Grafting of Different Monomers onto Nano Aluminum Surface and Studying Their Biological Activities

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Abstract

The research includes the preparation of two nano polymer (NP_1, NP_2) through a grafted nano ceramic material (aluminum oxide Al_2O_3)(80 nm) by acrylic acid monomer. The latter was extended with two different ester monomers using free radical polymerization. The antibacterial activity of the prepared compounds) performed according to the agar diffusion method. All compounds (1, 2, 3, 4, NP_1, NP_2) showed inhibition against bacterial.

Key words:-Aluminum oxide, polymers, grafting, antibacterial

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Introduction

For decades, surface chemical modifications have intensively been studied. Recently, surface nanostructuring has increasingly got attention in view of its various technological applications in the fields of microelectronics, biomaterials, and medicine in which modification of the surface is made to enhance the interaction with cells [1-3]. Polymer nanocomposites are widely studied because of their potential utility to modify the properties of polymeric matrixes to meet the requirements for various applications [4−7]. Alumina has attracted a particular attention as a filler to augment the properties of polymer materials due to its high refractive index, its high thermal conductivity, and the absence of light absorption in the visible range [8−11]. There are only few studies on introducing polymer brushes onto the surface of α-alumina [12,13]. Van der Waals forces and the electrostatic repulsive energy between colloidal particles are significantly favorites domination of ceramic particles dispersion characteristics. The negative or positive charge of the ceramic particles surface depends on the fraction of the dissociated surface-hydroxyl groups. In acidic suspension, metal oxide surface possesses positive charge due to the presence of MOH^{2+} sites (M: metal atom), while in basic medium a negatively charged surface is formed due to the presence of MO^- sites [14].

In this work, a commercial nano-ceramic material, aluminum oxide (alumina, Al_2O_3), was grafted by acrylic acid. The latter was extended with three different monomers using free radical polymerization and biological activity was study for the compounds.

Experimental

Chemical

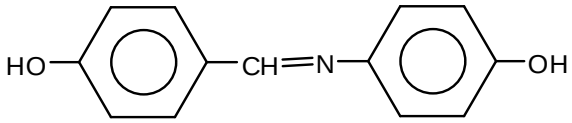
Alumina Nano(80nm) from (BDH), 4-Amino phenol 4-Hydroxy benzaldehyde Benzoylchloride from (BDH), Benzoyl peroxide from (MERK), p-Phenylenediamine from (BDH).

Preparation procedures

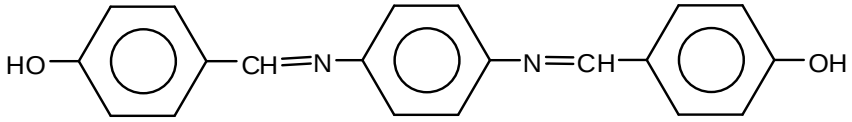
1) Preparation of Schiff-bases [15]

A solution of (0.01 mol) of (4-hydroxybenzaldehyde) in (20) ml of absolute ethanol, (0.01 mol) of (4-aminophenol)and a solution of (0.01 mol) of (4-hydroxybenzaldehyde) in (20) ml of absolute ethanol, (0.01 mol) of (p-Phenylenediamine) was added;so we will have two different reactions, to then number of drop glacial acetic acid was added as a catalyst. The reactions mixture was heated under reflux for [4] hours. The reactions cooled and the product precipitated, to then filtered and purified by recrystallization from water.

(1)



(2)



2)Preparationof acryloyl chloride [16]

