Original Article

Synthesis, Characterization and Study Electrical Conductivity of New Poly Thiadizole Derivatives, Silica Nanocomposites

Nasir Sadoon Abid[1], Maha T. Sultan[2]

[1]Department of Medical Instrumentation Engineering, College of Medical Techniques, Al- Farahidi University, Baghdad, Iraq.

[2]Department of Chemistry/College of Education for Pure Science (Ibn Al-Haitham), University of Baghdad, Baghdad, Iraq

Abstract

Heterocyclic polymers / silica nanocomposite one of important materials because of excellent properties such as thermal , electrical , and mechanical properties , so that hybrid nanomaterial are widely used in many fields, in this paper nanocomposite had prepared by modification of silica nanoparticals by using acrylic acid and functionalized the surface of nanoparticles, and using free Radical polymerization by AIBN as initiators and anhydrous toluene as solvent to polymerize functionalize silica nanoparticles with heterocyclic monomers to prepare heterocylic polymers / silica nanocomposite and study electrical conductivity , The nanocomposite which had prepared characterized by many analysis technique to study thermal properties such as (TGA , DSC) and study surface morphology by use Scanning electron microscopy and atoms forces microscopy (SEM , and AFM) ,and study structure of Nanocomposite by using (XRD) Analysis and study others advantages by other common methods.

Keywords: Heterocyclic polymers, 1,3,4 thiadiazole ,Silica Nanoparticals , nanocomposite , SEM , XRD , and electrical conductivity.

1. INTRODUCTION

Nanocomposites its materials mead up of inorganic nanoparticles and organic polymers represent a new class of materials that exhibit improved performance when compared with their microparticle counter parts (1). polymer Nanocomposite materials had been used in all fields of technology (2) . Recently, inorganic-polymer composites have been studied widely because of their particular applications and properties (3). In electrical failed polymer nanocomposite used as electeomagnatic materials in electronic device (4). The surface modification of nanoparticles in order to change their physical and chemical properti(es has become an area of significant research in industry(5). Heterocyclic Polymer/silica nanocomposites have been extensively used in many applications because of their excellent properties (6).

Most of Heterocyclic polymer /silica nanocomposite synthesis by using thermal polymerization method (7) .combined heterocyclic polymer with silica nanoparticles have been extensively used in many applications because of their excellent properties such as superior mechanical properties, ,good thermal stability and good creep resistance(8).[1,2,3] thiadiazole and [1,2,5] thiadiazole dervatives is a known as heterocyclic polymers that finds in many applications(9-10).

Access this article online	
Quick Response Code:	**Website:** www.pnrjournal.com
	DOI: 10.47750/pnr.2022.13.04.182

Address for correspondence: Nasir Sadoon Abid
College of Medical Techniques, Al- Farahidi University, Baghdad, Iraq
Email: n.abid@uoalfarahidi.edu.iq

For reprints contact: pnrjournal@gmail.com

How to cite this article: N S Abid, M T. Sultan, Synthesis, Characterization and Study Electrical Conductivity of New Poly Thiadizole Derivatives, Silica Nanocomposites, J PHARM NEGATIVE RESULTS 2022;13: 1295-1306.

2. Experimental:

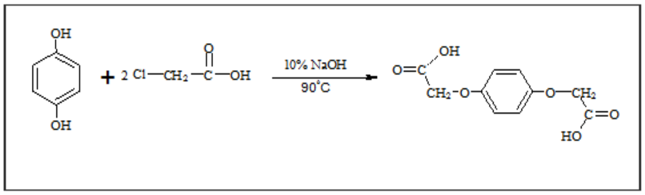
2.1 Material

Silica nanoparticles was purchased from nano sky company , toluene , triethylamine , benzoyl peroxide , solufoniyl chloride , metha acryloyl chloride , tetra hydro furan and thio semi carbazide were purchased from sigma Aldridge.

2.2 preparation of compounds :

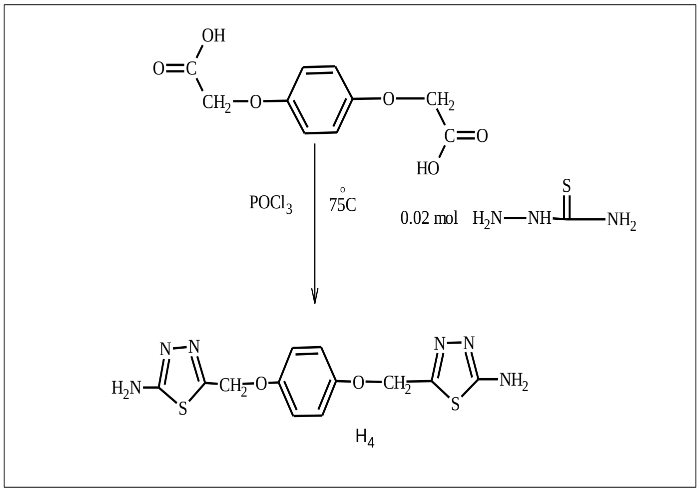
2.2.1 Preparation of 2,2–[benzene-1,4-diylbis (oxy)]diacetic acid (S2).

This compound [S2]was prepared according to literatures. through the reaction of hydroquenon with α -chloroacetic acid with10% Sodium hydroxide Solution (NaOH) at 90°C.(11)



2.2.2 preparation of 5,5-[benzene-1,4-diylbis (oxymethanediyl)] bis(1,3,4-thiadiazol-2-amine) [H4] (12).

0.01mol, 2.26g of [2,2 –(benzene-1,4-diylbis (oxy) di acetic acid] was mixed with 0.02 mole ,1.82 g of thiosemicarbazide and refluxed with 15ml of phosphorous oxy chloride (POCl3) for 5 hours , after that the mixture cooled and added to 50ml of Cold water gradually in hood station, The precipitate neutralized by sodium bicarbonate , filtered , washed by water and dried as shown in scheme (1) .



Scheme (1) preparation of (H4) Compound

2.3 Perparation of monomers [III , IIII] … (14)

2.3.1 Preparation of N-[5-({4-[(5-amino-1,3,4-thiadiazol-2-yl) methoxy] phenoxy} methyl)-1,3,4-thiadiazol-2-yl]-2-methylprop-2-enamide [M1] .

This compound was prepared following the procedure described in (2.6.1) with one different by using 0.01mol , 3.3g of compound (H4) .

.

2.3.2 2.6.8 Preparation of 2-methyl-N-{5-[4-({5-[(2 methylacryloyl amino]-1,3,4-thiadiazol-2-yl}phenoxy) phenyl]-1,3,4-thia diazol-2-yl}prop-2-enamide. [M2].

Monomer [M8] was prepared by same preparation procedure of [M7] but used 0.02mol, 2.08g of methacryloyl chloride .

all physical properties and structure of preparation monomers showed in Scheme 2.

2.4 Preparation of polymers and their composites by Free radical polymerization (15,16).

Benzoyl peroxide was used as initiator .It was purified by dissolving certain amount in minimum quantity of chloroform unit got 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.

2.4.1 Preparation of polymer P1.

flask contain (20ml) of dry toluene as solvent was placed in controlled water bath at (75°C) under nitrogen atmosphere , after 5 minutes (0.1) g benzoyl peroxide was added , followed by addition of (3 g) of monomer [M1] ,with stirring for (5) hours. The product was filtered and washed firstly with (15) ml of toluene and secondly with (15) ml of acetone than left to dry at room temperature .m.p (243°C) , yield (94%) .

2.4.2 Preparation of polymer P2.

Polymer (P2) was prepared by using monomer [M2] with the same procedure for preparation polymer (P1) .m.p (325-326)°C yield (92%) .

2.4.3 Preparation of Nanocomposite (C1)

flask contain (20) ml of dry toluene as solvent was placed in controlled water bath at (75°C) under nitrogen atmosphere after 5minutes (0.1) g benzoyl peroxide was added , followed by addition of (3 g) of Silica –grafted acrylic acid monomer and (3 g) of monomer [M1] with stirring for (5) hours . The product also filtered and washed firstly with (15) ml of toluene and secondly with 15 ml of acetone than left to dry at room temperature.

