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New Nanocomposite Derivatives from Thiadiazole Polymers /Silica Synthesis and Characterization using Free Radical Polymerization

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Abstract

A new class of thiadiazole /silica nanocomposites with chemical bonds between thiadiazole monomers and modified nanosilica surface were synthesized by free radical polymerization. Presence silica nanoparticles in the structure of nanocomposite showed effectively improve the physical and chemical properties of Producing polymers. A nanocomposite material with feature properties comparison with their polymers. The structure and morphology of the synthesis materials were investigated by FT-IR spectrum which display preparation new thiadiazole compounds and polymerization monomers. FT-IR showed disappeared double bond (C=C) of monomers, due to produce long chains of thiadiazole polymers and nanocomposite. X-ray diffraction gave idea about crystalline structure of nanoparticles and nanocomposite, X-ray showed that silica nanoparticles have high intensity at 18000, due to nanoscale of particles which allowed for particles aggregation together. While nanocomposite show low intensity due to reacted thiadaizole polymer chains with silica nanoparticles surface. The distribution of nanoparticles had characterized by Atomic forces microscopy AFM. AFM results shown roughness in the surfaces of nanocomposites C_1 and C_2, comparison with silica nanoparticles which gave smooth surface. The roughness attributed to reaction between functionalized surface of silica nanoparticles and chains of thiadaizole polymers, which led to change in size particles distribution and surface of particles that refer to nanocomposite.

Keywords: Thiadiazole, polymers, surface modification, nanocopmposite

1. Introduction

Nanocomposite materials, especially hybrid organic/inorganic, have been extensively studied for a long time in a different field such as electronic, aerospace, medical, and industries [1]. Shouji, and Buttry, discovered a method have described by which the disulfide dimer of 2,5-dimercapto-1,3,4-thiadiazole can be oxidatively intercalated into the layered structure of a V_2O_5 gel. This reaction produces a new organic-inorganic composite material [2]. Biswas and SinhaRay, synthesized and evolution of composite from montmorillonite and some heterocyclic polymers by use The cationic polymerization of N-vinylcarbazole (NVC) can be initiated directly by montmorillonite (MMT) [3]. Dias Filho et al, used Silica gel with a specific area and an average pore diameter of 60 Å which was chemically modified with 2-amino-1,3,4-thiadiazole, for the purpose of selective adsorption of heavy metals ions [4]. Liu et al, synthesized as a new electro responsive electrorheological (ER) polymer/inorganic nanocomposite material and polyaniline (PANI)/nano-silica nanocomposite was synthesized via an in situ chemical oxidative polymerization method [5]. The organic/inorganic nanocomposites with different ingredients of the two components have invest important academic and technological characterized because they have interesting physical properties such as strength, rigidity and potential applications such as photo cell and semiconductors [6]. Generally, they are organic polymer composites with inorganic nanoscale particles to produce new materials different in their characterization and properties comparing with characterize of neat polymer. Moreover, they contain special properties of nanofillers leading to Improve the properties such as lightweight, easy fabrication, exceptional processability, durability and relatively low cost [7]. The advantage of polymer nanocomposites is that the small size of the fillers leads to a dramatic increase in interfacial area. In comparing with traditional composites. This interfacial area gives a significant volume fraction of interfacial polymer with properties different from the bulk polymer even at small loadings [8]. The combination of the two components at a molecular level provides polymeric materials, potentially useful in multiples domains, such as optical biosensors, catalysts, and nanotechnology [9]. Heterocyclic aromatic polymers have attracted a great deal of attention in many Fields such as heat resistant non-metallic materials and aerospace [10]. Thiadiazole is one of heterocyclic type that used as a nanocomposite due to the structure of thiadiazole components [11], one of important method to prepare polymer/ silica nanocomposite its modification by chemical interaction, in this work polymer chains covalent attachment with surface of nanosilica, by functional groups to produce new nanocomposite [12].

2. Materials and Methods

2.1 Materials

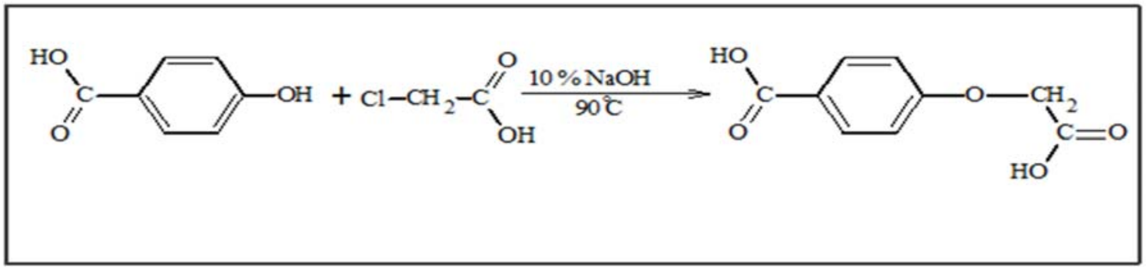
Nano sized silica powders were supplied by sky Co. Ltd (USA) with average particle sizes of 30 nm. Acrylic acid was obtained by Merck Co, methacryloyl chloride, thiosimecarbazide, tetrahydrofuran (THF), 4-hydroxybenzoic acid, tri ethylene diamine and soduime hydroxide (NaOH) were obtained by sigma Aldridge. Benzoyl Peroxide was supplied by Fluke Chemical Company. Phosphorous oxy chloride was obtained by Merck Company.

2.2. Techniques:

The FTIR spectra were recorded on Shimadzu 8300 Fourier Tran ranging from 400-4000cm^{-1}. Atomic Force Microscope (AFM)-SPM AA3000 USA-2008. 7000 / 6000 S-type X-ray Diffract meter recorded in Shimadzu / Japan.

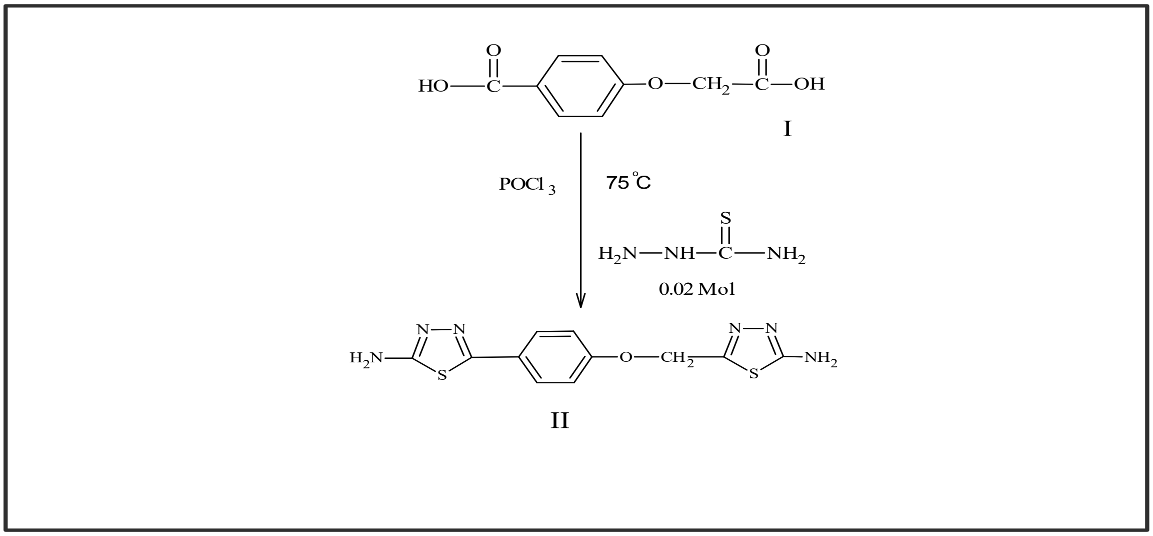
2.3. Preparation of 4-(carboxymethoxy) benzoic acid (I).

4-(carboxymethoxy) benzoic acid compound was prepared from the following procedure, the 4-(carboxymethoxy) benzoic acid was prepared by dissolved mixture of p-hydroxybenzoic acid 1.38 g, 0.01ml and 0.94 g, 0.01 ml of chloroacetic acid in 40 mL of sodium hydroxide 10%. The reaction was continued for 6 h at reflux at 80°C temperature and cooled to 5°C. The mixture was then acidified with dilute HCI to precipitate 4-(carboxymethoxy) benzoic acid, the precipitate filter, wash and dry. m.p (210-212) °C, yield 87% [13].



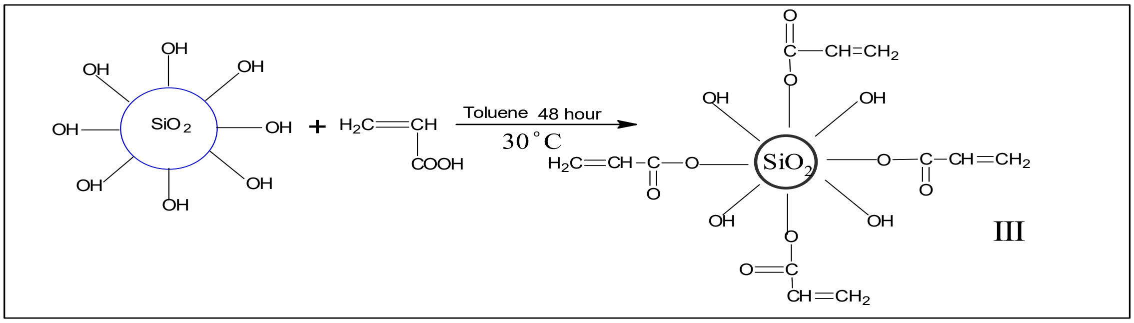
2.4. Preparation of 5-{4-[(5-amino-1,3,4-thiadiazol-2-yl) methoxy] phenyl}-1,3,4-thiadiazol-2-amine [II].

