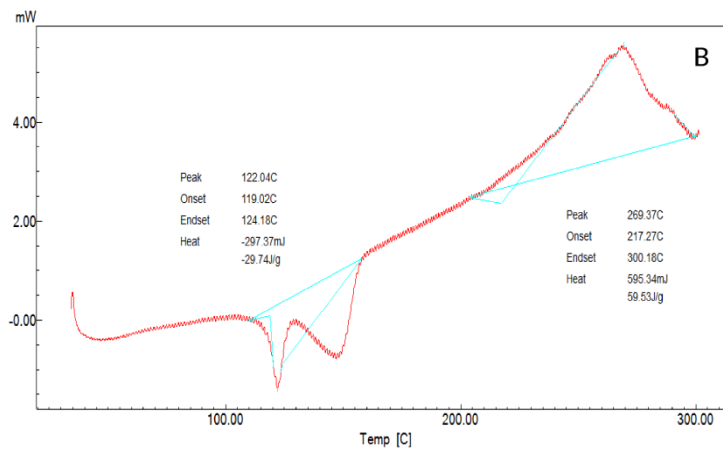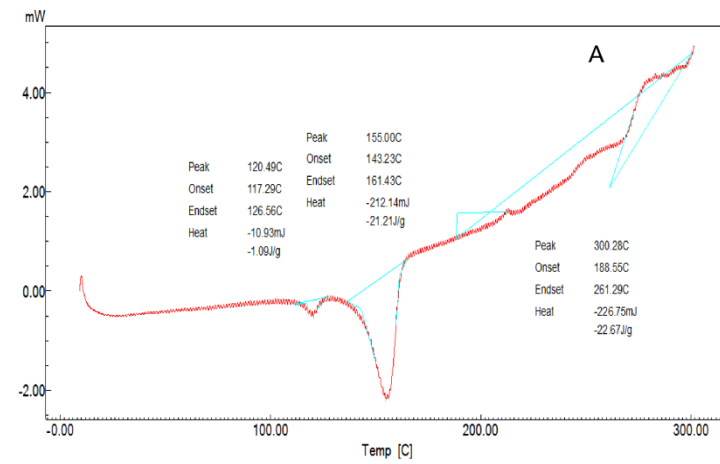Fig.(4) Impact Strength Behavior of WPP at Different SiO$_2$ NPs Concentration
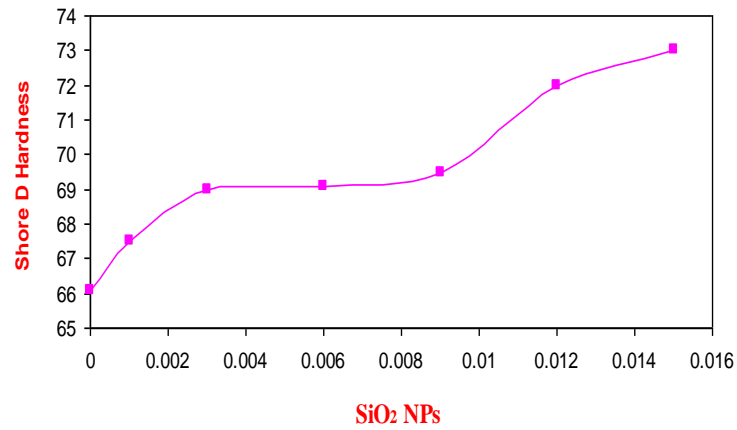
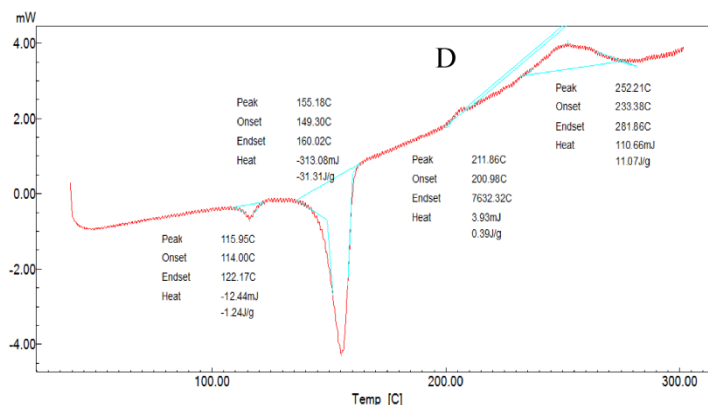Fig.(5):-The Hardness Behavior of WPP nanocomposite at Different SiO$_2$ NPs Concentration
