



## Synthesis New Polymeric Composite Materials Derivatives from thiosemicarbazide

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### Abstract

In this work two monomers were prepared by using Thiosemicarbazide free-radical polymerization was used to polymerize monomers one with itself to produce two polymers ( $P_1$ ,  $P_2$ ) and the second with Nano silica grafted meth acrylic acid to produce two Nano composite ( $C_1, C_2$ ) All the prepared compounds were characterized by FT-IR Spectroscopy. The structures of standard Nano silica and Nano composite were studied by Atomic Forces Microscopy (AFM). The X-ray diffraction offer information on molecular structure configuration of the Nano composite after modification which showed different in intensity between Nano silica and their Nano composite.

**Keywords:** *Triazole polymer, Nano composite, Modification.*

### Introduction

Polymer Nano composites are a class of hybrid materials composed of an organic polymer matrix with dispersed inorganic Nano fillers. Polymer Nano composite shows unique properties, combining the advantages of the inorganic Nano fillers (e.g., rigidity, thermal stability) and the organic polymers (e.g. Flexibility, dielectric, ductility, and process ability) [1].

Although the intercalation chemistry of polymers when mixed with appropriately modified layered silicate and synthetic layered silicates has long been known [2]. The organic/inorganic Nano composites 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 [3].

Nano composite materials have emerged as suitable alternatives to overcome limitations of micro composites and monolithic, while posing preparation challenges related to the control of elemental composition and stoichiometry in the Nano cluster phase [4]. Recently, Nano composites have attracted considerable interests due to the possibility of improving the mechanical [5], and thermal

properties of polymers [6], and have even generated certain properties, for example, low dielectric constant, low thermal Expansion property [7], excellent friction and wear performance [8]. The dispersion was considered stable in organic solvent because of the increase in affinity between the particle surface and the polymer due to the surface modification of the colloidal  $SiO_2$ .

The agglomeration of colloidal particles dispersed in an organic solvent with polymers that exhibit only weak hydrogen bonding or similar interactions has long been discussed on the basis of the theory of depletion aggregation [9]. One of important method to prepare polymer/ silica Nano composite its modification by chemical interaction, in this work polymer chains covalent attachment with surface of Nano silica, by functional groups to produce new Nano composite[10].

### Experimental

#### Materials

Nano sized silica powders (30 nm) were supplied by sky Company Ltd (USA), thiosemicarbazid was obtained by TCI, meth acrylic acid was obtained by Merck Company,

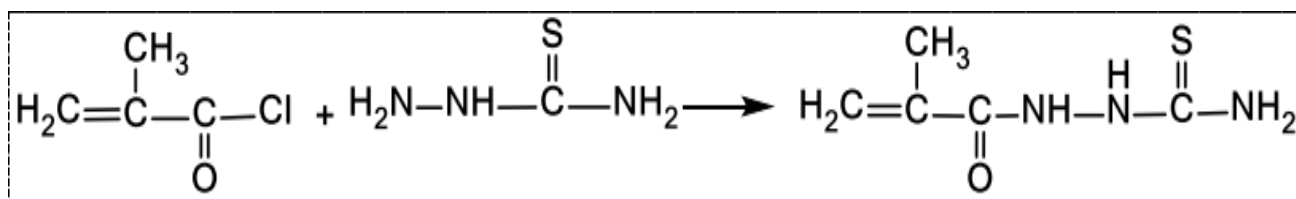
methacryloyl chloride, and Benzoyl Peroxide were supplied by Fluke Chemical Company.

### Preparation

#### Preparation of 2-methacryloyl hydrazine-1-carbothioamide (I)

To a stirred solution of compound

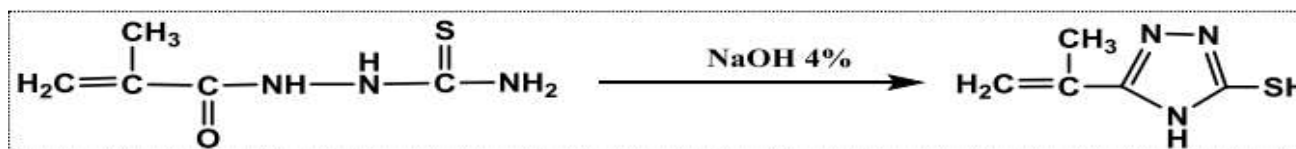
thiosemicarbazide (0.91 g, 0.01M) in dry pyridine 15 mL at -5 °C, was added dropwise of methacryloyl chloride (1.05 g, 0.01M) at -5 °C. The stirring was continued for half an hour at -5 °C and then overnight at room temperature. Then added 30 mL dulit hydrochloric acid the precipitate was washed by water and then by sodium bicarbonate.



#### Preparation of 5-(prop-1-en-2-yl)-4H-1, 2, 4, Triazole-3-Thio (II)

A solution of compound [I] (1.59 g, 0.01M) and 20 mL 4%aqueous sodium hydroxide

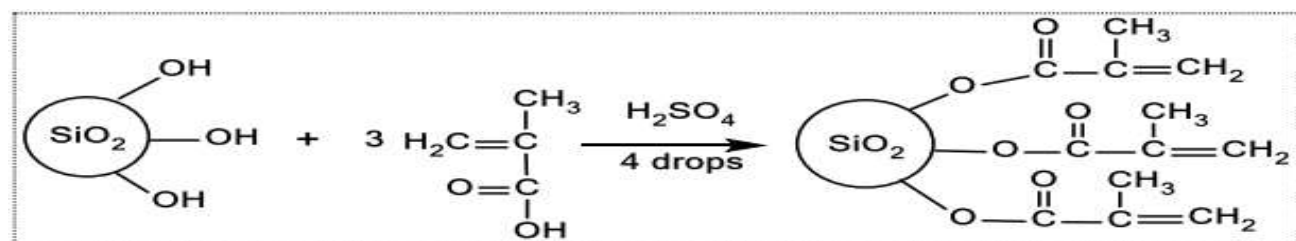
solution was refluxed for 6 h. After that, the mixture was filtered, and then the resulting filtrate was acidified with 10% HCl. The product was filtered and washed with water, then recrystallized from ethanol.