The 1.96 g, 0.01mol of 4-(carboxymethoxy) benzoic acid was mixed with 0.91g, 0.01 mol of thiosemicarbazide and refluxed at 75°C with 10mL of phosphorous oxy chloride ($POCl_3$) for 5 hours. To the cold mixture 50 mL of ice water was add. The precipitate was neutralized by sodium bicarbonate, filtered, washed by water and dried m.p 189°C, yield 93% [14].



2.5. Preparation of nano Silica –Graft acrylic acid monomer (III).

The 1.0 g of silica placed in one-neck round bottom flask followed by addition of 20 mL dry-toluene. 3.0 g, 0.01 mol of Acrylic acid monomer was added to the solution of silica-toluene drop wise at room temperature. Then the mixture left to stirring for overnight. The product was filtered and washed with 20 mL of distilled water, and 20mL acetone respectively. The solid product left to dry at room temperature [15].



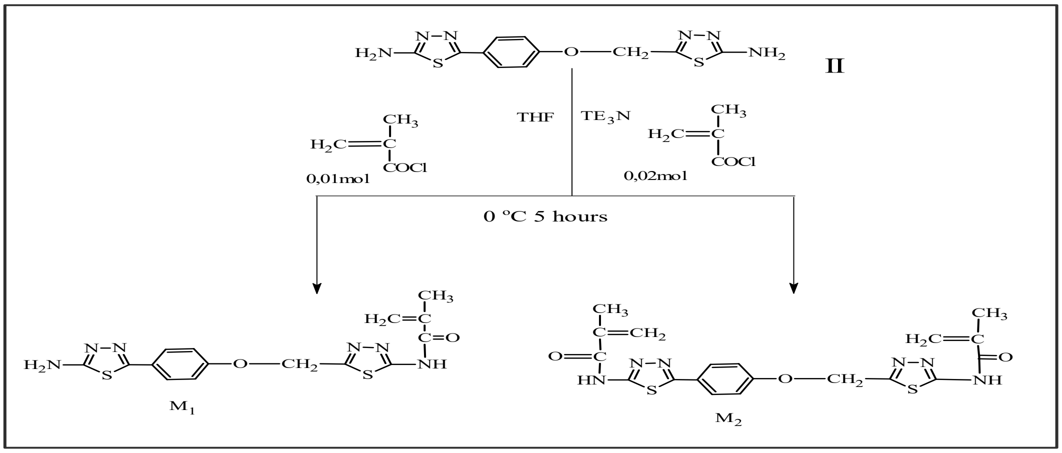
2.6. Preparation of monomers.

2.6.1. Preparation of N-(5-{[4-(5-amino-1,3,4-thiadiazol-2-yl) phenoxy] methyl}-1,3,4-thiadiazol-2-yl)-2-methylprop-2enamide [M$_1$].

The 2.5 g, 0.01 mol of heterocyclic compounds (II) was dissolved in 10mL tetrahydrofurane (THF) with 2 ml of trietheylamine (TE$_3$N). Then 1.04g, 0.01mol of methacryloyl chloride was added drop wise with stirring in (0°C) for 5 hours. To the cold mixture 50 mL of ice water was add, the precipitate was filtered, washed by water and dried at room temperature [16].

2.6.2 Preparation of 2-methy l-*N*- {5- [4-({5- [(2 methylacryloyl amino] 1,3,4-thia diazol-2-yl} methoxy) phenyl]-1,3,4-thiadiazol-2-yl} prop-2 enamide. [M$_2$].

The 2.5g,0.01mol of heterocyclic compounds (II) was dissolved in 10 mL tetrahydrofurane (THF) with 2ml of trietheylamine (TE$_3$N). Then 2.08 g, 0.02 mol of methacryloyl chloride was added drop wise with stirring in (0°C) for 5 hours. To the cold mixture 50 mL of ice water was add, the precipitate was filtered, washed by water and dried at room temperature [16].



2.7. Preparation of Polymers and their nanocomposites by Free Radical Polymerization.

Benzoyl peroxide was used as initiator it was purified by dissolving certain amount in minimum quantity of chloroform until turns to a clear solution. Petroleum ether (60-80)°C was added drop-wise until white precipitate started to appear, then the solid product filtered and left to dry in desiccator at room temperature [17].

2.7.1 Preparation of Polymers [P_1 and P_2]

In all of those preparation a two-neck round-bottom flask contains 20 ml of dry toluene as solvent was placed in controlled water bath at 75°C under nitrogen atmosphere. After 5 minutes 0.1g,0.01mol of benzoyl peroxide was added, followed by addition of 3.0g ,0.0mol of each of following monomers M_1, M_2 was added separately with stirring for 5 hours. The product was filtered and washed firstly with 15mL of toluene and 15mL of acetone then dried at room temperature [17].

2.7.2 Preparation of Nanocomposite [C_1 and C_2]

In all of those preparations a two-neck round-bottom flask contain 20 ml of dry toluene as solvent was placed in controlled water bath at 75°C under nitrogen atmosphere. After 5 minutes 0.1g benzoyl peroxide was added, followed by addition of 3.0g of nano silica-grafted acrylic acid monomer after that 3.0g,0.01mol of each monomer M_1, M_2 was added separately to give two different reactions, with stirring for 5 hours. The product was also filtered and washed firstly with 15mL of toluene and dried such as last method of the preparation of polymers [17]. All structures of polymers and nanocomposites had showed in **Table 1**.

3. Results and Discussion

3.1. FT-IR of compounds

The FT-IR spectrum of compound (I) **Figure1**, shows the appearance stretching vibration band of aliphatic υ C-H between 2918 cm^{-1}, 2794 cm^{-1}. FT-IR shows strong band at 1221 cm^{-1} which attributed to stretching vibration of υ (C-O-C) [13].

The characteristic of FT-IR absorption bands for compound [II] **Figure 2.** shows the disappearance of absorption band due to O-H stretching of compound (I) together with the appearance of a stretching band at 3226cm^{-1}, 3159 cm^{-1}, assignable to υ NH_2. The spectrum shows the band at 1620 cm^{-1} due to υ C=N [14].

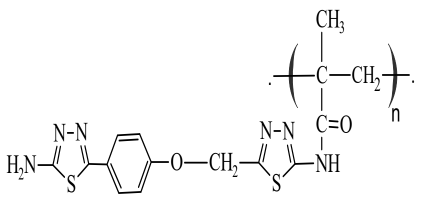
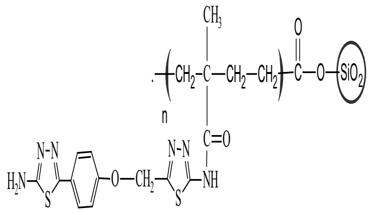
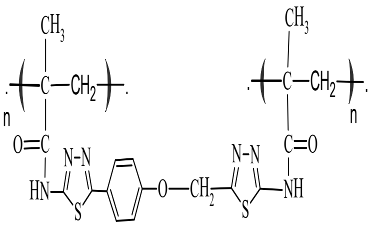
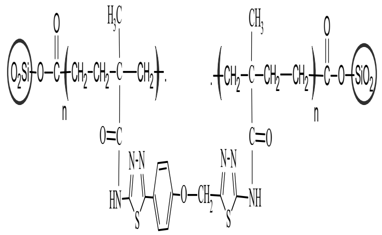
Nanosilica-graft acrylic acid monomer [III] was characterized by FT-IR, **Figure 3.** The spectrum shows a decrease of peak intensity at 3390 cm^{-1} due to grafting process, which refer reaction of acrylic acid with hydroxyl group of nanosilica surface. The FT-IR displayed a sharp C-H stretching absorption in the region between 2968cm^{-1}- 2850 cm^{-1}, as well the υ C=O absorption at 1724 cm^{-1} , the spectrum also shows appearance υ C=C stretching vibration at 1637 cm^{-1} . peak at 1053 cm^{-1} to υ Si-O-C.

The FT-IR spectrum of N-(5-{[4-(5-amino-1,3,4-thiadiazol-2-yl) phenoxy] methyl}-1, 3, 4-thiadiazol-2-yl)-2-methylprop -2enamide (M_1), **Figure 4** shows a significant bands at 3280 cm^{-1}, which could be attributed to the stretching vibration of υ NH_2 of compound [II].The spectrum shows band at 3124cm^{-1} due to secondary amine and also appearance band at 1695cm^{-1}. The spectrum also shows the band at 1570 cm^{-1} due to υ C=C of methacryloyl chloride.

The FT-IR spectrum of 2-Methyl-N- {5- [4-({5- [(2 methylacryloyl amino]1,3,4-thia diazol-2-yl} methoxy) phenyl]1,3,4-thiadiazol-2-yl} prop-2enamide(M_2) **Figure 5.** shows disappearance of absorption band of υNH_2 of compound [II]. FT-IR spectrum shows C=O band at 1695 cm^{-1} and stretching vibration at 1605cm^{-1} attributed to C=C of methacrloyl chloride.