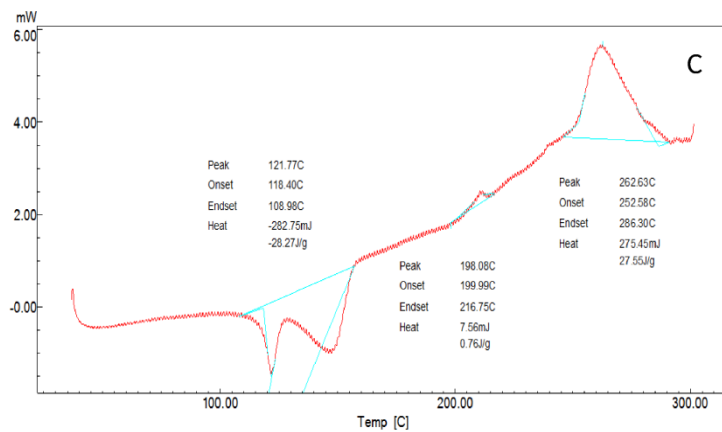
Fig.(6): Thermal history of WPP Nanocomposite(A) WPP, (B)
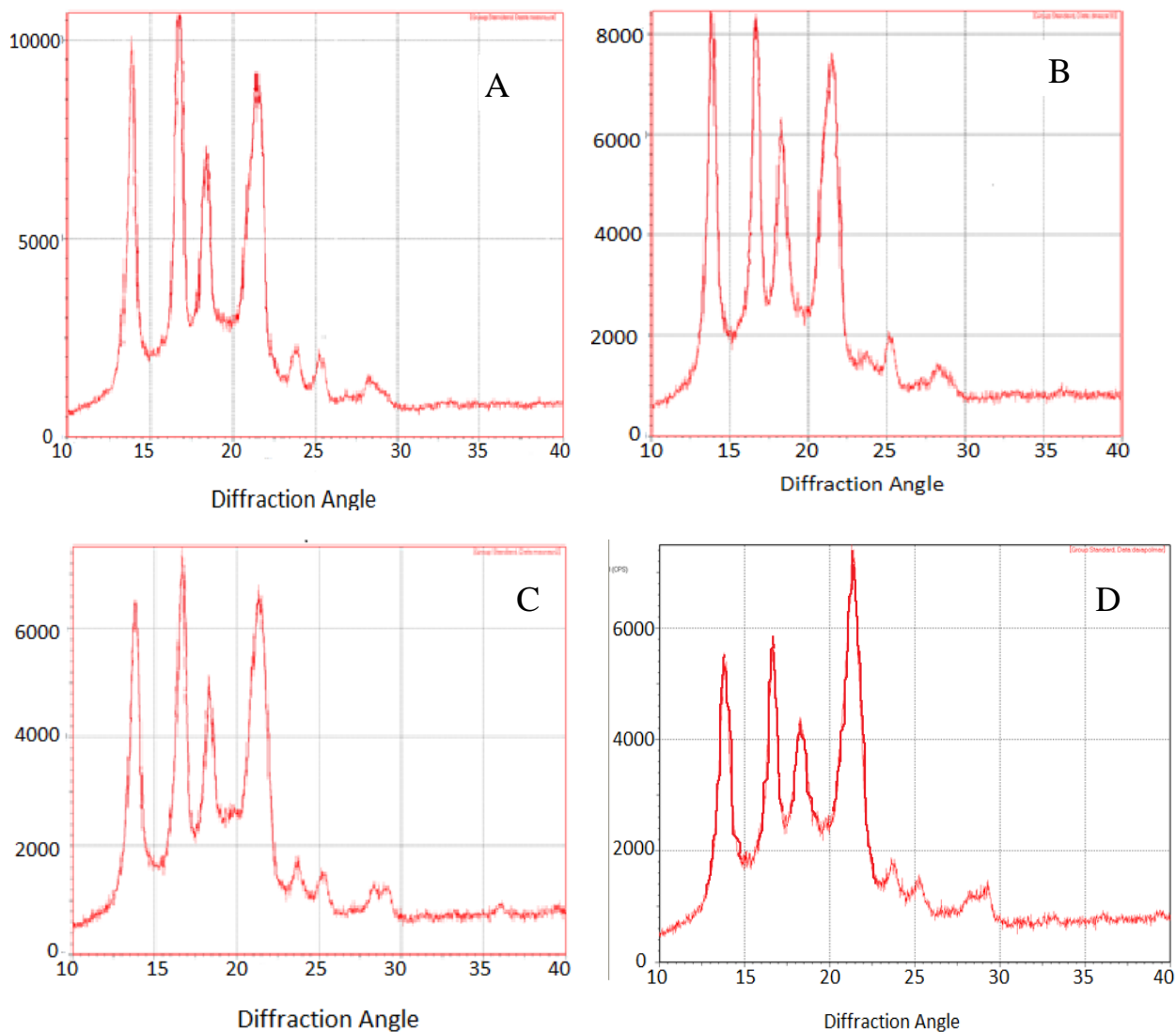0.003, (C)0.009 and (D) 0.015 of SiO$_2$ NPs

Fig. 7: XRD for (A) WPP, (B) 0.003%SiO$_2$, (C) 0.009%SiO$_2$ and (D)
0.015% SiO$_2$ nanocomposite.