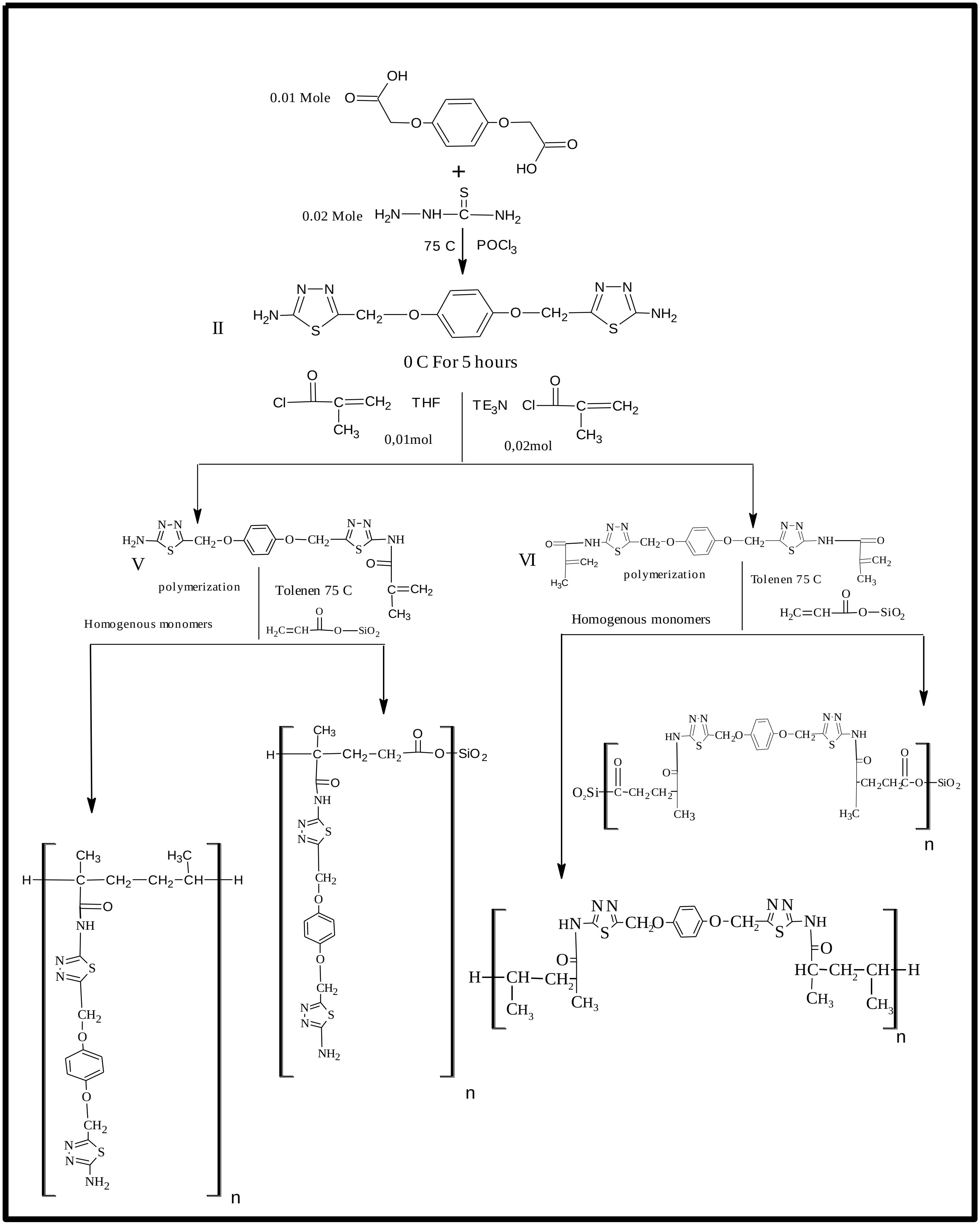
2.4.4 preparation of Nanocomposite (C2)

Nanocomposite (C2) was prepared by using (3g) of monomer [M2] with the same procedure for preparation Nanocomposite (C1)

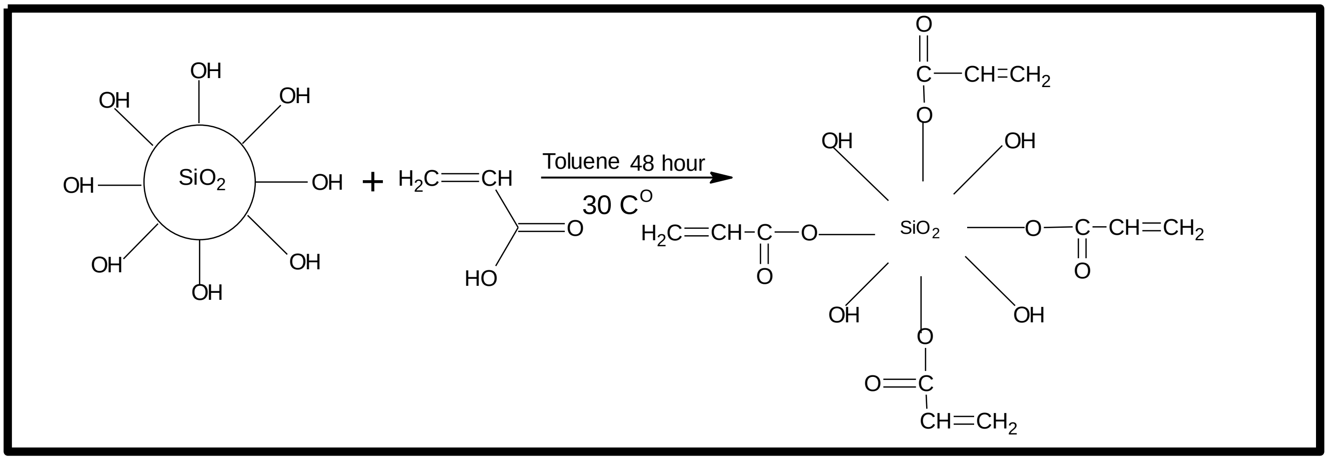
Scheme (2) Synthesis and polymerize of (V, VI) Monomers

2.5 Synthesis of Silica –Graft acrylic acid monomer …

(1g) of Silica was weight and placed in (one–neck round



bottom flask) followed by Addition of (20 ml) dry – Toluene . Acrylic acid monomer (3g) was added to the solution of Silica – Toluene drop wise at room temperature , than left the mixture was stirring for overnight . The product was filtered and washed with (20ml) distilled water , than (20ml) acetone . The Solid product left to dry at room temperature (16.17.18).



Scheme (3) modification of silica nanoparticles by acrylic acid monomers

3. Result and discussion

3.1 IR of silica-Grafted acrylic acid

The FT-IR spectrum in Figure (3-1) showed decrease of the peak intensity at 3390 cm-1 due to grafting process , FT-IR displayed sharp (C-H) stretching absorption in the region between 2968cm-1- 2850 cm-1 , as well the (C=O) absorption at 1724 cm-1 , FT-IR spectrum too showed appearance (C=C) starching vibration at 1637 cm-1 , feature peak at 1053 cm-1 belong to Si-O-C

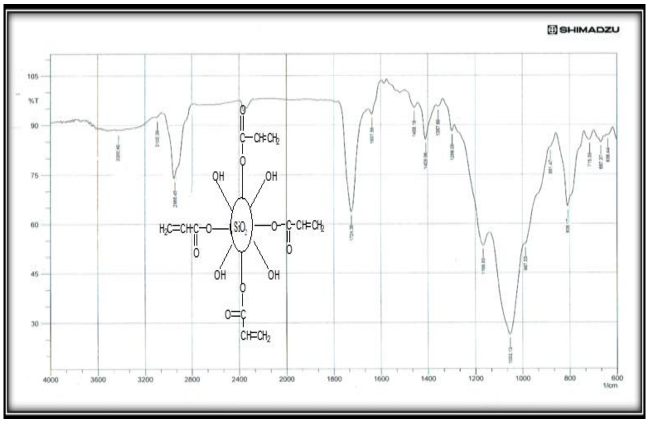


Figure (3-1) FT-IR spectrum of silica-Grafted acrylic acid

3.2 IR of compound (S2) :

The compound [I] was prepared by reaction α- Chloroacetic acid with 4-hydroxy Benzoic acid at (90°C) , This compound was characterized by FT-IR spectra., Figure (3-2) , showed browed peak at (3400) cm-1 which is attributed to the (O-H) stretching vibration , bands around 2999 cm-1 and 2918 cm-1assignible to aliphatic (C-H) stretching , FT-IR spectrum appearance band at 1738 cm-1 assigned stretching to (C=O) of carboxylic acid , FT-IR obtained strong band at 1221cm-1 attributed to stretching vibration of (C-O-C) (16) .