The FT-IR spectrum of the polymers and their nanocomposite shows disappeared C=C stretching of methacryloyl chloride of monomers, the spectrum shows absorption strong aliphatic C-H groups attributed to alkyl groups. strong band of stretching vibration at (1095) cm^{-1}shows which attributed to Si-O-C group for the nanocomposites [18] , **Figures 6-9.**

Table1. Structure of polymers and their nanocomposite

NO	Polymer	NO	Nanocomposite
P_1		C_1	
P_2		C_2	

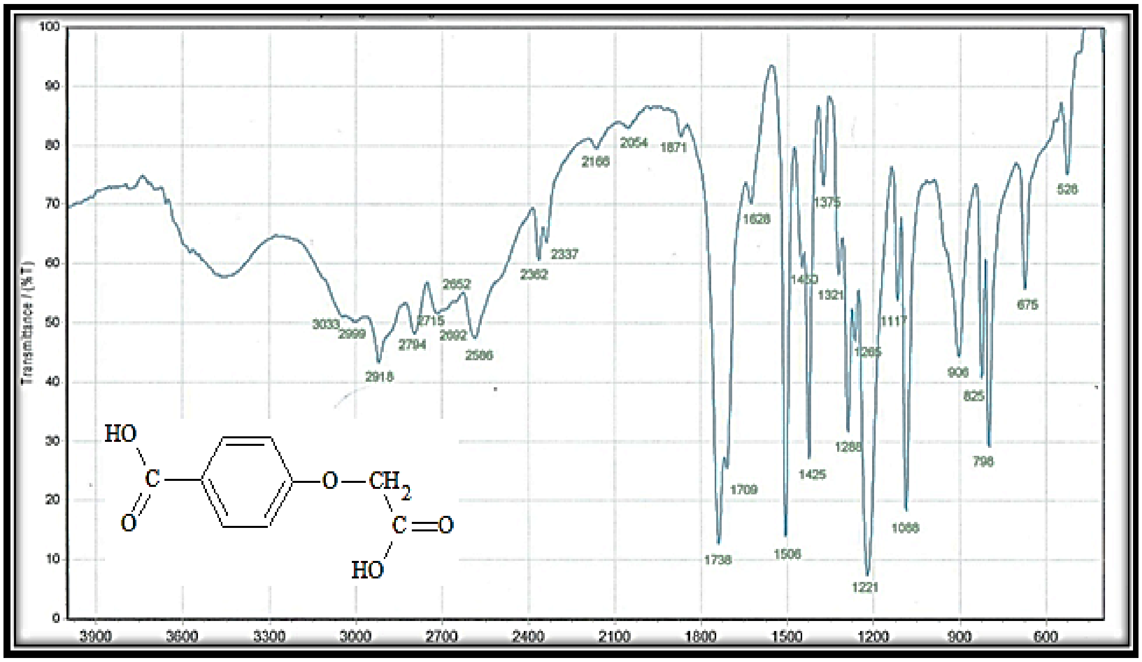


Figure 1. FT-IR spectrum of 4-(carboxymethoxy) benzoic acid(I).

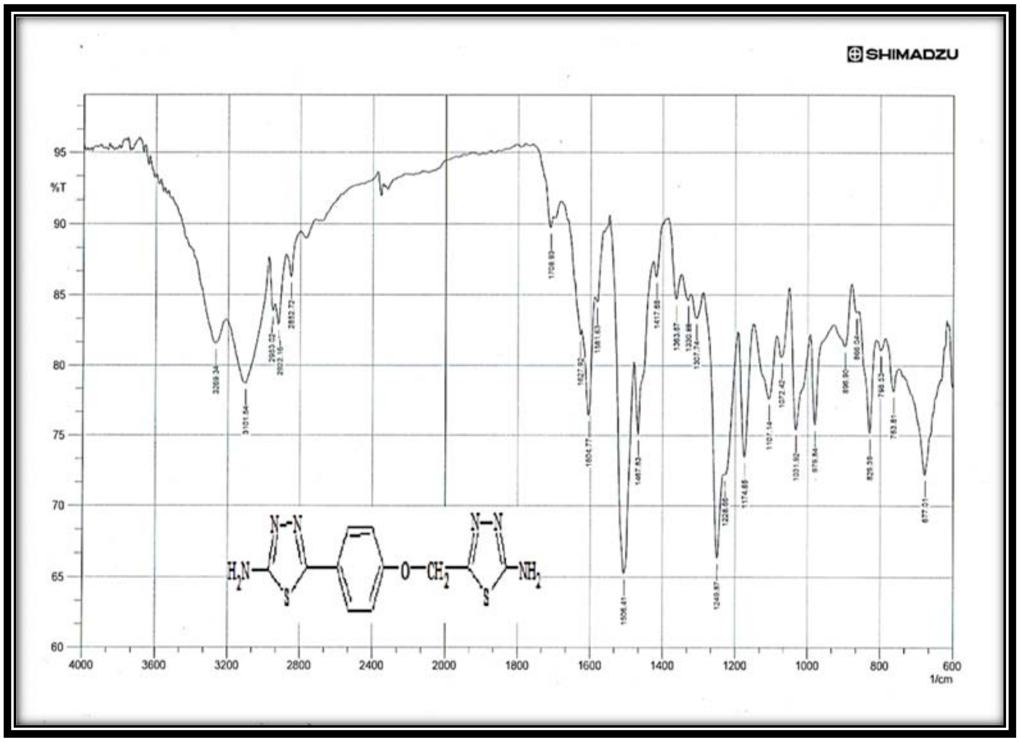


Figure 2. FT-IR of heterocyclic compound [II].

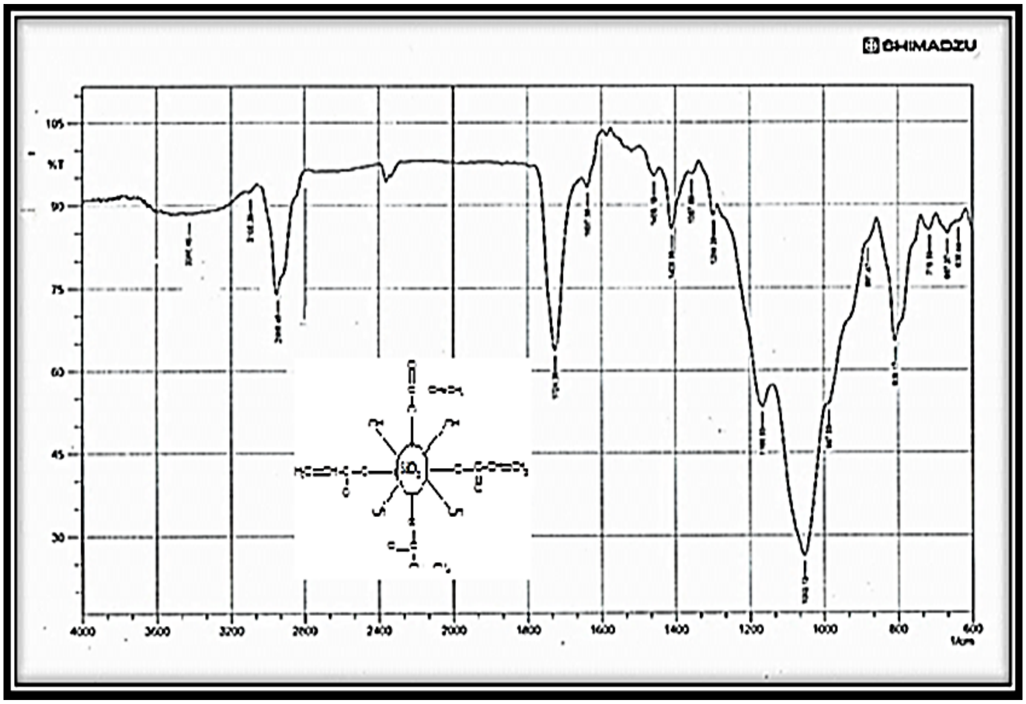


Figure 3. FT-IR of nanoSilica graft acreylic acid monomer (III).

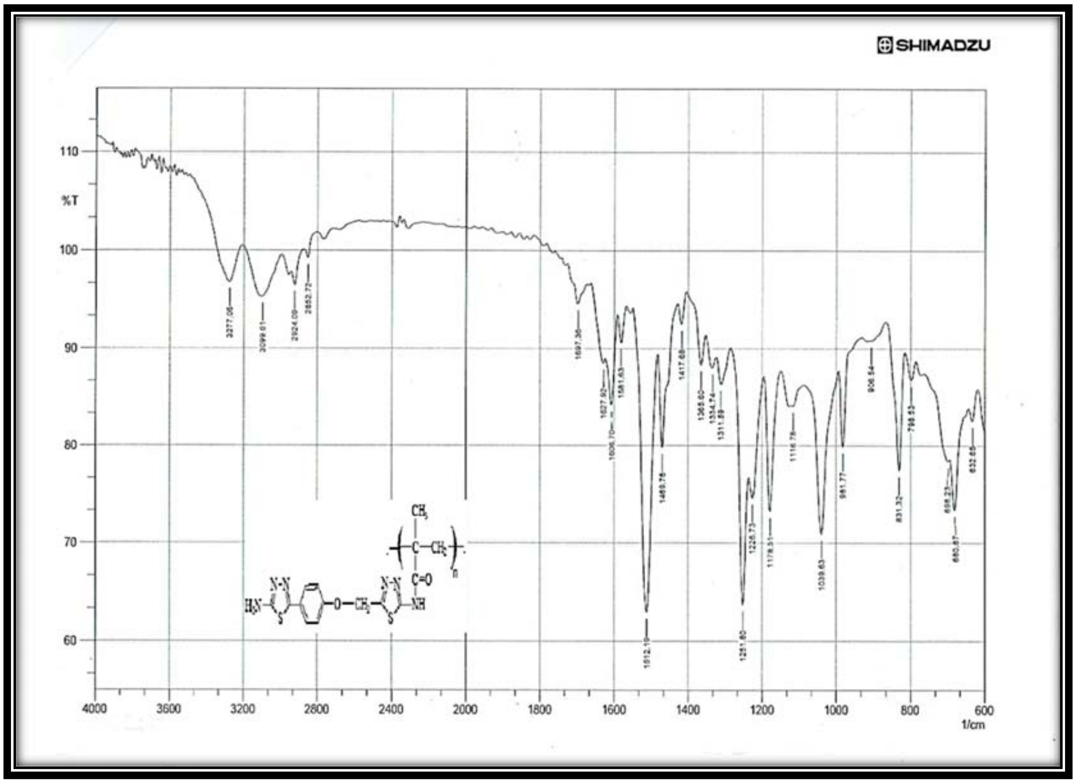


Figure 4. FT-IR Spectrum of monomer[M_1].