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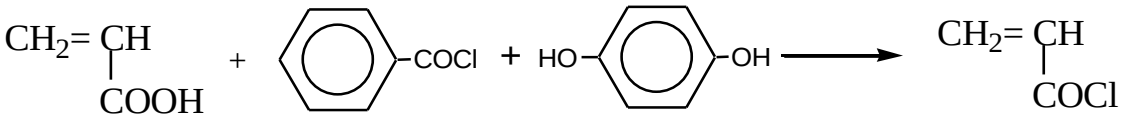
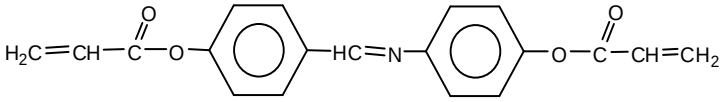


acrylic acid (4.32g, 0.06 mol) was mixed with benzoylchloride (16.88g, 0.12 mol), and hydroquinone (0.01 g). The mixture was distilled quite rapidly via a 25cm-efficient distilling column. A receiver containing 0.5 g of hydroquinone, in cooled ice-bath, was used to collect the distillate obtained when the top of the column temperature was between (60-70) ºC. The distillation process was stopped when this temperature was raised to reach 85ºC, yield (3) (68-72) %.

3)Preparation of Esters [17]

4-(hydroxybenzylidene-4-aminophenol)4-(hydroxyybenzylidene-4-phenyleneDiamine) (1,2) (0.01 mol) was dissolved in (10 ml) of [tetrahydrofurane] with (2) ml triethylamine in two different flask, then acryloyl chloride was added dropwise to each one with stirring in (0°C). The reactions mixture left stirring in the same temperature for (5) hours, the ammonium salt was precipitated, then the mixture was added to (50 ml) water, the oil phase was continued, then (50 ml) chloroform was added, separated the water as completely as possible and was dried the organic phase over {anhydrous magnesium sulphate} over night the filtered evaporated to yield (4, 5)75-80%.

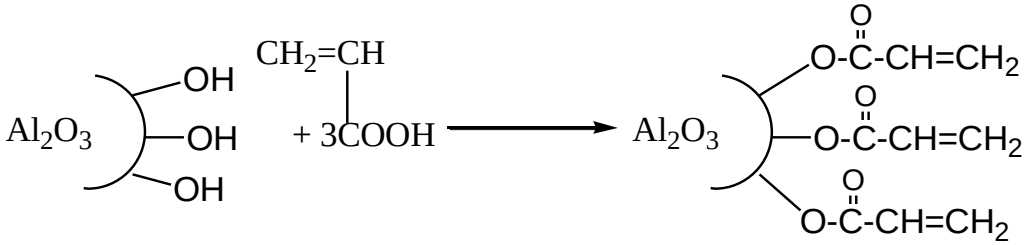
(4)



(5)

4) Preparation of Alumina-graft acrylic acid monomer [16]

7 g (Alumina) was weighted and placed in one-neck round bottom flask, followed by addition of -30- ml dry-toluene. The monomer acrylic acid 21 g was added to the standard solution of Alumina-toluene dropwise at room temperature, then the mixture was left stirring for (3) hours. The product was filtered and washed with (20) ml distilled water, then (20) ml of acetone. The solid produced was left to dry at room temperature.



5) Preparation of polymers by free radical polymerization [16]

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

In all of those preparations a two neck round-bottom flask contains (20) ml of dry-toluene as a solvent was placed in controlled water bath at (75°C) (±2) under nitrogen atmosphere, after (5) minutes (0.1) g[benzoyl peroxide] was added, followed by addition