#### Preparation of Nano Silica-graft Meth Acrylic Acid Monomer (III) [11]

(1g) Nano Silica was weight and placed in round bottom flask followed by Addition of (20ml) dry-Toluene, meth acrylic acid monomer (3g) was added to the solution of

Nano Silica-Toluene drop wise with few drops sulfuric acid at room temperature than left the mixture with stirring for overnight .The product was filtered and washed with (20ml) distilled water, than (20ml) of acetone. The Solid product left to dry at room temperature.

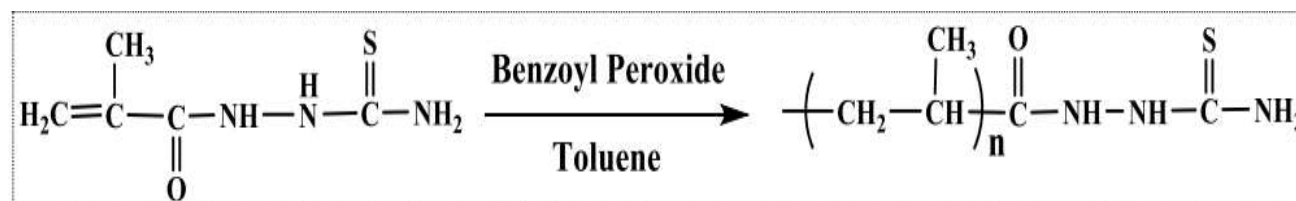


#### Preparation of Polymers and their Composites by Free radical Polymerization [12]

##### Preparation of Polymer P1

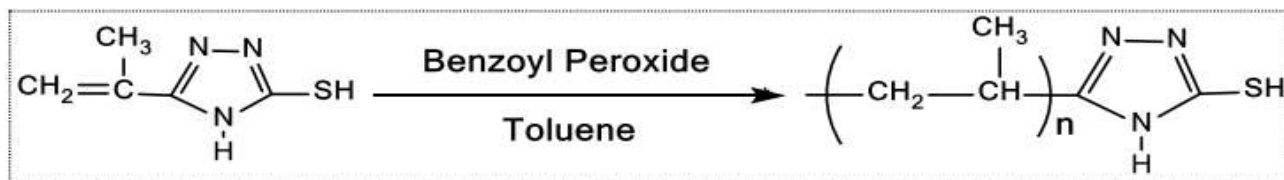
flask contain (10ml) of dry toluene as solvent was placed in controlled water bath at (80°C) under nitrogen atmosphere , after 5 minutes

(0.1) g benzoyl peroxide was added , followed by addition of (0.5 g) of compound (I).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.



### Preparation of Polymer P2

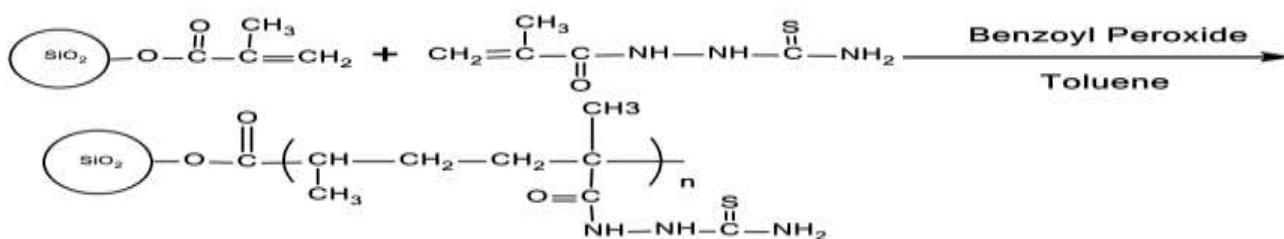
Polymer (P2) was prepared by using compound (II) with the same procedure for preparation polymer (P1).



### Preparation of Nano composite (C1)

Nano composite (C<sub>1</sub>) was prepared by using (0.25g) of silica-grafted acrylic acid monomer

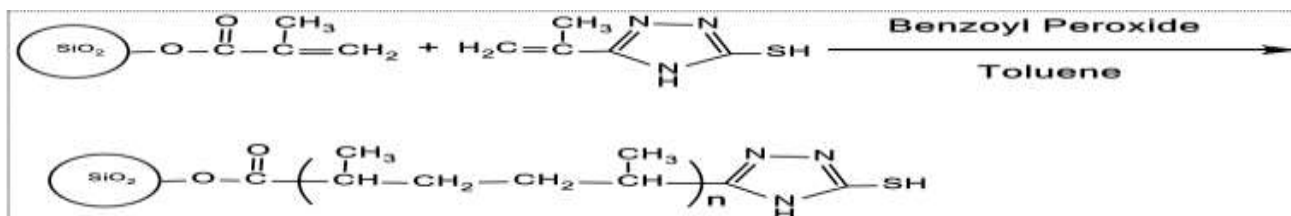
and (0.5 g) of compound (I) with the same procedure for preparation polymers.



### Preparation of Nano composite (C2)

Nano composite (C<sub>2</sub>) was prepared by using (0.5g) of compound (II) with the same

Procedure for preparation Nano composite (C<sub>2</sub>).



## Result and Discussion

### FT-IR Spectroscopy

The structures of all synthesized compounds were confirmed by using FT-IR spectral. it was good evidence which corresponds to the structure of suggested compounds. The compound [I] was prepared by reaction thiosemicarbazide with of meth acryloyl

chloride The FTIR spectrum of compound [I] showed absorption stretching band at 1267.27 cm<sup>-1</sup> that could be assigned to C=S group in addition to new bands for asymmetric and symmetric stretching vibration of NH<sub>2</sub> and NH groups appears between 3460 and 3178 cm<sup>-1</sup>, also showed stretching band of C=O (amide) group at 1656 cm<sup>-1</sup>.