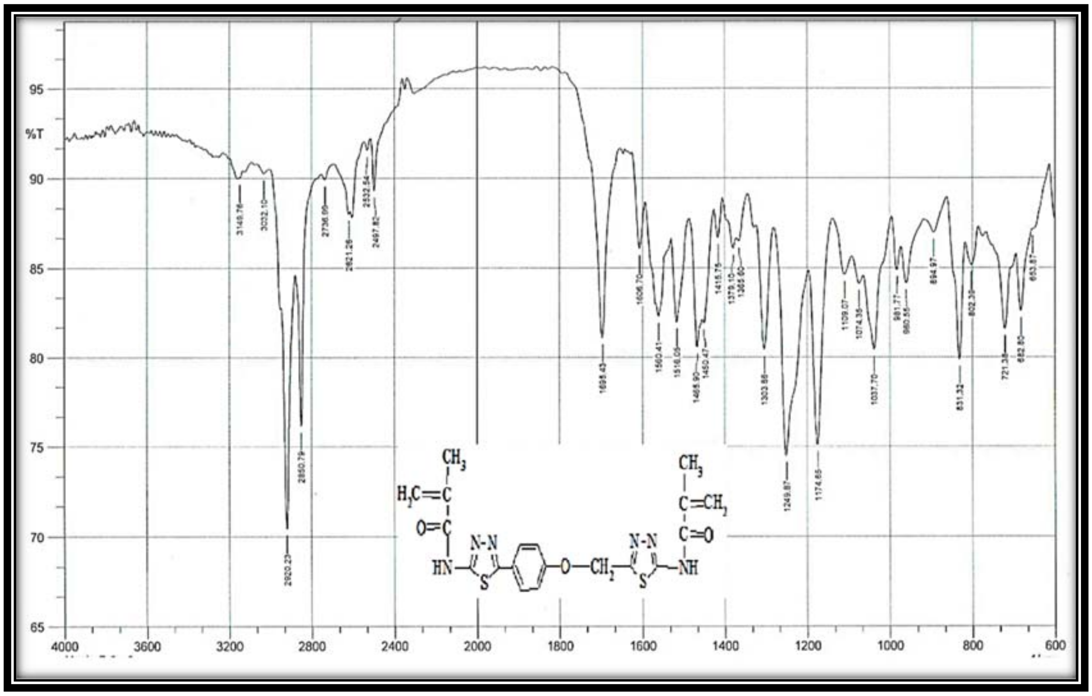


Figure 5. FT-IR Spectrum of monomer[M_2].

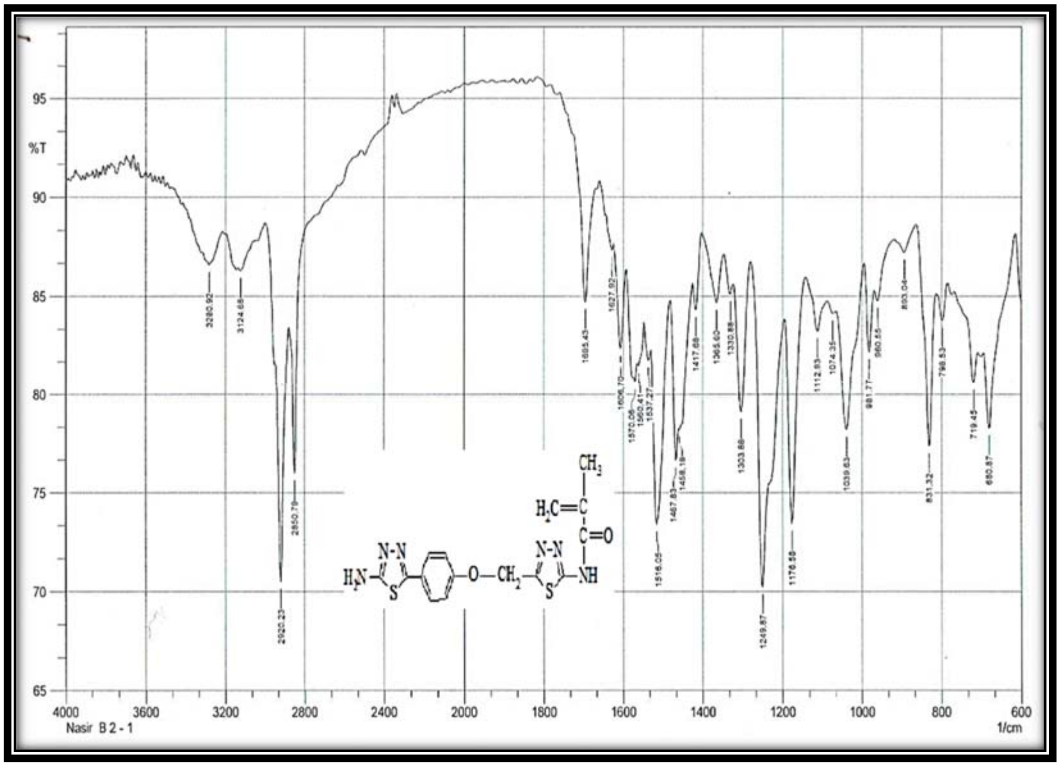


Figure 6. FT-IR Spectrum of polymer (P_1).

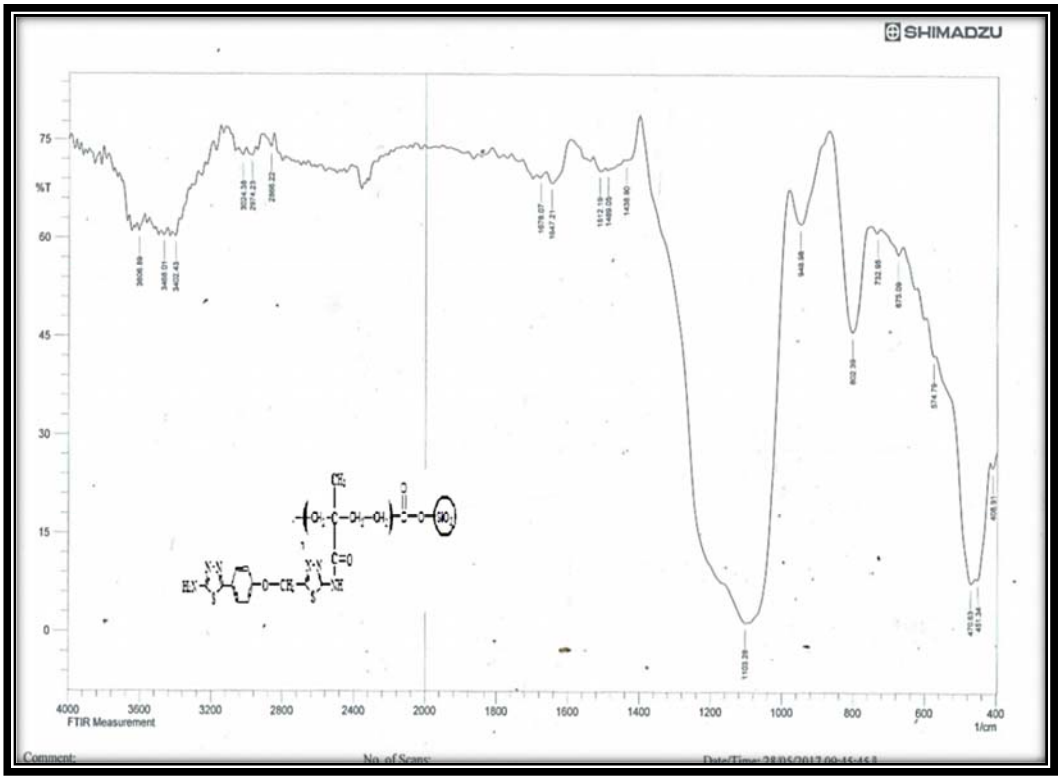


Figure 7. FT-IR Spectrum of Nano composite (C_1).