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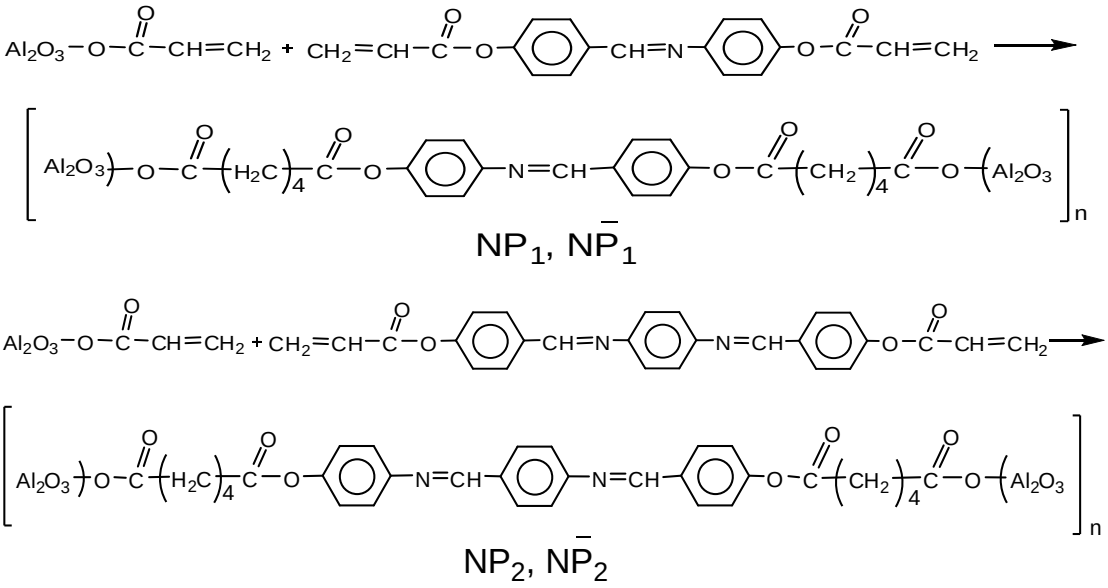
of (5) g of{ alumina-graft acrylic acid monomer}, after that (5) g of each of the following monomers was added, (i.e.4,5) separately. So we will have three different reactions, with stirring for (1) hour. The product was filtered and washed firstly with (15) ml of toluene and secondly with (15) ml of acetone, then left to dry at room temperature.
The following structures of these polymers are:



NP_1, $\overline{NP}_1$

NP_2, $\overline{NP}_2$

6) Biological activity

The antibacterial- activity of the prepared compounds (1,2,3,4, NP_1, NP_2) was performed according to the agar diffusion method. The prepared compounds were tested against Bacillus, Esherichia coli (E. coli). Each compound was dissolved in DMSO in concentration (0.024 M). The plates were then incubated at 37ºC and examined after 24 hrs.

Results and discussion

Schiff- base compounds (1,2) was synthesized by refluxing of 4-hydroxybenzaldehyde with(4-aminophenol) and with (p-Phenylenediamine) in two different reactions in glacial acetic acid as a catalyst. Table 1 and figure (1, 2) show a stretching band for Schiff base.

The compound acryloyl chloride was prepared by distilling of acrylic acid with benzoyl chloride and hydroquinone. This compound was characterized by FTIR spectra. The FTIR spectrum of compound, Figure (3), showed the strong peak at (1760) cm^{-1} which is attributed to the $\upsilon_{C=O}$ stretching.

The compounds (4,5) was prepared by the two different reactions between compounds 1 and compound 2 with {acryloyl chloride} at ($0^{\circ}C$). Table 2 and figure-(4,5) show a stretching band for esters. The -Alumina-graft acrylic acid monomer was prepared by the reaction between alumina and _acrylic acid monomer in dry toluene. The structure of this compound was studied by FTIR spectroscopy, the FTIR spectrum of this compound Figure (6) showed the following absorption bands: C=O -stretching at (1728) $cm^{-1.}$ It also shows the peak at (3487) cm^{-1} due to the υ_{O-H} group.

The polymers (NP_1, NP_2) were obtained by free radical polymerization. The structure assignment of the polymers was based on –FTIR- spectroscopy. Table 3 and figures (7,8) show a stretching band for polymers.

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The resulting data of biological activity are listed in table 4. All compounds (1, 2, 4, 5, NP_1, NP_2) showed inhibition against bacterial the best inhibition on Esherichia coli was the polymerNP1and to the Bacillus bacterial was the first Schiff-base(1).

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Table (1) : The stretching bands of Schiff-bases.

Schiff-bases	$\upsilon_{-C=N}$	υ_{-OH}
1	1587 **cm^{-1}**	3182 **cm^{-1}**
2	1595 **cm^{-1}**	3271 **cm^{-1}**

Table (2) : The stretching bands of esters.

Esters	$\upsilon_{-C=O}$	$\upsilon_{-C=N}$	υ_{-OH}
3	1604 cm^{-1}	**1523**cm^{-1}	**3149**cm^{-1}
4	**1591**cm^{-1}	**1523**cm^{-1}	**3045**cm^{-1}

Table (3) : The stretching bands of polymers.