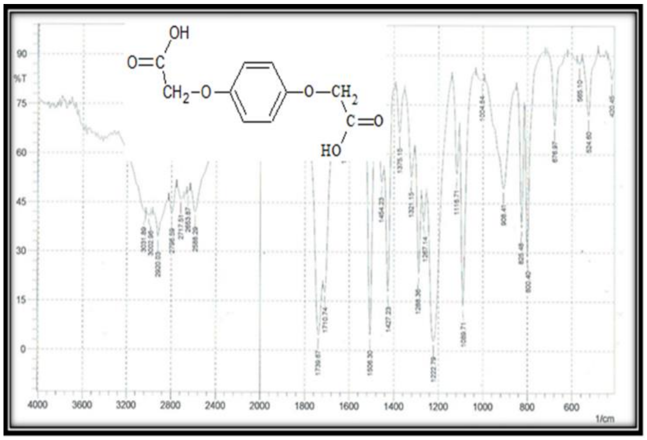


Figure (3-2) FT-IR spectrum of (S2) compound

3.3 IR of of compound 5,5-[benzene-1,4-diylbis(oxymethanediyl bis (1,3,4-thiadiazol-2-amine) [H4] .

The characteristic FT-IR absorption bands of compound [H4] (Figure 3.3) showed the disappearance of absorption band due to O-H stretching of compound (S2) together with the appearance of stretching bands at 3340cm-1 , 3221 cm-1 , assignable to υ NH2. The spectrum shows a band at 1587 cm-1 which is due to υ C=N.

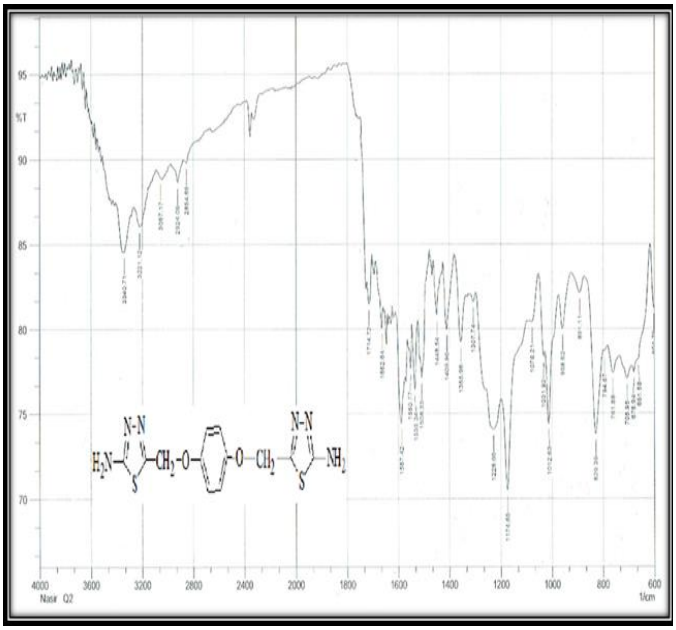


Figure (3-3) FT-IR spectrum of (H4) compound

3.4 FT-IR Spectrum of monomers

3.4.1 Preparation of N-[5-({4-[(5-amino-1,3,4-thiadiazol-2-yl) methoxy] phenoxy} me thyl)-1,3,4-thiadiazol-2-yl]-2-methylprop-2-enamide [M1] .

Monomer [M1] was prepared by the reaction compound [H4] with methacryloyl chloride 1:1;The FT-IR spectrum of monomer (M1) (Figure 3.4) respectively shows a significant bands at 3305cm-1, which attributed to stretching vibration of υ NH2 of compound [H4].the spectrum shows band at 3116cm-1 due to secondary amine , appearance also band at 1697cm-1due to C=O of amide, a spectrum shows also the band at 1620 cm-1 due to υ C=C of methacryloyl chloride .

3.4.2 Preparation of 2-methyl- N-[5-({4-[(5-amino-1,3,4-thiadiazol-2-yl) methoxy] phenoxy}methyl)-1,3,4-thiadiazol-2-yl]-2-methylprop-2-enamide [M2].

Monomer [M2] was prepared by the reaction compound [H4] with methacryloyl chloride1:2; The FT-IR spectrum of monomer (M2) (Figure 3.5) respectively shows a significant band at 3194 cm-1 which attributed to stretching vibration of secondary amine υ N-H , also shows the disappearance of absorption band of υ NH2 of compound [H4], FT-IR display band of υ C=O of amid at 1695cm-1, υ C=C group shows stretching vibration at 1604 cm-1 of methacryloyl chloride .(18, 19, 20)

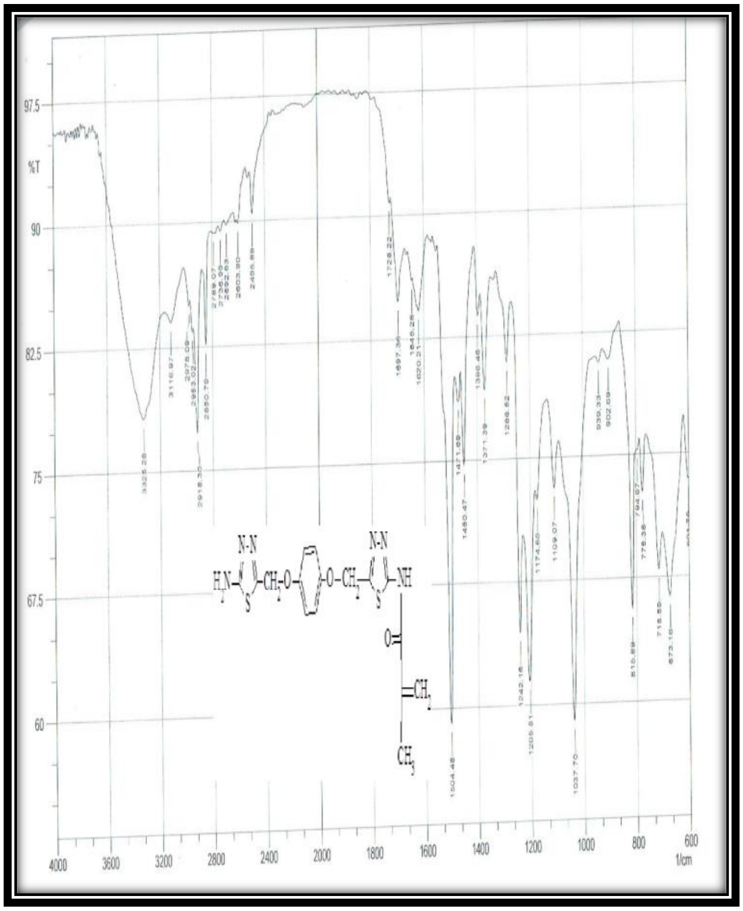


Figure (3-4) FT-IR Spectrum of monomer[M1]

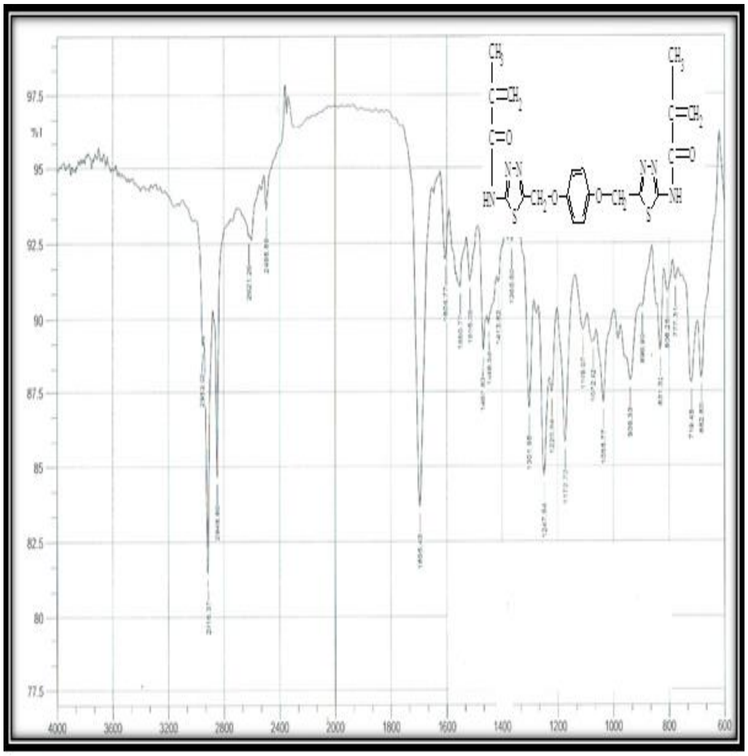


Figure (3-5) FT-IR Spectrum of monomer[M2]