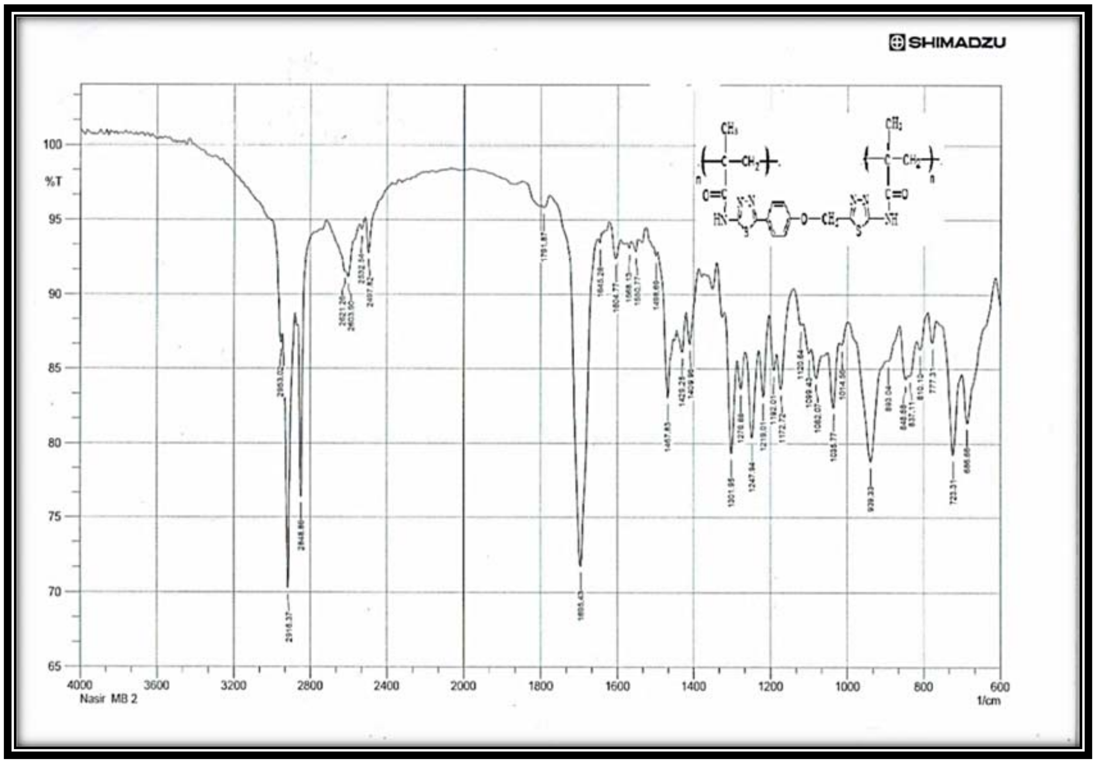


Figure 8. FT-IR Spectrum of polymer (P_2).

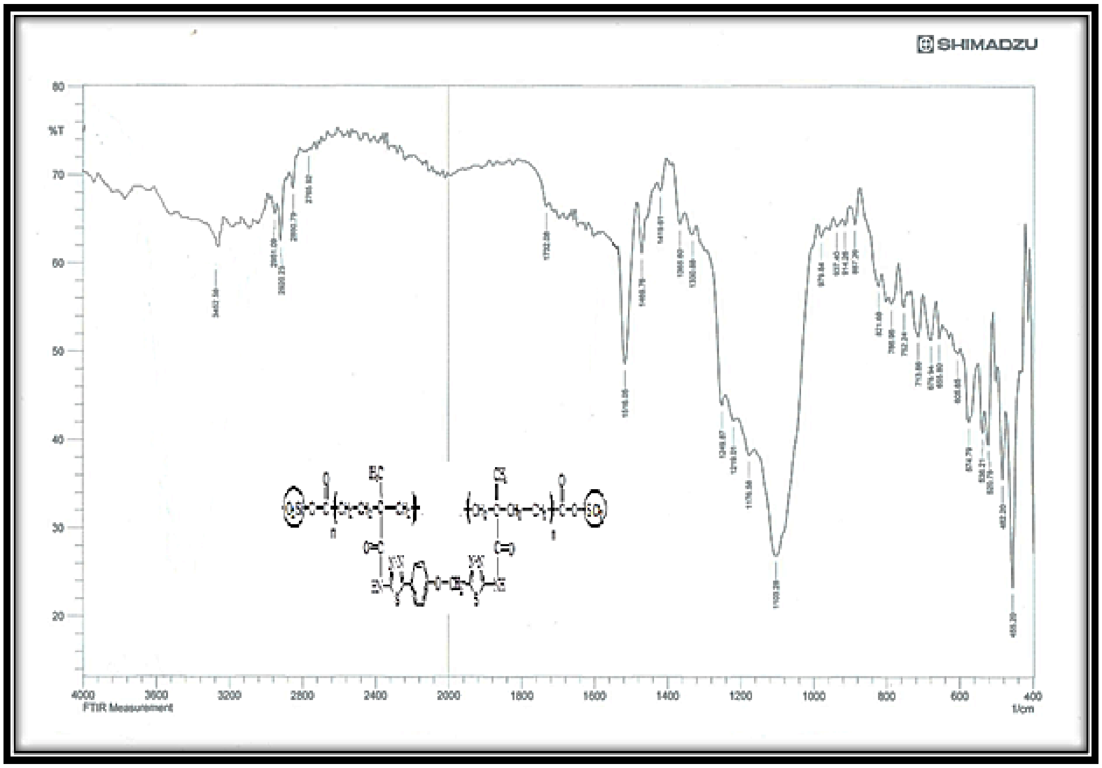


Figure 9. FT-IR Spectrum of Nano composite (C_2).

3.2. X-ray diffraction of nanocomposite.

X-ray diffraction of silica nanoparticles and their nanocomposite show in **Figures10-13**. The structure of silica nanoparticles, **Figure 10**. show intensity at 18000 with broad peak at 2θ=23. While the structure of grafted nanosilica and nanocomposite through X-ray pattern **Figure 11.** show presence of wide range peak with low intensity at 2θ=23 with intensity at 150 compared with standard nanosilica. **Figure 12**. of nanocomposite C_1 show broad peak at 2θ=22 with intensity at 120 and sharp peaks at 2θ=32, 2θ=41 attributed to the crystalline polymers chains which grafted on the silica surface. While Nanocomposite C_2 in **Figure 13**. show broad peak at 2θ =22 with intensity at 140 with small peak also at same area 2θ=22 which refers to polymer chains grafted covalent with silica nanoparticles.

Change in intensive and sharp peak refers to high crystalline of chain and crystalline structure of nanosilica. All figures of X-ray diffraction show there are similar to that of the standard silica nanoparticles there are no changes in the positions of the diffraction peaks. The difference was shown in the intensity of peaks which indicating that the crystalline structure of the mineral silica nanoparticles remained intact and has not been destroyed after the grafted with thiadiazole polymers chains. The change in the relative intensities of peaks can be mostly attributed to the two types of forces . The first one is the chemical modification between grafted silica surface and thiadiazole polymer chains .The second type is the force of attraction of Van-der-Waals force between thiadiazole chains in the nanocomposite structure. These results are in good agreement with those reported in the literatures [19, 20].

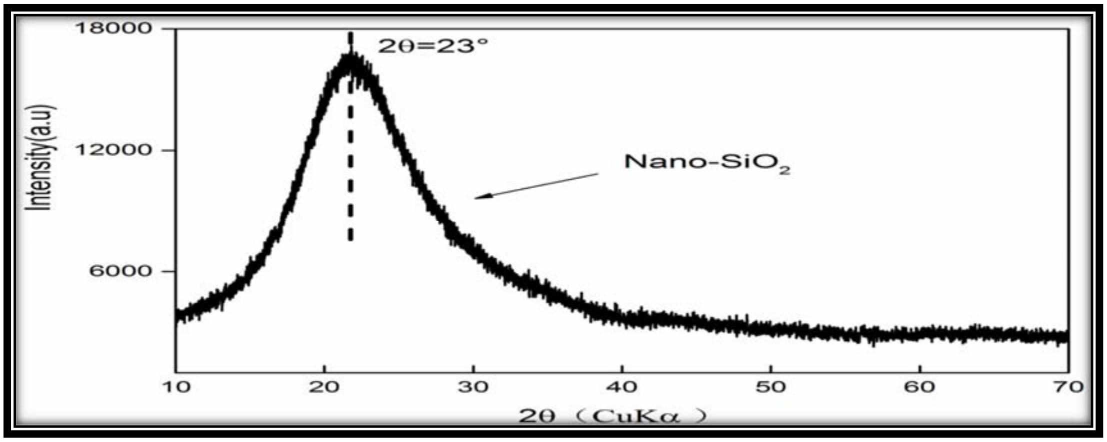


Figure 10. X-ray diffraction of standard nanosilica.

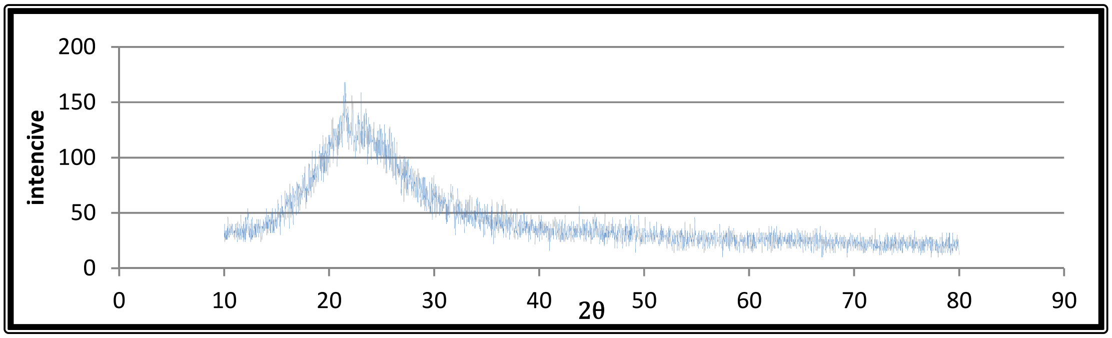


Figure 11. X-ray diffraction of grafting nanoSilica.