Nano polymers	$\upsilon_{-C=O}$	$\upsilon_{-C=N}$	υ_{-OH}	υ_{-C-H}
NP_1	**1734**	**1622**	**3467**	**---**
NP_2	**1599**	**1523**	**2963**	**2931**

Table(4): Biologcal activities of the compounds.

No.		Esherichia coli	Bacillus
1	Schiff $_1$	13	22
2	Schiff $_2$	19	18
3	Ester 3	15	16
4	Ester $_4$	17	13
5	NP1	22	12
6	NP2	13	12

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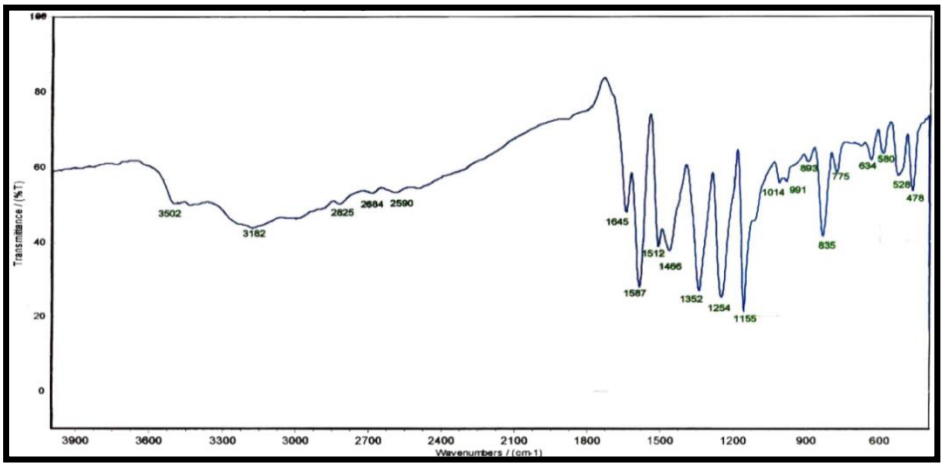

Figure (1): FTIR for compound (1).

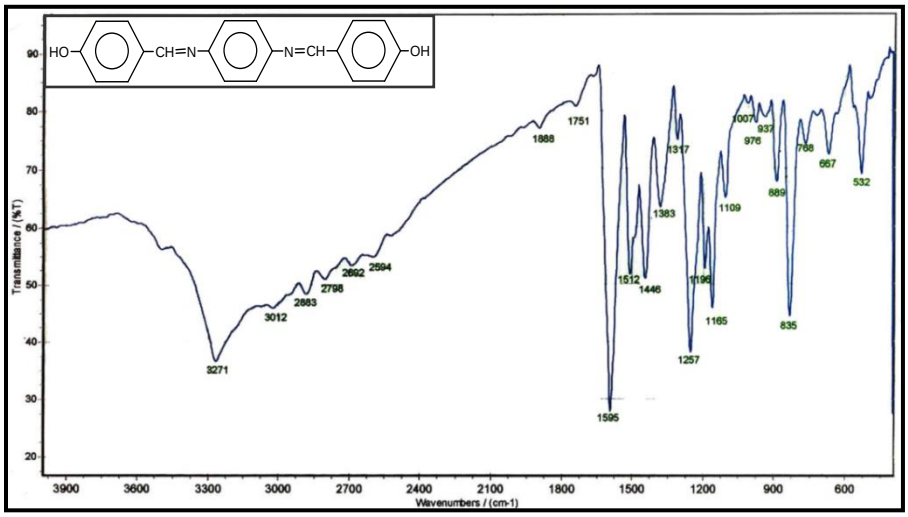

Figure (2): FTIR for compound (2).