3.5 The FT-IR spectra of these polymers and their nanocomposite) P1,P2,C1,C2) (21,22)

The FT-IR spectra of these polymers and their nanocomposite shows disappeared C=C stretching of methacryloyl chloride of monomers , spectrum of absorption showed strong aliphatic C-H groups attributed to alkyl groups due to polymerization process . also display strong band at range (1095) cm-1 which attributed to Si-O-C group in the nanocomposites

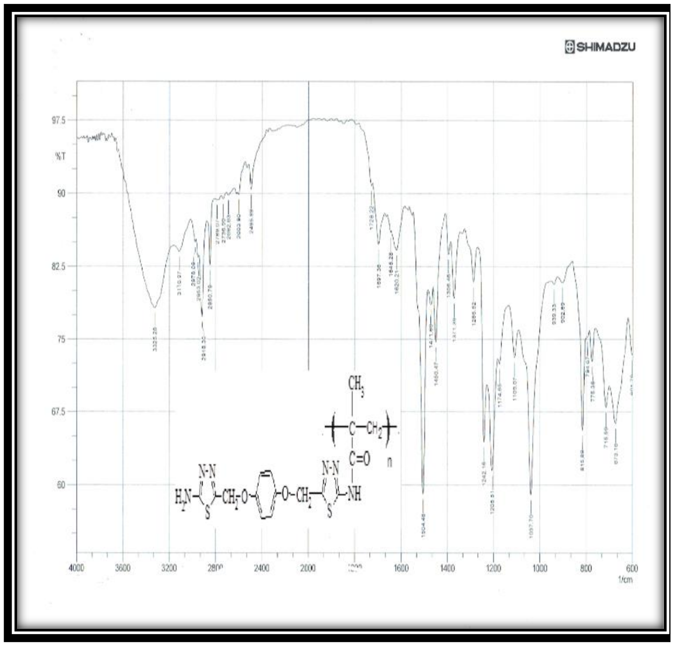


Figure (3-6) FT-IR Spectrum of polymer (P1)

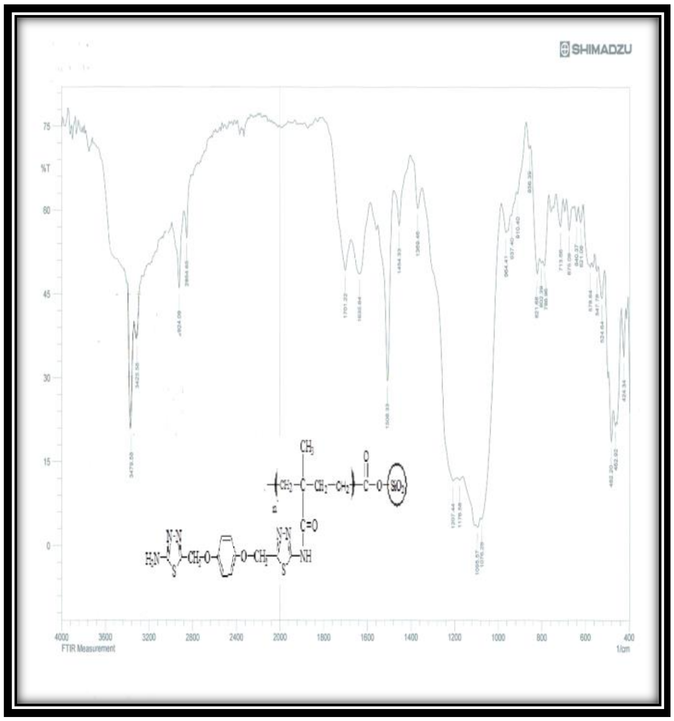


Figure (3-7) FT-IR Spectrum of nanocomposite (C1)

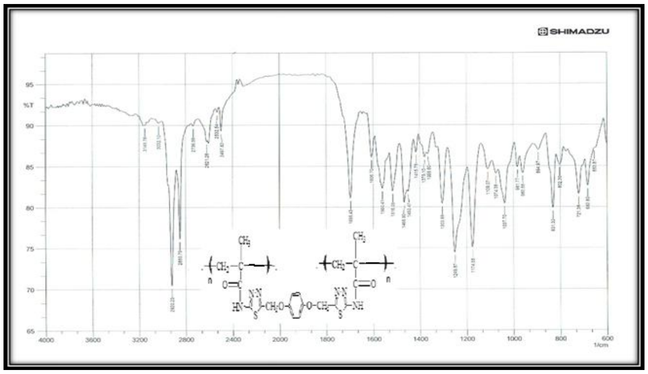


Figure (3-8) FT-IR Spectrum of polymer (P2)

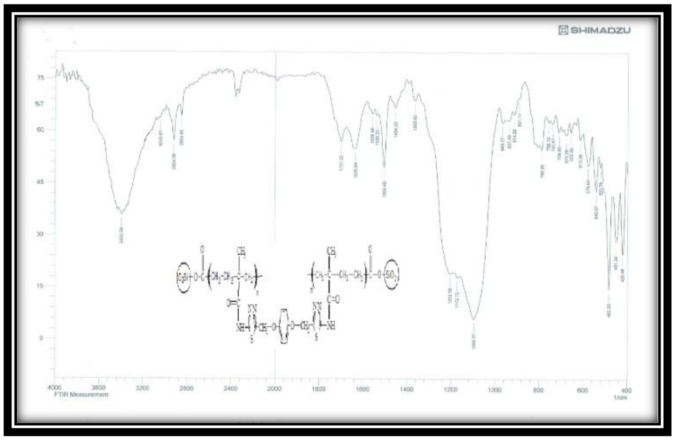


Figure (3-9) FT-IR Spectrum of nanocompsite (C2)

3.6 X-ray diffraction of nanocomposite .

X-ray diffraction (XRD) is one of the most powerful techniques to investigate the structural geometry of nanocomposite .The(XRD)results can also offer information on molecular structure configuration of the nanocomposite after modification , The X-ray diffraction spectrum gives the relationship between intensity and diffraction angle (2θ) in Bragg's low.

Figures show X-ray diffraction which refer to silica nanoparticles and their nanocomposite , The structure of grafted silica and nanocomposite through X-ray pattern show presence of wide range peak with low intensity peak compared with standard nanosilica. Modification of silica show broad peak at 2θ=23 with intensity at 150 . of C2 show broad peak at 2θ=22 with intensity at 130and sharp peaks at 2θ=32, 2θ=41 which refer to the crystalline polymers chains .

Figure of C1 show broad peak at 2θ =22 with intensity at 130 with small peak also at same 2θ which also refers to polymer chains grafted covalent with silica nanoparticles ,.