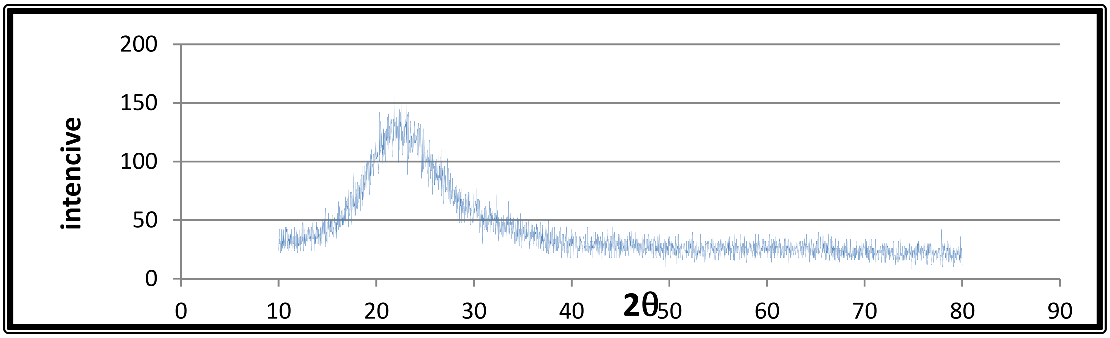


Figure 12. X-ray diffraction of nanocomposite (C_1).

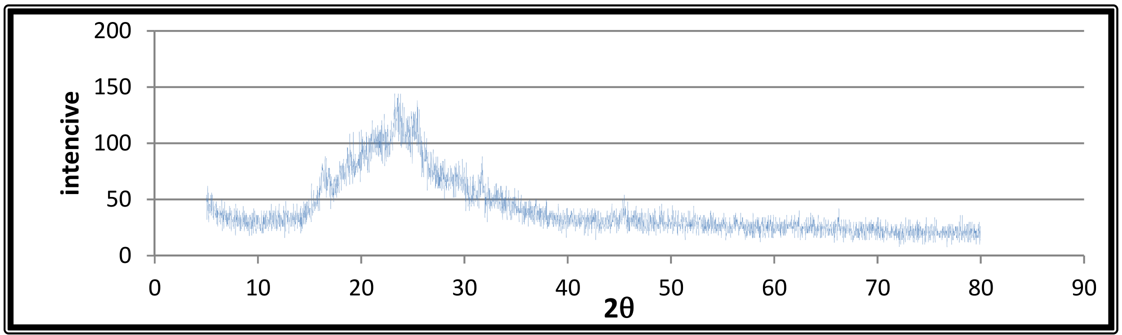


Figure 13. X-ray diffraction of nanocomposite (C_2).

3.3. Atomic Forces microscopy of nanoComposites (AFM).

The surface morphology of nanosilica and nanocomposite **Figures 14-15**. shows the three-dimensional image of the silica nanoparticles before modification of nanosilica surface by acrylic monomer with rang diameter between (55-110 nm) and height up to (9.68 nm). **Figures 16-17**. shows the three-dimensional image of the grafting silica nanoparticles with range diameter between (60-135) nm and height up to (22.9) nm. The surface morphology of nanocomposite for height profile as well as the three-dimensional surface structure. **Figures 18-21**. shows the existence of irregular surface roughness. This roughness and height up diameters of the nanocomposite, can be attributed to linkage of different synthesized chains of heterocyclic thiadiazole polymers, with surface of grafting silica to formation nanocomposite [21]. It is strongly dependent on the growing conditions and the surface processing methodologies [22]. Particles size distribution of samples display that the particles of modified silica in **Figure 16**. and all figures of nanocomposites show increase in size of particles. In contrast the modification of nanosilica with polymers lead to increase diameter in fact the reaction of chains polymers with modified SiO_2 surface can run through the polymer linkage and distribution on to the modified silica surface. As the chains of polymers is very long that lead to high rough and big diameter in the particles size distribution [23]. Photograph image of nanocomposites, shows present high a rough surfaces and high diameter compared with silica nanoparticles which appeared to modification by polymer chains but varying degrees. These result which attributed to the linkage between functionalized surface of grafted nanosilica with along polymer chains because of polymer chains with different lengths attach to the silica surface. They will increase the size of the particles, thus obtain surfaces with different forms of roughness that can be shows through AFM photo of nanocomposite and particles size distribution. **Figure 14**. of nanosilica particles shows small particles with a little roughness due to nanoscale size of particles. While **Figure 20**. of nanocompositeC_2 shows height up to 49.76nm with particle size distribution (60.135) nm comparison with grafted nanosilica surface and nanocomposite C_1. These characterization of nanocomposite C_1 and C_2 attributed to cyclic structure of thiadaizole chains. Due to react chains with grafted nanosilica surface led to the high roughness with wide range particles size distribution [20].

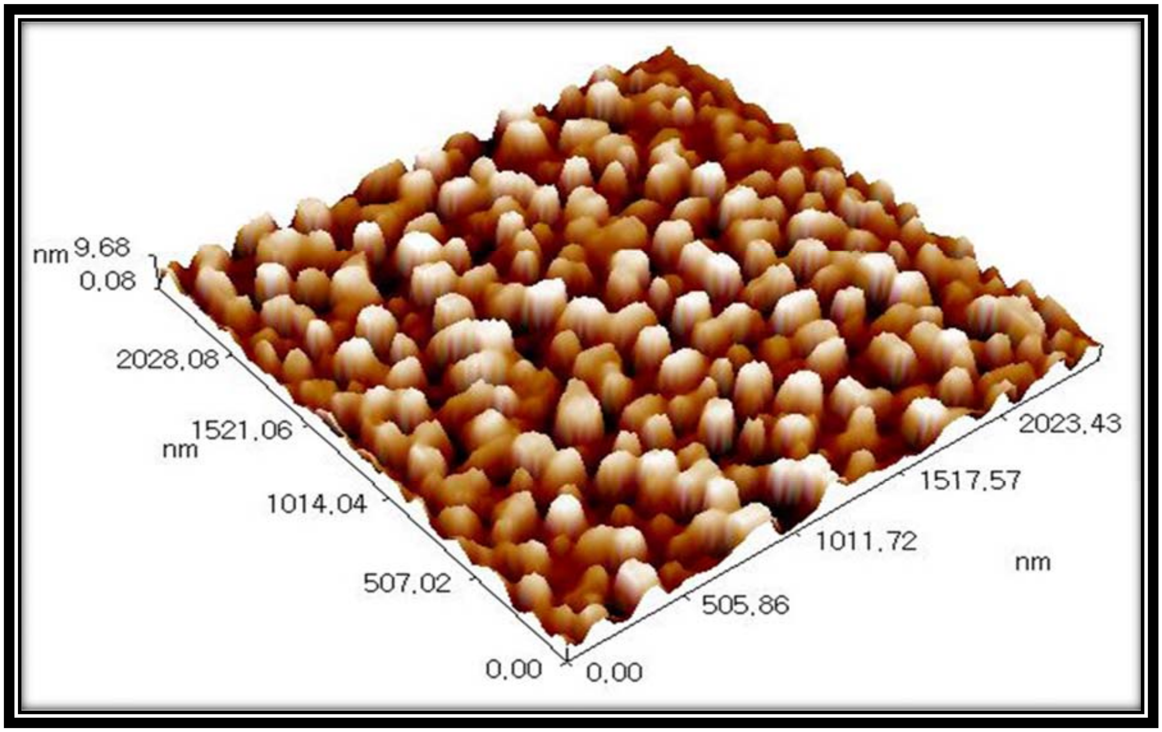


Figure 14. AFM photo of nano silica.

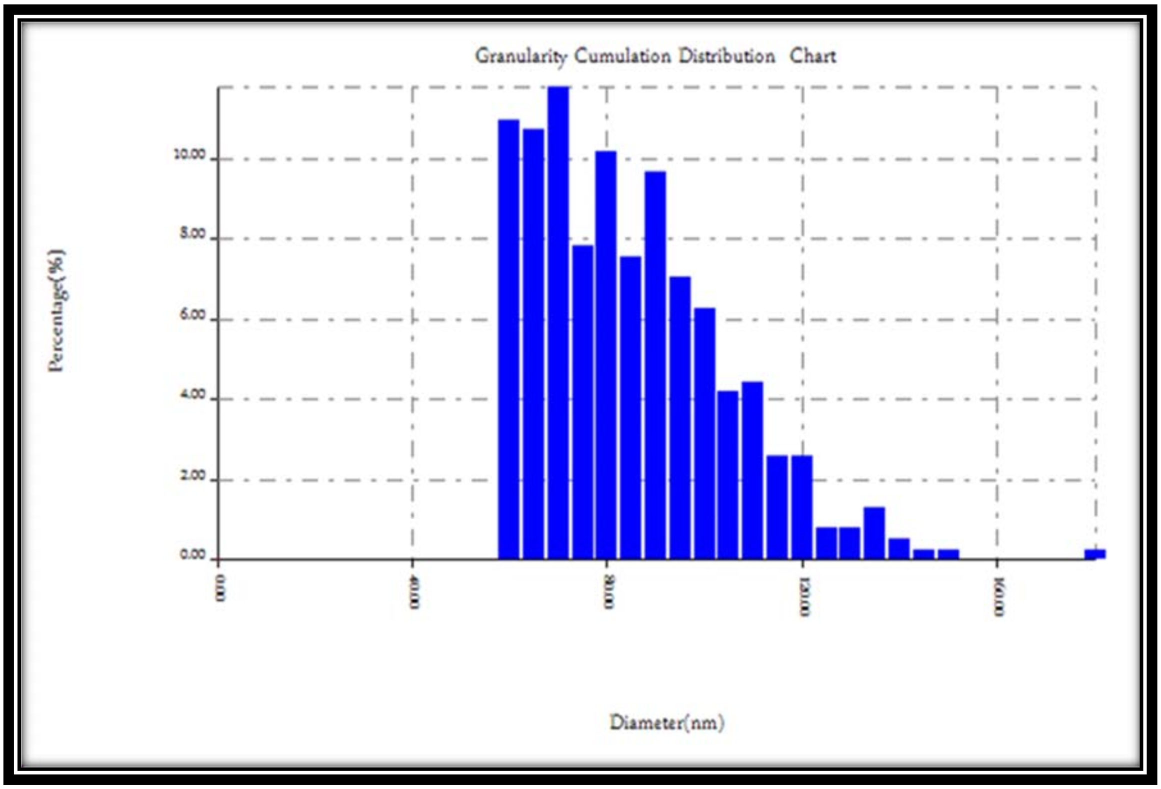


Figure 15. particle size distribution for nanosilica.