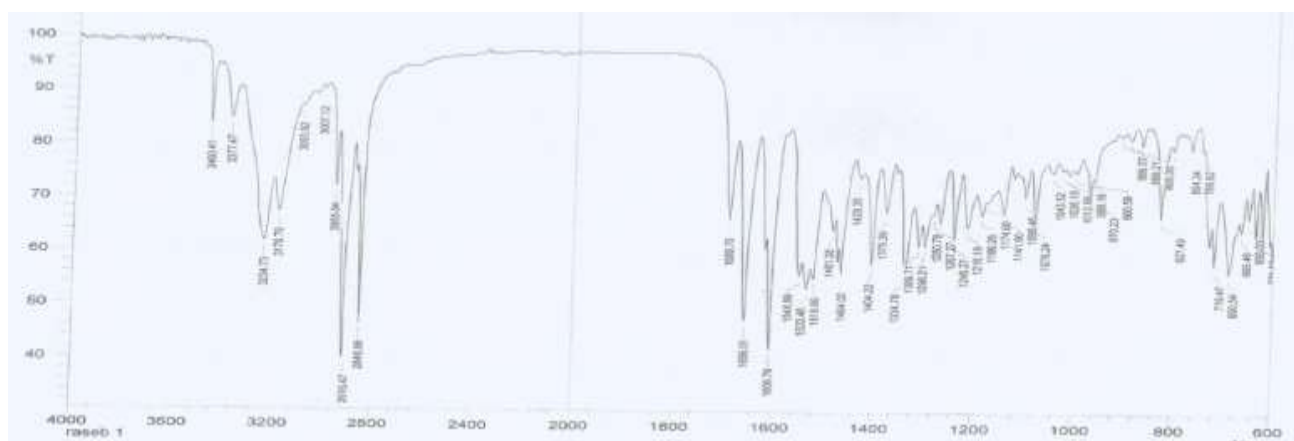


Figure 1: FT-IR spectrum of compound (I)

The cyclization of carbothioamide [I] in medium of aqueous sodium hydroxide then acidification with hydrochloric acid led to formation of principal key heterocyclic compound, 5- (prop- 1- en- 2-yl)- 4H-1, 2, 4-Triazole-3-thio [II]. The FTIR spectrum for compound [II] showed disappearance

bands of the C=O (amide) groups, that observed in the starting material and showed new absorption stretching band at 2525 cm<sup>-1</sup> that attributed to the SH and 1207.44 cm<sup>-1</sup> for C=S group. Also, showed stretching bands at the 3124 cm<sup>-1</sup> and 1600 cm<sup>-1</sup> for N-H and C=N (endocyclic) of 1, 2, 4-triazole ring [13].

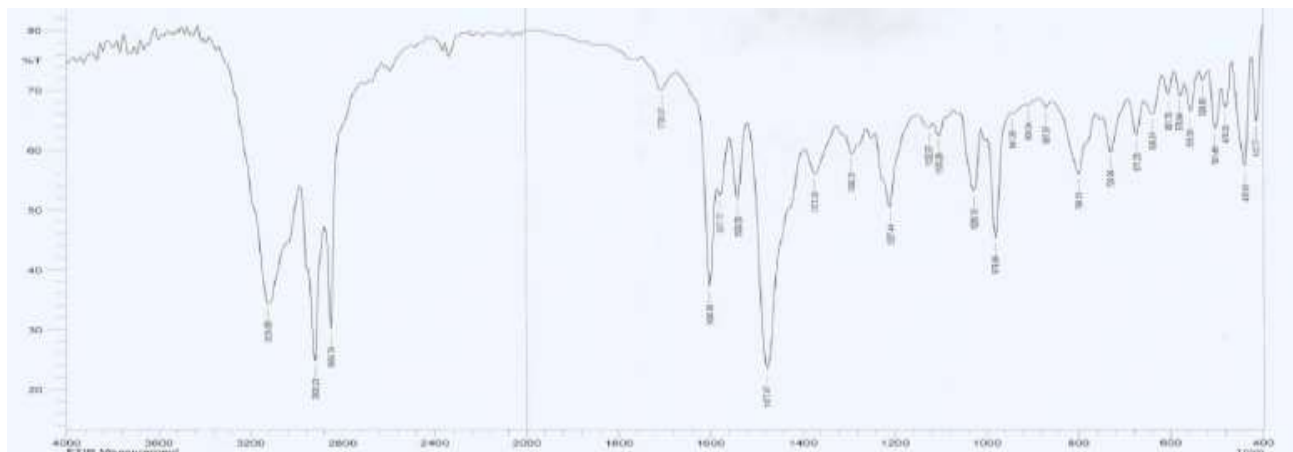


Figure 2: FT-IR spectrum of compound (II)

Nano silica -graft acrylic acid monomer (III) was prepared by grafted silica nanoparticles with meth acrylic monomer in toluene as solvent, the structure of this compound was studied by FT-IR spectroscopy, the FT-IR

spectrum Figure 3 showed the following absorption bands C=O stretching at 1697cm<sup>-1</sup>, with appearance (C=C) starching vibration at1635 cm<sup>-1</sup>, feature peak at 1099 cm<sup>-1</sup> belong to Si-O-C.