. High intensive and sharp peak refer to high crystalline of chain and crystalline structure of silica . As noticed from all Figures 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 ascribed to the two types of forces the first one : is the chemical modification between grafted silica surface and thiadiazole polymer chains and the second 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 (21,22, 23)

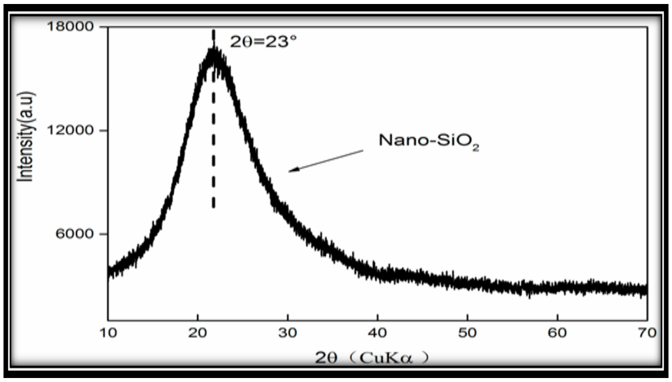


Figure (3-10) X-ray diffraction of silica nanoparticles

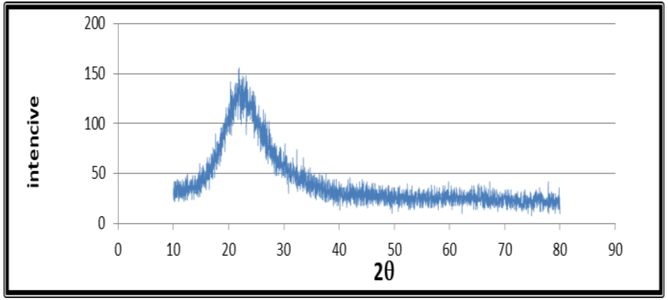


Figure (3-11) X-ray diffraction of grafting Silica

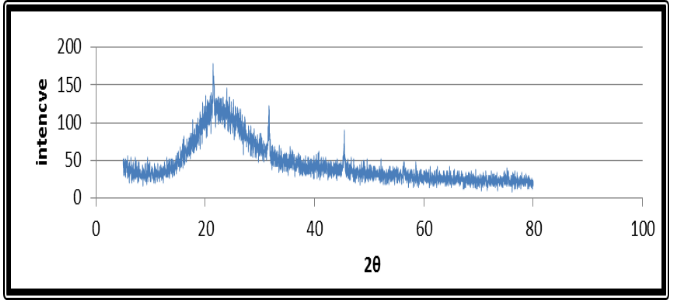


Figure (3-12) X-ray diffraction of nanocomposite (C1)

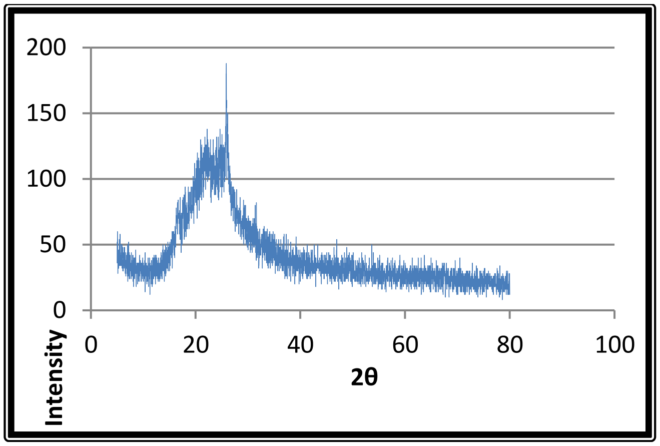


Figure (3-13) X-ray diffraction of nanocomposite (C2)

3.7 Atomic Forces microscopy of nanocomposite (AFM).

Atomic Forces microscopy(AFM), is a technique allows characterization of topography, and it also provides some information on surface mechanical properties via the phase image . In its basic function, AFM provides high resolution imaging of the surface relief of the specimen between lateral scales of a few nanometers to about hundred micrometers as demonstrated(18). In this work silica nanoparticles grafted by acrylic acid monomer, (Figure shows the three-dimensional image of the silica nanoparticles before grafting process with rang diameter between 55-110 nm and Height up to 9.68 nm . While image of the grafted nanosilica shown range diameter between 60-135 nm, height up to 67.32 nm . The surface morphology of nanocomposite of Figures showed the existence of uniform surface roughness. This roughness and great high in diameters of the nanocomposite attributed to linkage of different synthesized chains of heterocyclic thiadiazole polymers with surface of grafted nanosilica and formation nanocomposite(19). The surface morphology of the nanocomposite is strongly dependent on the growing conditions and the surface processing methodologies(18). Generally, from particles size distribution of samples , we notice that the particles of grafted nanosilica and nanocomposite showed increase in size of particles , in contrast the modification of silica with polymers lead to increase in (diameter). The reaction of chains polymers with modified SiO2 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)(19) . Form photographic image of nanocomposites , we notice the present of a rough surfaces and high diameter compared with silica nanoparticles which related 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 (20) . From the results the roughness of surface increased with the increase of loading polymer chains on the silica surface modification to product nanocomposite which can be seen by high roughness in the photograph image of AFM of nancomposite

Compering with AFM images of surface modification of silica. images of (Figure showed decrease in height of peaks due to the absence of polymers chains responsible roughness and height in peaks(20,21) .