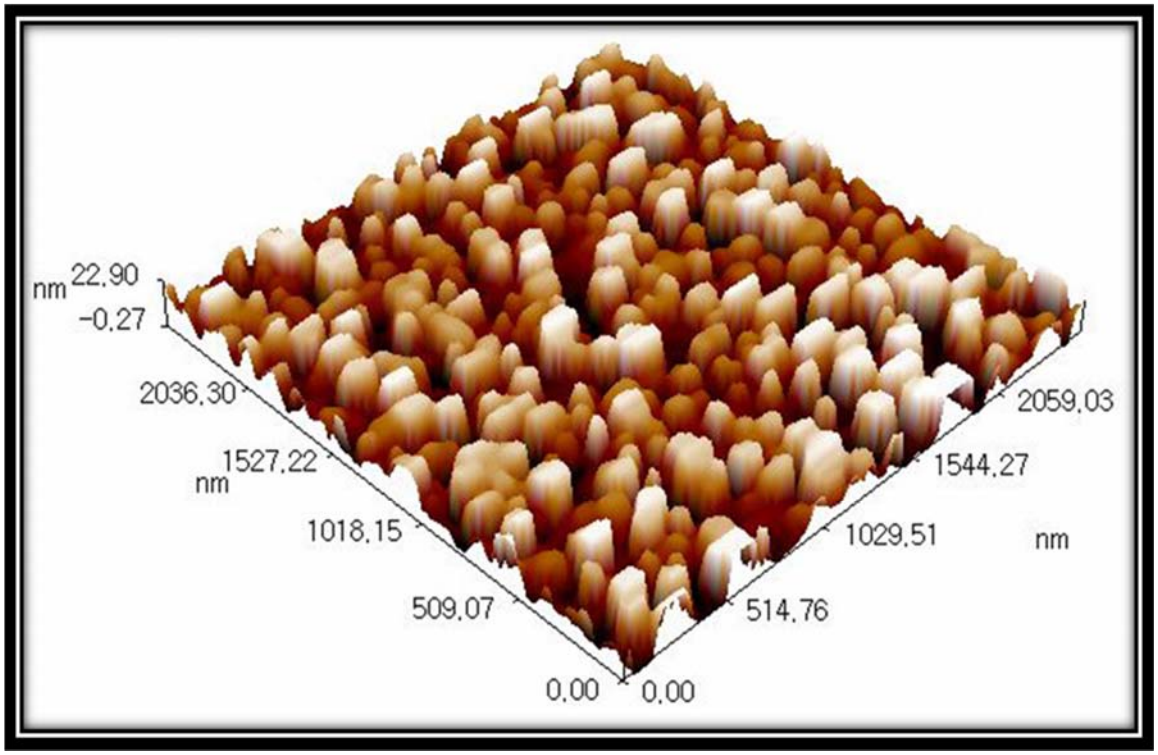


Figure 16. AFM photo of grafted nano silica.

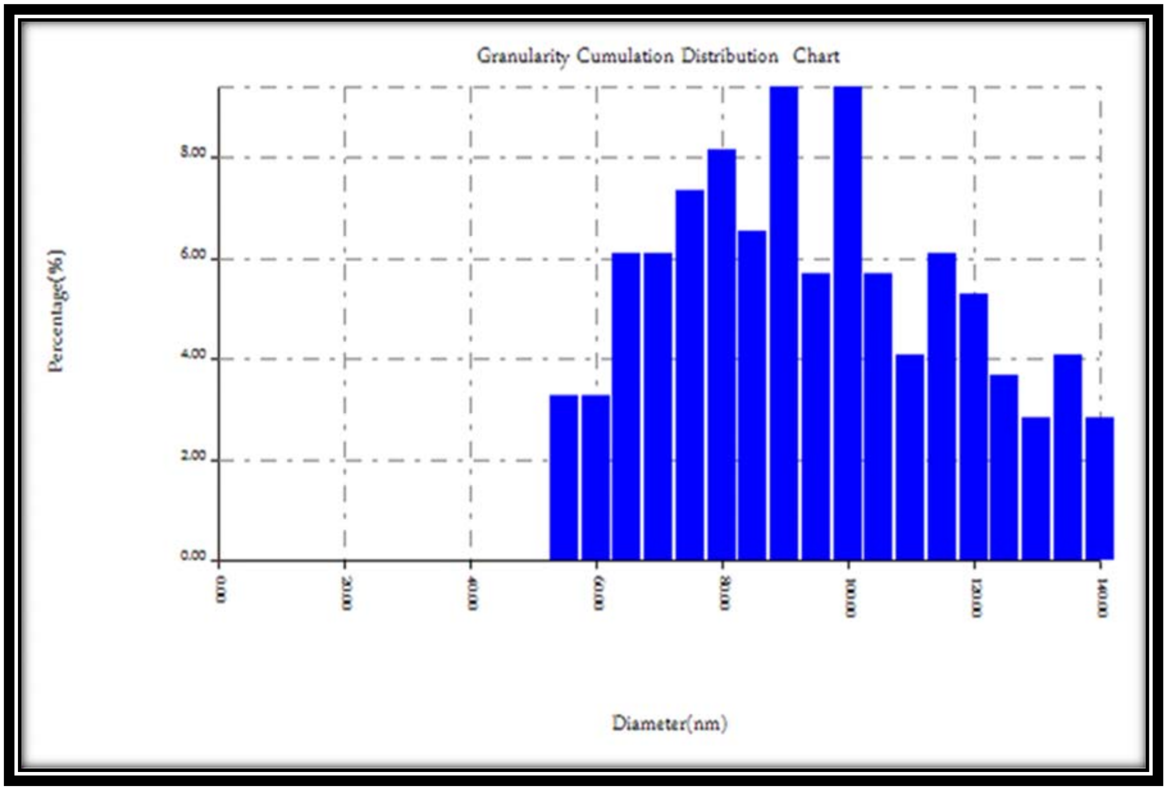


Figure 17. Particle size distribution for grafted Nano silica.

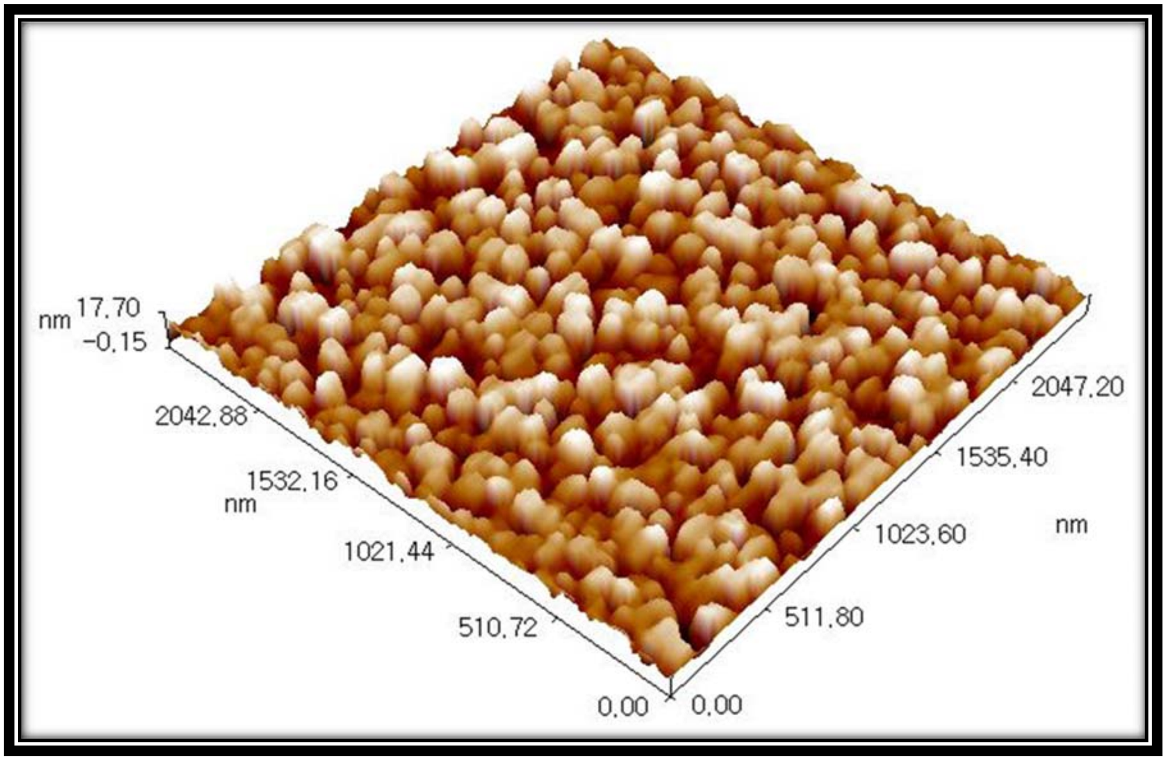


Figure 18. AFM photo of Nano composite (C_1).