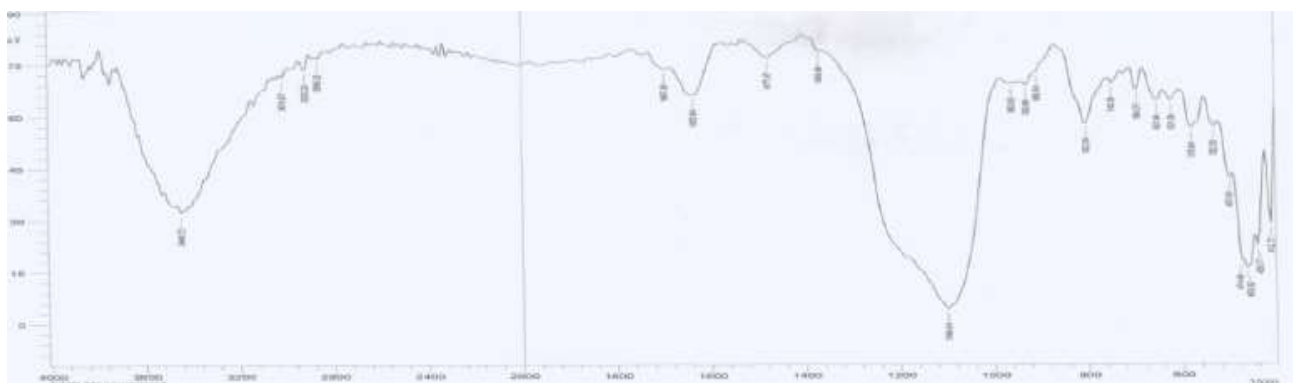


Figure 3-3: FT-IR spectrum of compound (III)

Table 1: The polymers (P<sub>1</sub>, P<sub>2</sub>) were prepared by use free radical polymerization to compounds (I, II) respectively Table (1) showed the characteristic absorption bands of the polymers

Polymer	$\nu(\text{N-H}) \text{ cm}^{-1}$	$\nu(\text{N-H}) \text{ cm}^{-1}$	$\nu(\text{C-H}) \text{ cm}^{-1}$	$\nu(\text{C=O}) \text{ cm}^{-1}$	$\nu(\text{C=N}) \text{ cm}^{-1}$	$\nu(\text{C-S}) \text{ cm}^{-1}$	$\nu(\text{C=S}) \text{ cm}^{-1}$
P <sub>1</sub>	3437-3309	3151	2916-2850	1678	-	-	1606
P <sub>2</sub>	-	3132	2920-2850	-	1577	1435	-

Table 2: The Nano composites (C<sub>1</sub>, C<sub>2</sub>) were prepared by polymerization of Nano silica grafted - meth acrylic acid with compounds (I, II) respectively Table (3-2) showed the characteristic absorption bands of the Nano composites

Nanocomposite	$\nu(\text{N-H}) \text{ cm}^{-1}$	$\nu(\text{N-H}) \text{ cm}^{-1}$	$\nu(\text{C-H}) \text{ cm}^{-1}$	$\nu(\text{C=O}) \text{ cm}^{-1}$	$\nu(\text{Si-O-C}) \text{ cm}^{-1}$	$\nu(\text{C=S}) \text{ cm}^{-1}$	$\nu(\text{C=N}) \text{ cm}^{-1}$	$\nu(\text{C-S}) \text{ cm}^{-1}$
C <sub>1</sub>	3444-3317	3163	2920-2850	1676	1103	1608	-	-
C <sub>2</sub>	-	3120	2920-2850	1600	1095	-	1469-1435	-

Figures 4 to 7 showed the appearance of stretching bands of the polymers and Nano composites.

### X-ray Diffraction Analysis

The structure of modification silica and Nano composite through X-ray pattern show Presence of wide range and low intensive peaks compared with stander Nano silica Figure (8) which have  $2\theta = 23$  and intensive at 18000, Figure (3-9) of modification silica showed broad peak at  $2\theta = 23$  and intensive at 150. All figures shows there was no obvious difference between stander Nano

silica and Nano composite, that the main crystallite structure of silica its stable even after modification process of silica surface by different polymers chains ,in contrast a general pattern was not significantly changed but two-theta value at a peak maximum was slightly shifted to a lower value, The increase of d-spacing upon grafting is presumably due to the fact that the grafted polymeric chains disturb the structures of silica [14, 15]. Figure 10 and 11 showed X-ray diffraction of Nano composite (C<sub>1</sub>,C<sub>2</sub>), Table 3 showed intensity and  $2\theta$  for C<sub>1</sub> and C<sub>2</sub>.