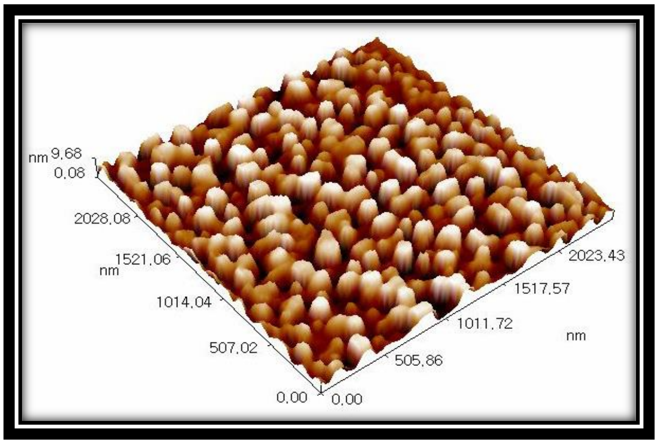


Figure (3-14) AFM Photo of Silica nanoparticles

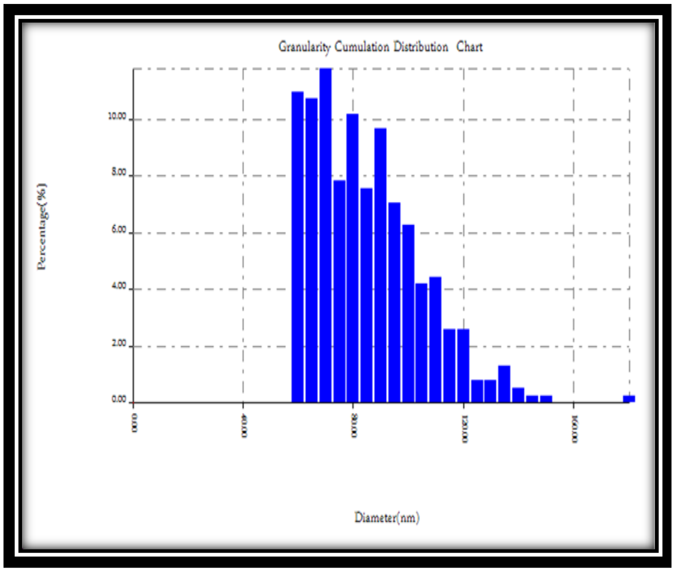


Figure (3-15) Particle size distribution for silica nanoparticles

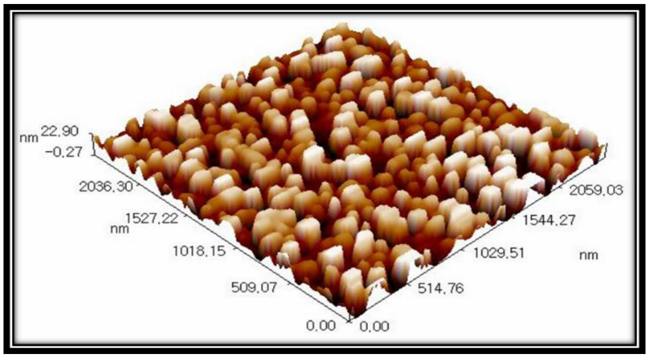


Figure (3-16) AFM Photo of surface modification silica

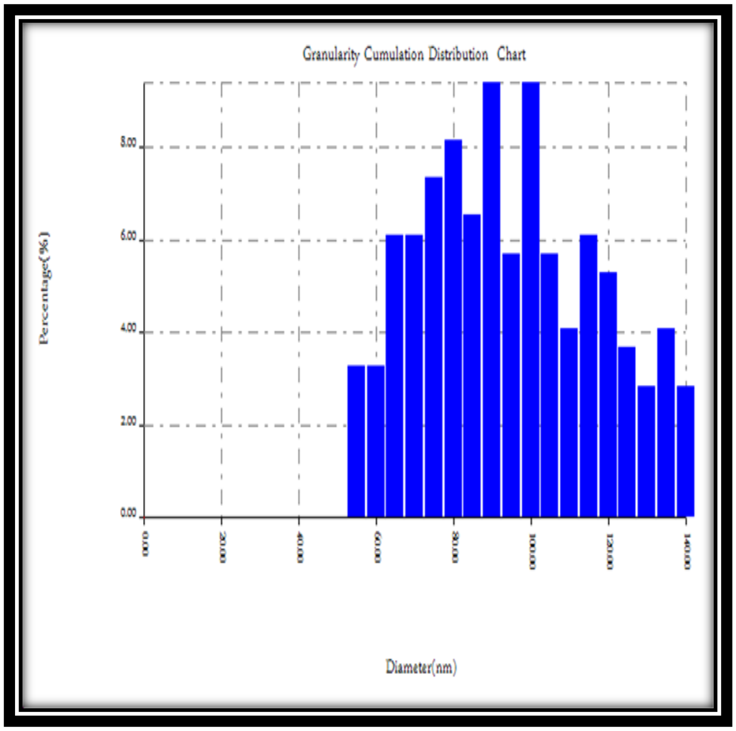


Figure (3-17)Particle size distribution for grafting silica nanoparticles

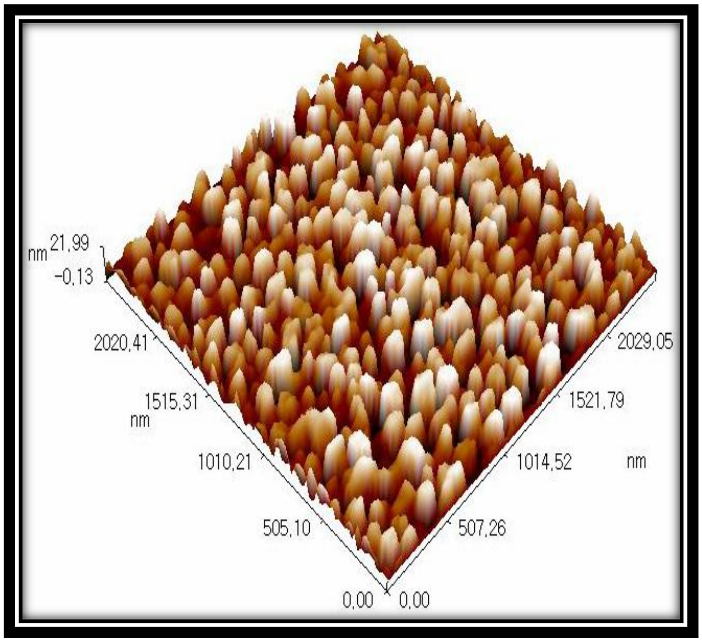


Figure (3-18) AFM photo of nanocomposite (C1)

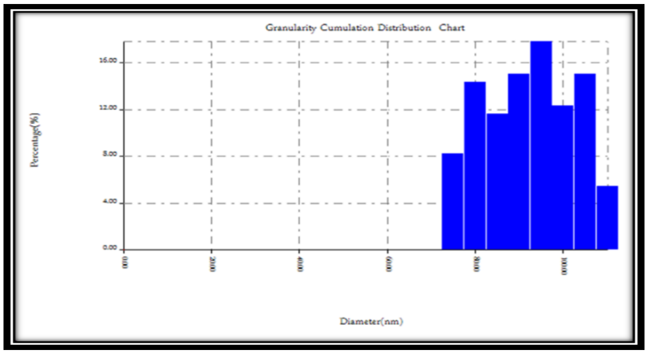


Figure (3-19) Particle size distribution nanocomposite (C1)

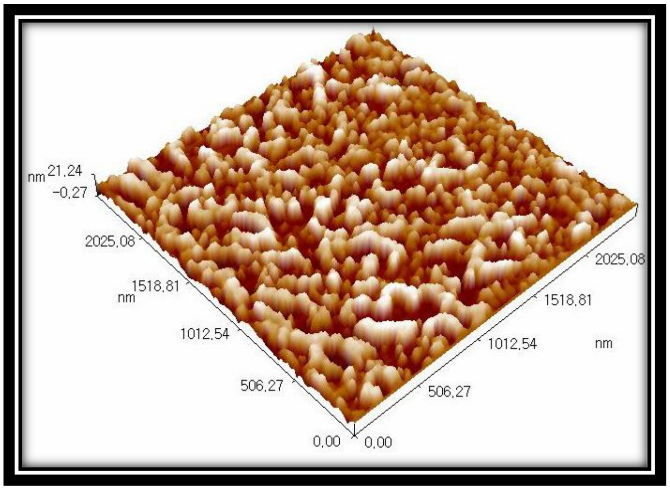


Figure (3-20)AFM Photo of nancomposite (C2)

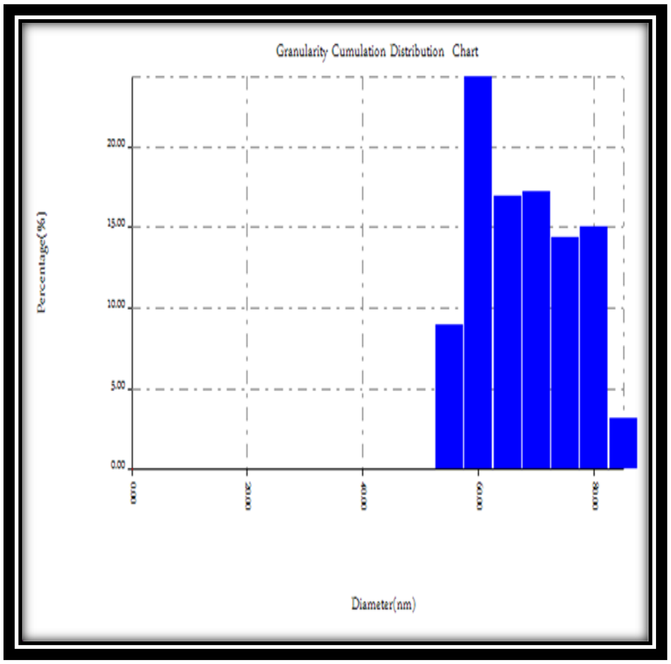


Figure (3-21) Particle size distribution of nancompositeb(C2)

3.8 Scanning electron microscope of nanocomposite (SEM)

Scanning electron microscope (SEM) is type of electron microscope of the analytical techniques which is used to perform surface morphology analysis on the samples that produce images of a sample by scanning it with a focused beam of electrons The SEM explains the crystalline structure ,surface texture and porosity of surface materials .

By this examination has a spherical particle morphology and the surface is smooth (19) , tend to gather to form a large aggregation , this phenomenon can be explained by the hydrogen bonds between (OH) groups on silica surface. Fingers (showed After modifying with acrylic acid monomer the nanosilica particles had changed but only slightly in size ,The reason is that the surface of silica reacted with organic groups Figures 3.89 , 3.90 and 3.92 show high agglomeration ,The main reason for these agglomerations that the polymerization of monomers with modified silica surface lead to increase significantly to form a large agglomeration , due to the surface interacted with organic groups and dispersed to form a large agglomeration(20)

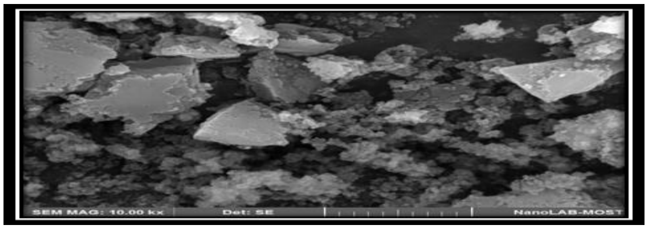


Figure (3-22) SEM of nanocomposite (C1)

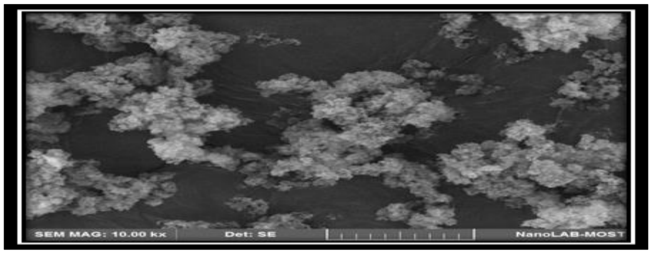


Figure (3-23) SEM of nanocomposite (C2)

3.9 Electrical conductivity of polymers and their Nanocomposite .

Due to their potential application as catalysts, adsorbents for large organic molecules, and chemical properties ,typical ceramic materials include amorphous or polycrystalline solids such as silica had been use as nanocomposite with some polymers had used (24) . A general strategy to address this challenge is to synthesize new semiconductor polymers by preparing organic-inorganic hybrid materials that couple the benefits of both inorganic and organic materials, which can prevent the semiconductor polymers (24 , 25) .