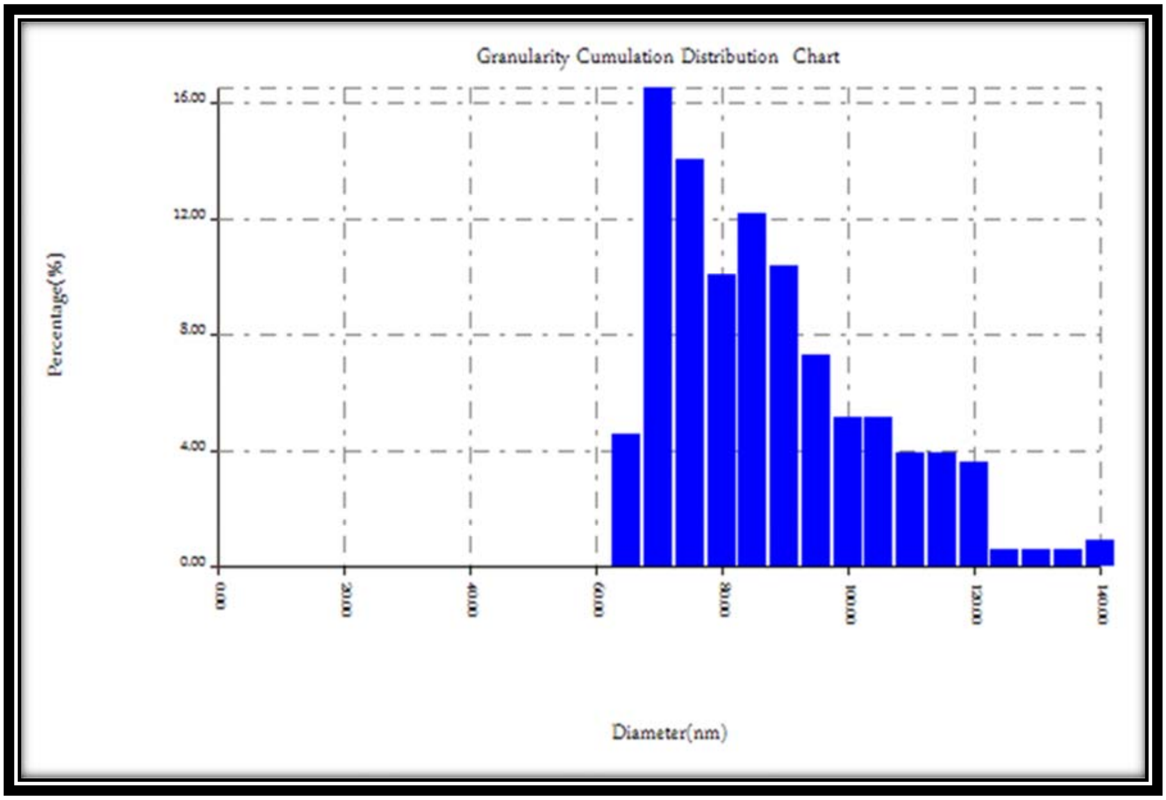


Figure 19. Particle size distribution of Nano composite (C_1).

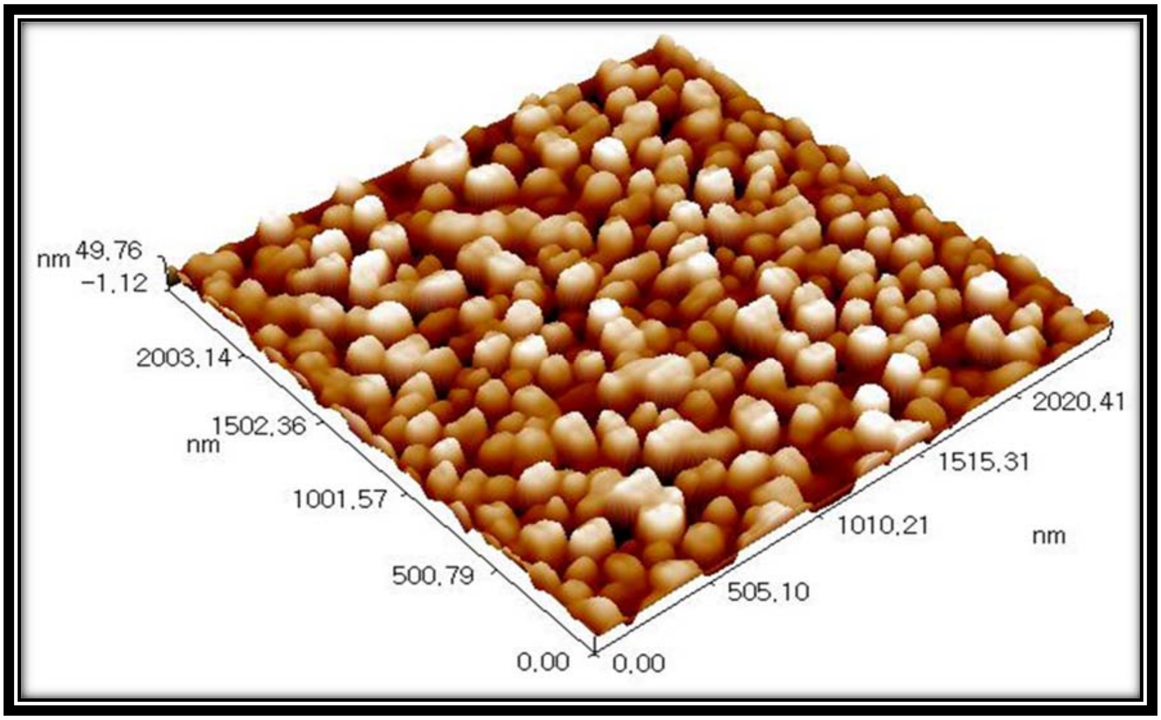


Figure 20. AFM photo of Nano composite (C_2).

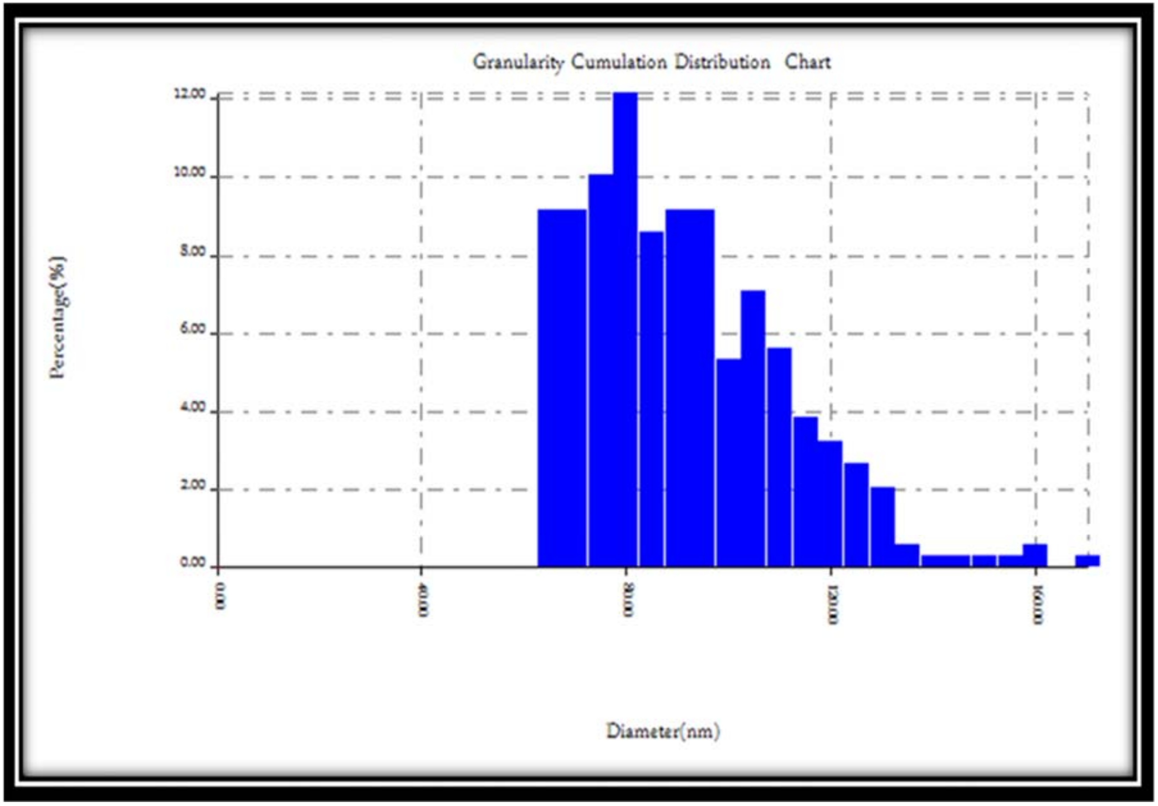


Figure 21. Particle size distribution Nano composite (C_2).

4. Conclusion

In recent years, nanocomposites have become a major part of new synthetic materials all over the world for industrial applications. Novel polymer and their nanocomposite were prepared by reaction thiadiazole monomers with nanosilica graft acrylic acid monomer by free radical polymerization. All prepared materials were identified by FT-IR spectroscopy, X-ray diffraction and atomic forces microscopy (AFM). FT-IR shows different in the structure of compunds, monomer, polymers and nanocomposite due to reacted of functional groups in these compounds. X-ray diffraction use to study the crystalline characterization. X-ray has shown the difference in the intensity of peaks with no change in area for grafted nanosilica and nanocomposite $C_1$and C_2 that indicate that the crystalline structure of the mineral silica nanoparticles remained intact and not destroyed after the grafted with thiadiazole polymers chains. AFM results shown high roughness in the surface of nanocomposites C_1 and C_2 comparison with silica nanoparticles that attributed to reaction between functionalized surface of grafted nanosilica with chains of thiadaizole polymers led to change in size particles distribution and surface of particles.

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