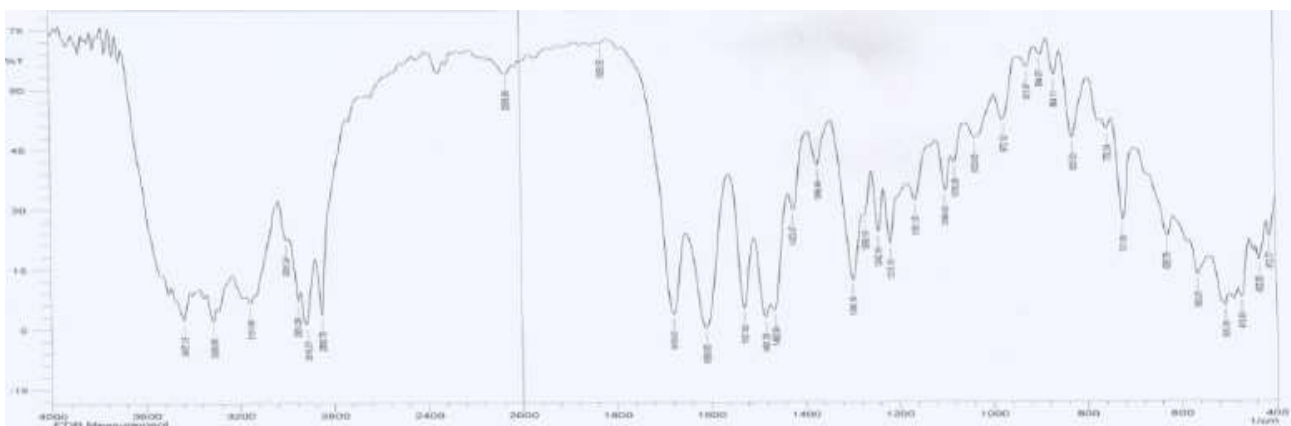


Figure 4: FT-IR spectrum of polymer P<sub>1</sub>

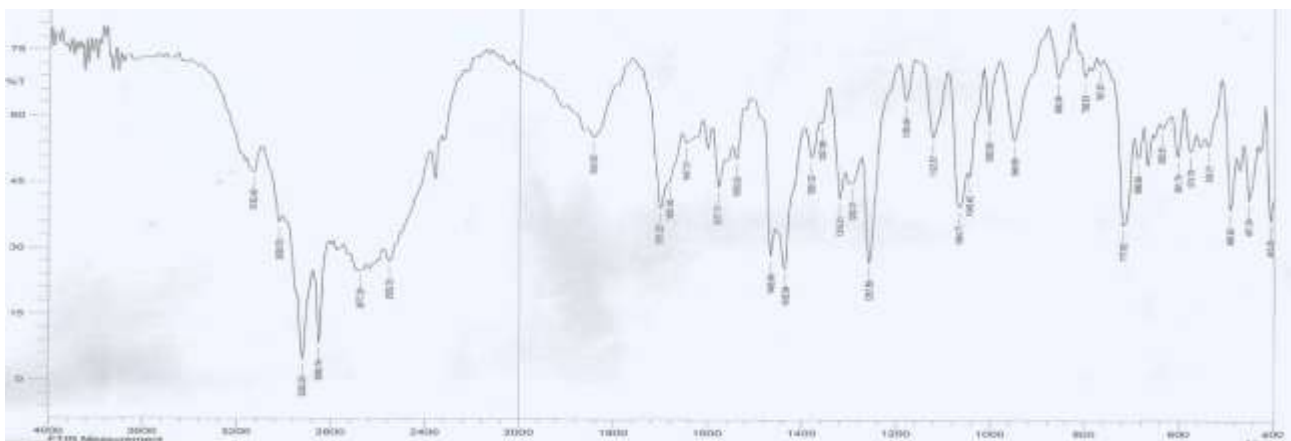


Figure 5: FT-IR spectrum of polymer P<sub>2</sub>

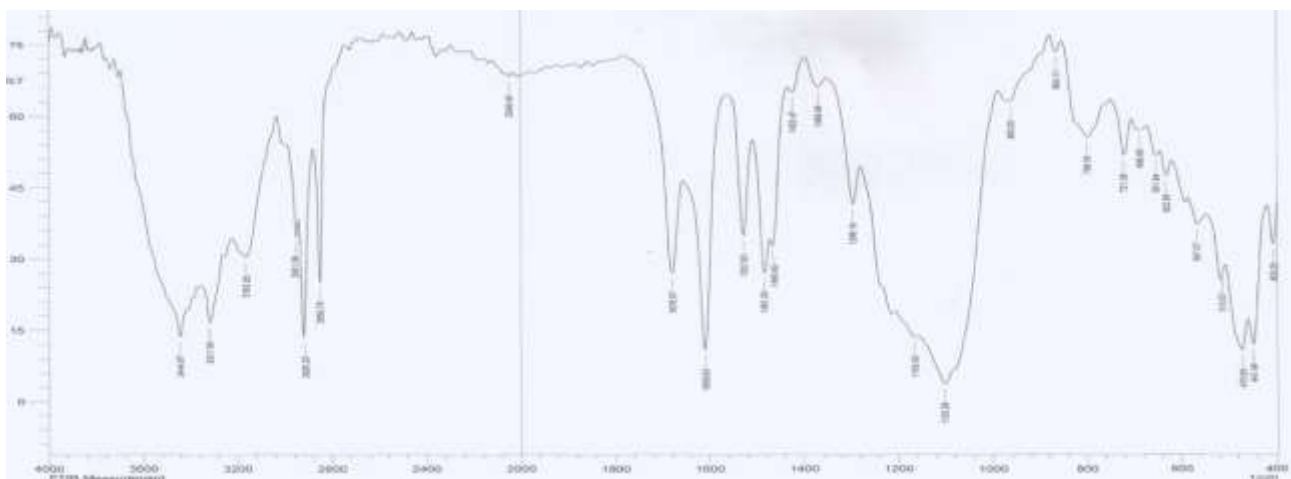


Figure 6: FT-IR spectrum of C<sub>1</sub>



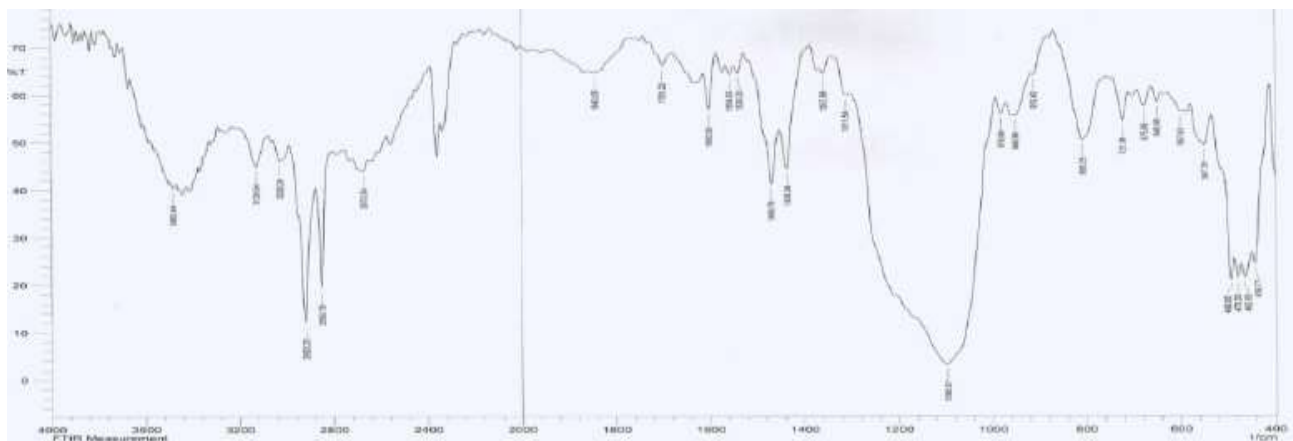


Figure 7: FT-IR spectrum of C<sub>2</sub>

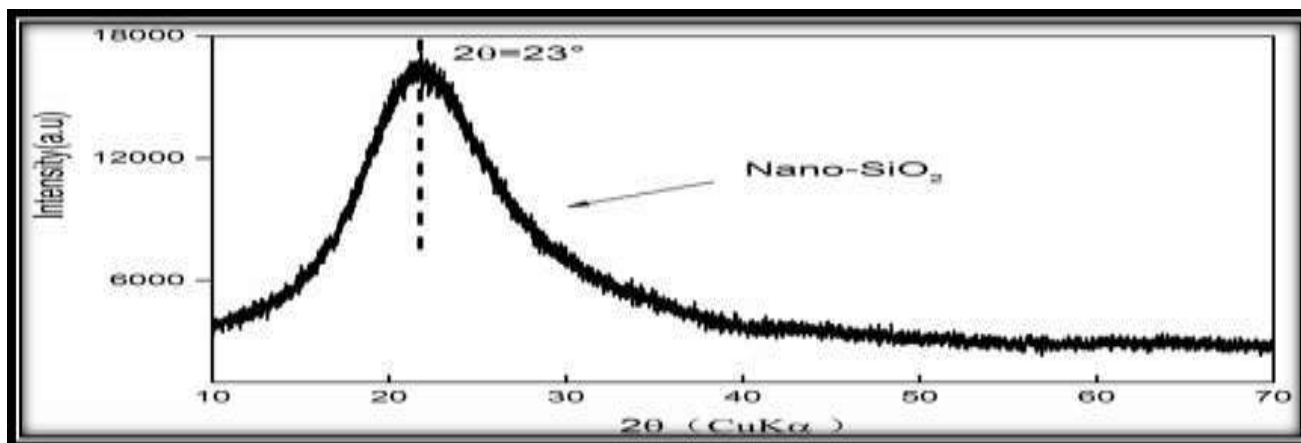


Figure 8: X-ray diffraction of silica nanoparticles

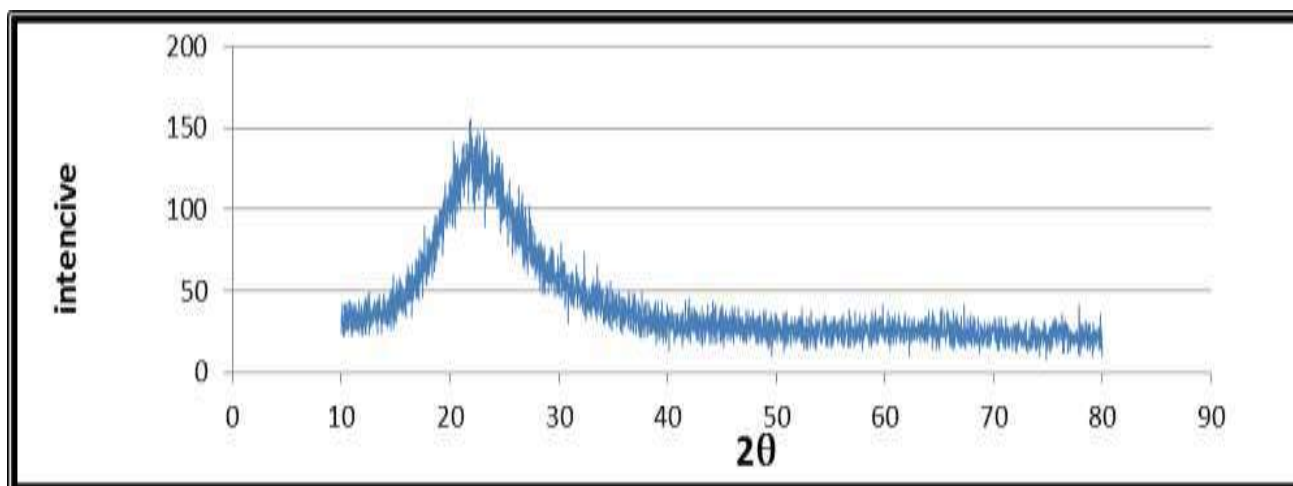


Figure 9: X-ray diffraction of grafting nano Silica

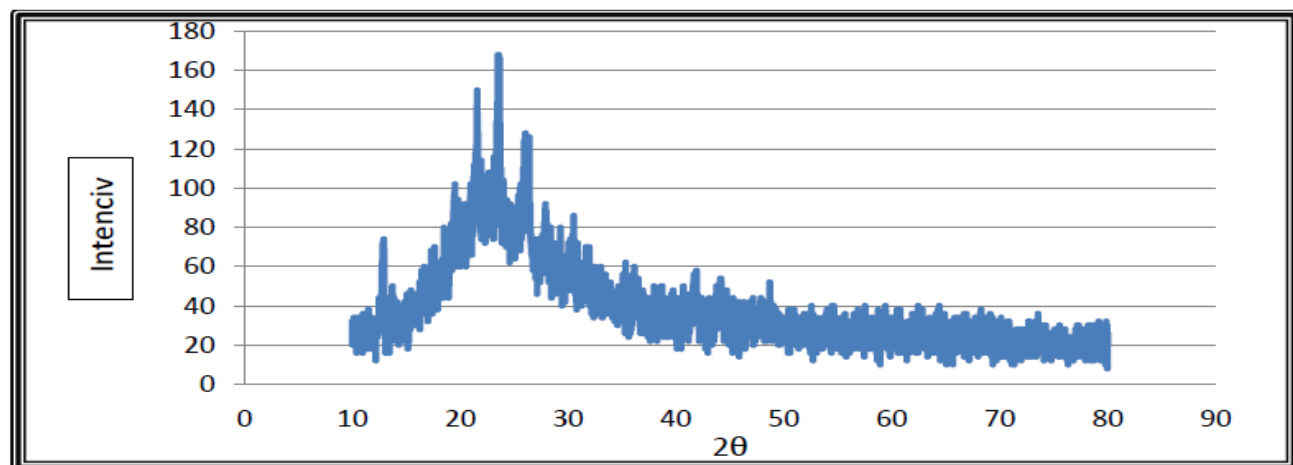


Figure 10: X-ray diffraction of C<sub>1</sub>