1- The plotting of conductivity (σ) against temperature as shown in figures of polymers giving electrical conductivity to neat polymers (P1-P2), H.K.Salih , ph.D.

Thesis,(1997), " synthesis , characterization and properties of liquid crystalline models and side chain polymers containing heterocyclic units " University of Baghdad , Collage of Education / Ibn- Al – Haytham .

because of The stability of semiconductor polymers largely depends on their chemical structures, Figures of neat polymers showed that conductivity of polymers increase with increase temperature even arrived to high value at one measured temperature after that begin decrease step by step due to decomposition chains of polymers and loss the doping and with drawing groups and charge .

Nanocomposite (C1-C2) showed stable electrical conductivity at varying temperature the reason that grafted silica nanoparticales improved thermal and electrical stability of nanocomposite (25)and showed that conductivity of polymers became better , Because of greater surface area and mechanical and electrical properties of grafted silica surface area which polymerized with heterocyclic monomers (26). The electrical conductivity of nanocomposites at lower values of SiO2 content was higher than that of neat polymers (27) .

All nanocomposites in this study showed conductivity at (0.3 S cm-1 -17.8 S cm-1). The mean reason of these high conductivity because of their small size, large specific surface area, high aspect ratio (length/diameter), good compatibility, facile processability (27), addition last features a doping and withdrawing groups in the structure of polymers and their nanocomposites, Electrical conductivity measurements for all nanocomposite samples revealed that direct Current(dc) conductivity (σ dc) increases with the rise temperature of the sample and Silica content ., the High value of electrical conductivity tow reason ..

1-modifying nanosilica surface which bonding with chains of polymer and the second season due to

2- doping groups such as (N-H , O-H , S-H) and the withdrawing groups such as C=O , C=C , C=N and C=S in the structure of nanocomposite caused to impreated in transfer the electrons and charge at along chains of nanocomposite(28) .

NO	T(C)	σ(S / cm)	NO	T(C)	σ(S / cm)
P_1	25	0.39663	**C_1**	25	13.9702
	35	0.47807		35	13.9702
	45	0.64149		45	13.9702
	55	0.82991		55	13.9702
	65	1.60168		65	13.9702
	75	0.44744		75	13.9702
	85	0.31083		85	13.4349
	95	0.25452		95	13.9702
	105	0.23339		105	13.2349
	110	0.18517		110	13.2349

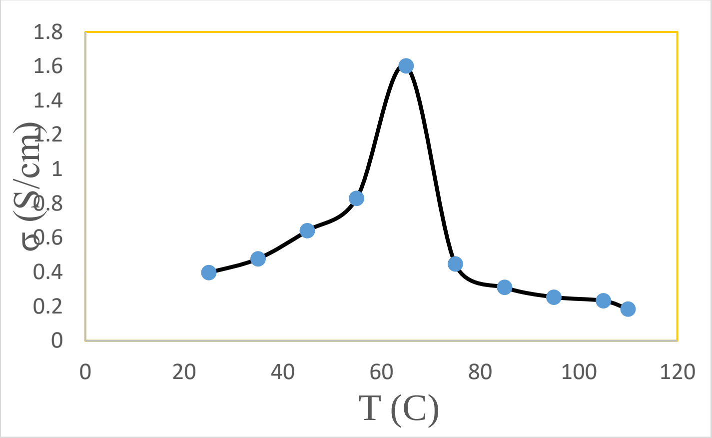


Figure (3-24) Electrical conductivity of polymer (P1)

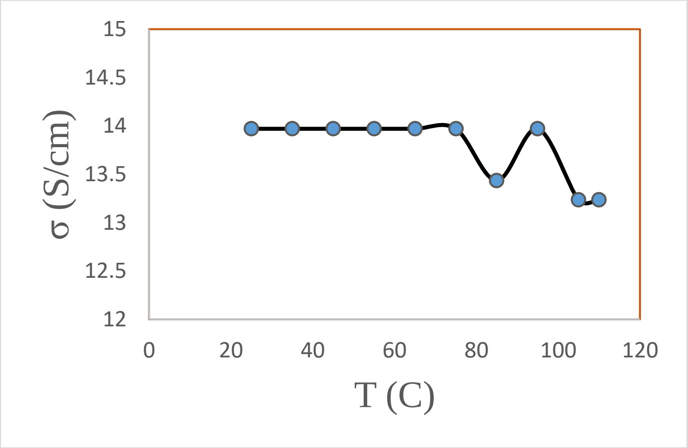


Figure (3-25) Electrical conductivity of nanocmposite (C1)

NO	T(C)	σ(S / cm)	NO	T(C)	σ(S / cm)
P_2	25	0.01577	**C_2**	25	0.29381
	35	0.01674		35	0.29383
	45	0.01812		45	0.29389
	55	0.02092		55	0.29388
	65	0.02525		65	0.29385
	75	0.03161		75	0.29382
	85	0.05519		85	0.29384
	95	0.04691		95	0.29382
	105	0.04348		105	0.29382
	110	0.04107		110	0.2301

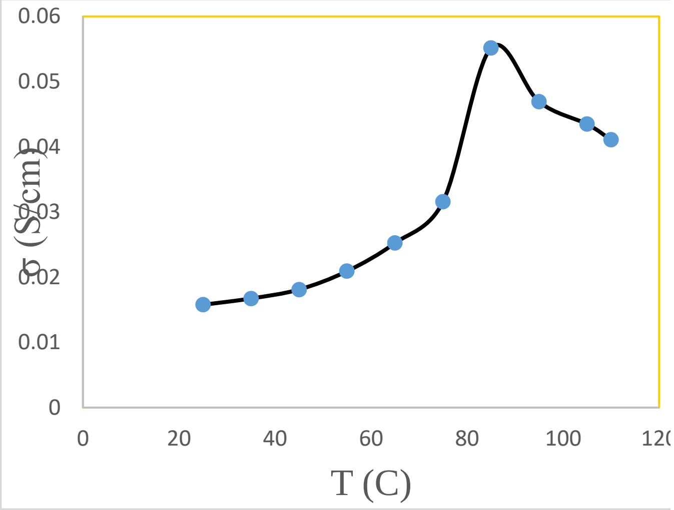


Figure (3-26) Electrical conductivity of polymer (P2)

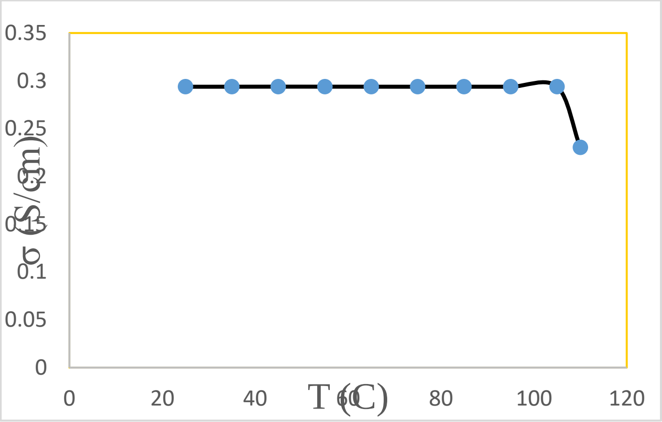


Figure (3-27) Electrical conductivity of nanocmposite (C2)

4. Conclusions

New thiadizole monomers have been prepared which used to prepare new poly thiadiazole polymers and thier nanocopmosite by using free radical polymerization , nanocopmosite prepared in the same procedure of polymers with use grafted silica nanoparticles. The chemical structures of these polymers and their nanocomposites were examined by FT-IR spectroscopy. The X-ray diffraction used to study The nanostructure of SiO2 which showed that no significantly changed upon grafting but there are decreased in intensity of the nanocomposite that refer the modification were on the surface without change the structure of particles in well as showed a better behavior than the neat polymers from thermo stability. According to Both components of the resulting nanocomposite can significantly profit from each other. On the other hand, the well-dispersed SiO2 nanoparticles helped in thermal stabilization of nanocomposite due to the surface modification and then polymer structure with functional groups such as (OH) and (C=N) help in increase the stability of nanocomposite.