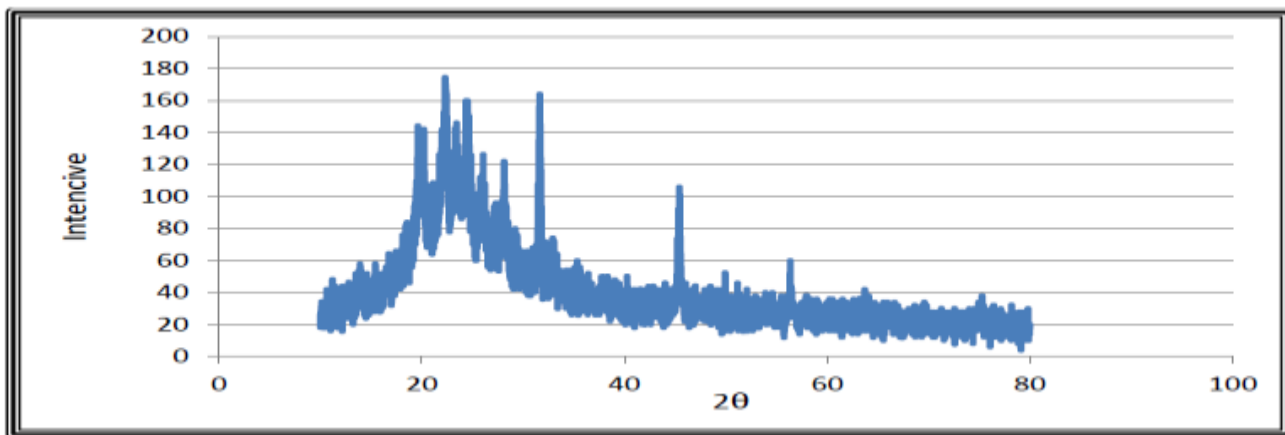


Figure 11: X-ray diffraction of C<sub>2</sub>

Table 3

Compound	2θ	Intensity
Silica nanoparticles	23°	170
Grafted nanosilica	23°	150
C <sub>1</sub>	23.56°	170
	21.58°	150
	25.98°	130
C <sub>2</sub>	22.33°	178
	26°	168
	44°	108

**Atomic Forces microscopy of Nano Composites (AFM)**

The surface morphology of Nano silica before and after modification by meth acrylic acid and Nano composite shows the three-dimensional image in Figures 12 to 15. The existence of irregular surface roughness Figures 14 and 15.

This roughness and height up diameters of the Nano composite can be attributed to linkage of different synthesized chains of heterocyclic triazole polymers, with surface of grafting silica to formation Nano composite [16], and all figures of Nano composites show increase in size of particles. In contrast the modification of Nano silica with polymers lead to increase diameter in fact the reaction

of chains polymers with modified SiO<sub>2</sub> 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 [17].

Photograph image of Nano composites, 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 Nano silica with along polymer chains, Table 3-4 shows average diameter and height for Nano silica, modified Nano silica and Nano composites(C<sub>1</sub>,C<sub>2</sub>).