REFERENCES

1. Sarita Kangoa, Susheel Kaliab,c,∗, Annamaria Celli b, James Njugunad, Youssef Habibie, Rajesh Kumara,(2013)," Surface modification of inorganic nanoparticles for development of organic–inorganic nanocomposites—A review",JPPS-778,1-30.
2. M . Hatami , M . Ahmadipour and S. Asghari , (2017) ," Heterocyclic Grafting Functionalization of Silica Nanoparticles:Fabrication, Morphological Investigation and Application for PVA Nanocomposites " , J Inorg Organomet Polym , DOI 10.1007/s10904-017-0557-1 , 1-12 ,
3. Md. Rezaur Rahman, J. Lai Chang Hui and S. Hamdan ,(2017) , " Physical, Mechanical, Thermal and Morphology Properties of " , MATEC Web of Conferences mateсconf/20178703005 .
4. Arslan .M and M. Atilla Tasdelen , (2017) , " Polymer Nanocomposites via Click Chemistry Reactions " , polymers , 9, 499, 1-24 .
5. R. V. Ghorpade*, C. R. Rajan, N. N. Chavan, S. Ponrathnam , (2015) " Synthesis of novel silica-polyimide nanocomposite films using aromatic-amino modified silica nanoparticles: Mechanical, thermal and morphological investigations
6. Kango S., Kalia S., Celli A., Njuguna J., Habibi Y., Kumar R. (2013)."Surface modification of inorganic nanoparticles for development of organic–inorganic nanocomposites – A review. Progress in Polymer Science ", 38, 1232–1261 DOI: 10.1016/j.progpolymsci.2013.02.003
7. H . Zou , L . Wang , X .Wang , P. Lv . and Y. u Liao , (2016) , " Chemical Oxidative Polymerization of 2 Aminothiazole in Aqueous Solution: Synthesis, Characterization and Kinetics Study " , Polymers , 8, 407 , 1-11 .
8. Paweł Sikoraa,*, Paweł Łukowskia, Krzysztof Cendrowskib, Elżbieta Horszczarukb, Ewa Mijowskab , (2015) , " The effect of nanosilica on the mechanical properties of polymercement composites (PCC) " , Procedia Engineering 108 , 139 – 145 .
9. K . Takagi , E . Kawagita , R . Kouchi , (2014) , " Synthesis and Characterization of Polythiophene Derivatives with Nitrogen Heterocycles on the Side Chain " , POLYMER CHEMISTRY, 52, 2166–2174 .
10. B. Derkowska-Zielinska , L. Skowronski2 , A. Biitseva , A. Grabowski , M. K. Naparty , V.Smokal , A. Kysil , O. Krupka , (2016) , " Optical characterization of hetero cyclic Azo dyes containing polymer thin film " , Applied surface science , ,1-23 .
11. V. reddy and T. M. aminabhav, (1993) , " synthesis of a new diisocyanate-basedpolyurethanne " , poly-plast. technol. Eng , Vol 32, (15-20) .
12. M. S. AL-Gwady, (2009) " Synthesis of 2-Amino-5-Substituted-1,3,4-Thiadiazoles (ATDA) and Their Derivatives Using Conventional and Microwave Techniques ",J. Raf. Sci., Vol. 20,(1- 7) .
13. Ping Yanga, An-Dong Xua, Jun Xiab, Jie Hea, , Hong-Long Xinga, Xiao-Mei Zhanga, Shu-Yang Weia, Ning-Ning Wanga ,(2014) , " Facile synthesis of highly catalytic activity Ni–Co–Pd–P composite for reduction of the p-Nitrophenol " , Applied Catalysis A: General 470 (2014) 89– 96 .
14. A. Duarte, W. Cunico, C.M.P. Pereira, A. F.C. Flores, R. A. Freitag and G. M. Siqueira, (2010) , "Ultrasound promoted synthesis of thioesters from 2-mercaptobenzoxa(thia) zoles ", Ultrasonics Sonochemistry, Vol 17(2), (281-283)
15. Ying-Mei Niu , Xiao-Li Zhu , Bing Chang,2 Zhao-Hui Tong , Wen Cao , Pei-Huan Qiao, Lin-Yuan Zhang , Jing Zhao , and Yu-Guo Song , (2016) , " Nanosilica and Polyacrylate/Nanosilica: A Comparative Study of Acute Toxicity " , BioMed Research International , Volume 2016, Article ID 9353275, 7 pages .
16. R. V. Ghorpade , C. R. Rajan, N. N. Chavan, S. Ponrathnam , (2015) " Synthesis of novel silica-polyimide nanocomposite films using aromatic-amino modified silica nanoparticles: Mechanical, thermal and morphological investigations
17. Sh. Mallakpour and F. Marefatpour , (2015) " Preparation and characterization of optically active and flame-retardant poly(amide–imide) / SiO2 nanocomposites having N-trimellitylimido-I-methionine linkages using ultrasonic irradiation" Designed Monomers and Polymers, Vol. 18, No. 2, (137–144) .

18. B. D. Fecchio , S. R. Valandro , M. G. Neumann and C.C. S. Cavalheiro , (2016) , " Thermal Decomposition of Polymer/Montmorillonite Nanocomposites Synthesized in situ on a Clay Surface " J. Braz. Chem. Soc., Vol. 27, No. 2, 278-284.
19. V. reddy and T. M. aminabhav, (1993) , " synthesis of a new diisocyanate-basedpolyurethanne " , poly-plast. technol. Eng , Vol 32, (15-20) .
20. A. Sidiki Sougoule , Ch. Abdoul balde , N. Keita , X. Xiao , X.Han, J.Liang , and D.Zhu , (2015) " A Novel Tetranuclear Organotin(IV) Carboxylate with Chain Structure: Synthesis,Crystal Structure, and Characterizations " ,Heteroatom Chemistry , Vol 26 , (1-9) .
21. M. S. AL-Gwady, (2009) " Synthesis of 2-Amino-5-Substituted-1,3,4-Thiadiazoles (ATDA) and Their Derivatives Using Conventional and Microwave Techniques ",J. Raf. Sci., Vol. 20,(1-7)
22. A. Zuh , A. Cai , Z. Yu and W. Zhou , (2008) , " Film characterization of poly (styrene - butylacrylate - acrylic acid) Silica nanocomposite", Journal of Colloid and Interface Science ,Vol 322 , (51–58).
23. Tetyana M Budnyak , Ievgen V Pylypchuk , Valentin A Tertykh , Elina S Yanovska and Dorota Kolodynska , (2015) , " Synthesis and adsorption properties of chitosan-silica nanocomposite prepared by sol-gel method " , Budnyak et al. Nanoscale Research Letters , 10:87 , 1-10 .
24. L. Almada, (2013) , " conducting polymer synthesis, properties and application" by Nova Science Publishers, Inc. P 201 .
25. K. Chang , X. Men, H. Chen , Z. Liu , Sh . Yin , W. Qin , Zh. Yuan and Ch . Wu , (2015) " Silica-Encapsulated Semiconductor Polymer Dots as Stable Phosphors for White Light-emitting Diodes" , J. Mater. Chem.C,Vol 3, (7281-7285) .
26. Ch. Wu , C. Szymanski , and J. McNeill , (2006) " Preparation and Encapsulation of Highly Fluorescent Conjugated Polymer Nanoparticles" , Langmuir, Vol 22 , (2956–2960) .
27. A. Kaur , A. Kaur and D.Saini , (2016) " review on synthysis of silica nanocomposite with conducting polyaniline " An International Journal of Engineering Sciences , ISSN: 2229-6913 (1-14) .
28. L. michaelson , (2014) , " advance in conducting polymers research " Published by Nova Science Publishers, Inc. New York , P24 .