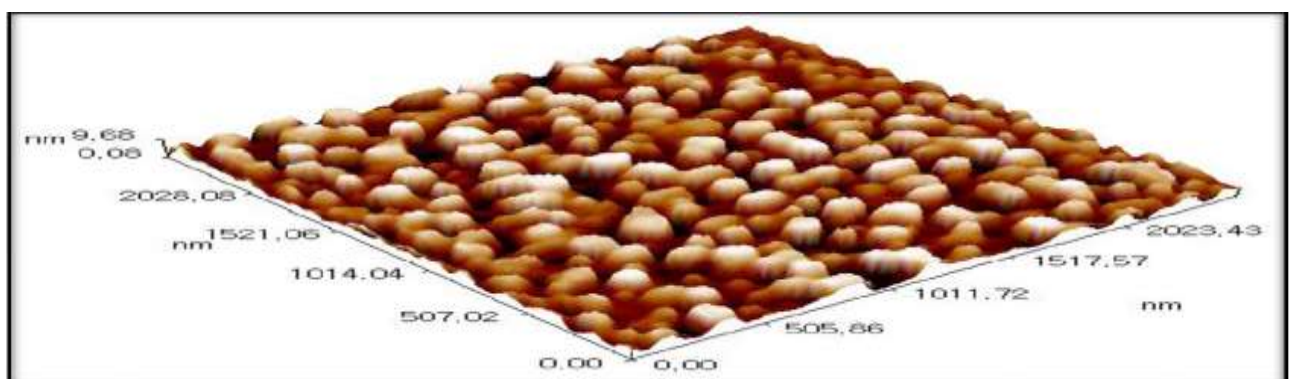


Figure 12: AFM photo of Nanosilica

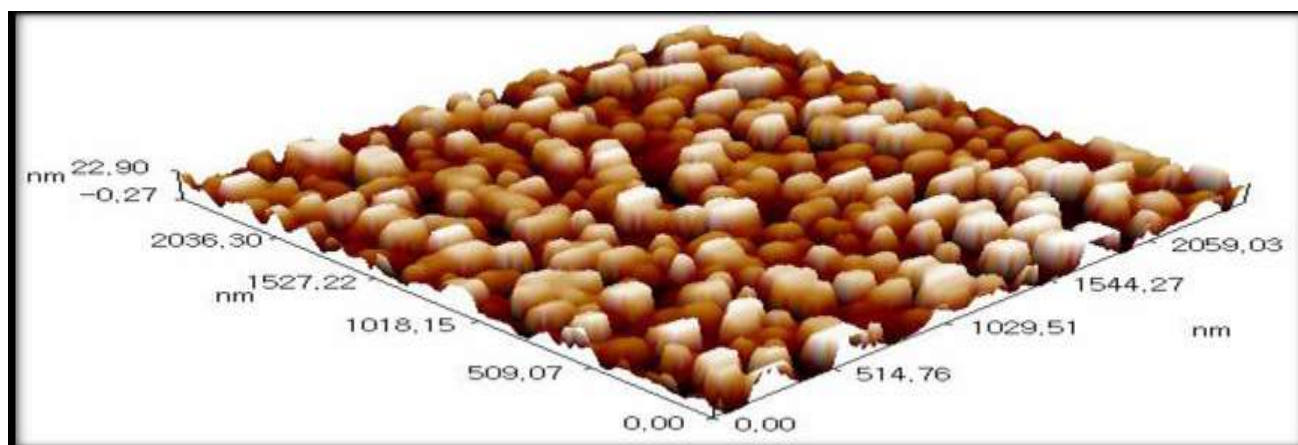


Figure 13: AFM photo of modified Nanosilica

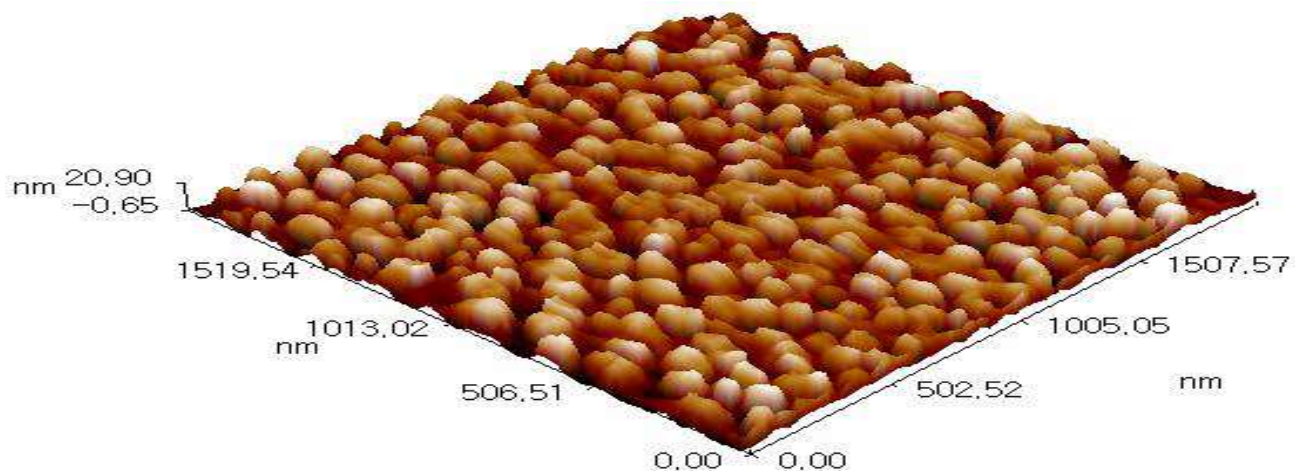


Figure 14: AFM photo of C1

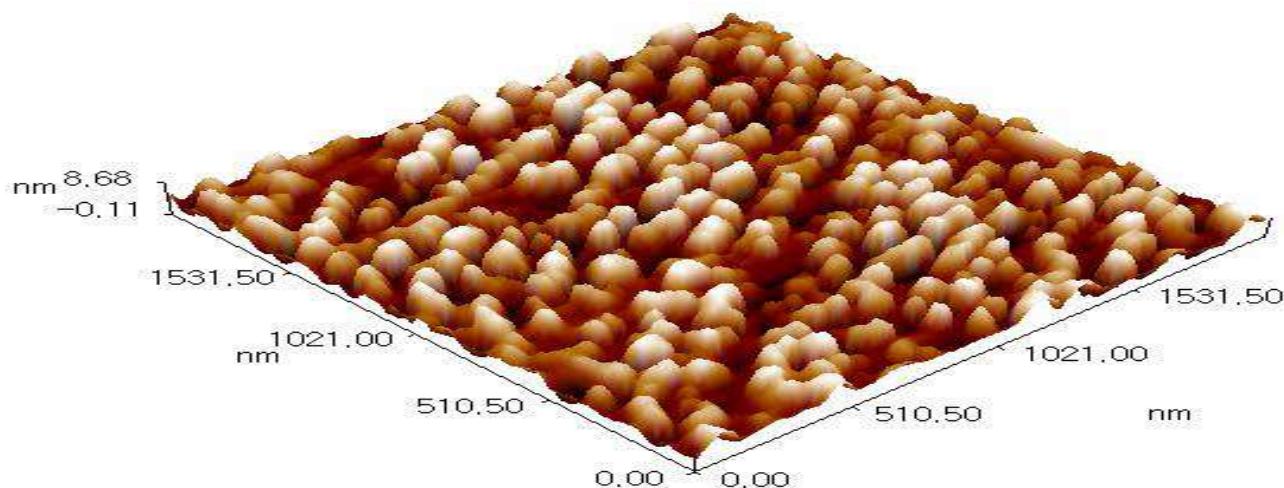


Figure 15: AFM photo of C2

## Conclusion

New triazole monomers have been prepared which used to prepare new polytriazole polymers and their Nano composite 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 compounds, monomer, polymers and Nano composite due to reacted of functional groups in these compounds. The X-ray diffraction used to study. The nanostructure of SiO<sub>2</sub> which

showed that no significantly changed upon grafting but there are decreased in intensity of the Nano composite that refer the modification were on the surface without change the structure of particles. AFM results shown high roughness in the surface of Nano composites C<sub>1</sub> and C<sub>2</sub> comparison with silica nanoparticles that attributed to reaction between functionalized surface of grafted Nano silica with chains of triazole polymers led to change in size particles distribution and surface of particles.



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