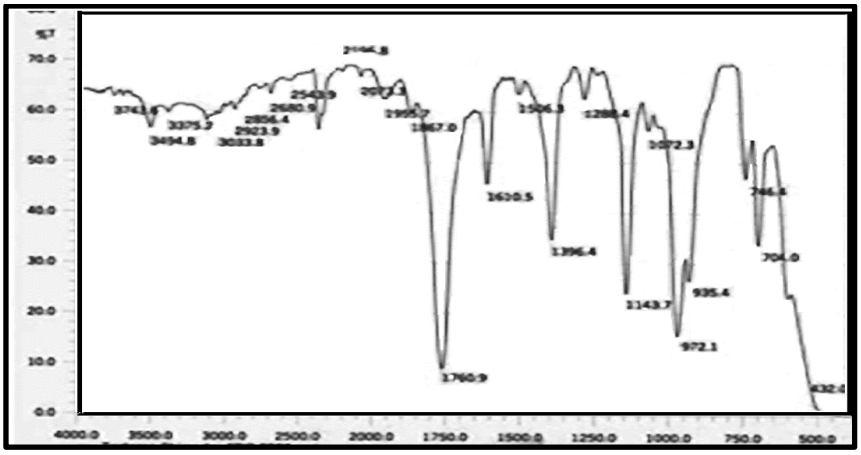

Figure (3): FTIR of Acryloyl chloride(3).

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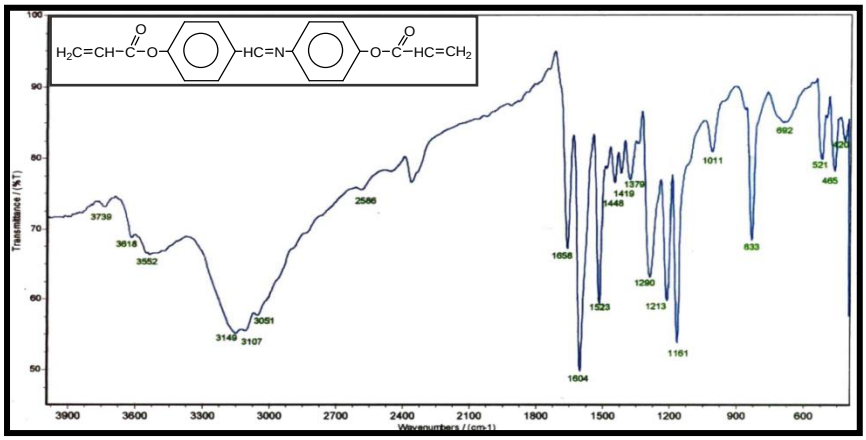

Figure (4):FTIR for compound(4)

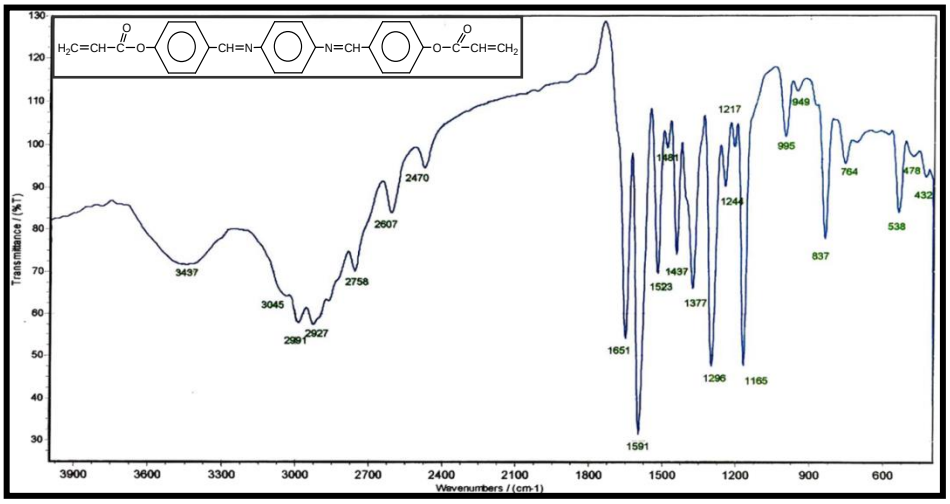

Figure (5): FTIR for compound (5).

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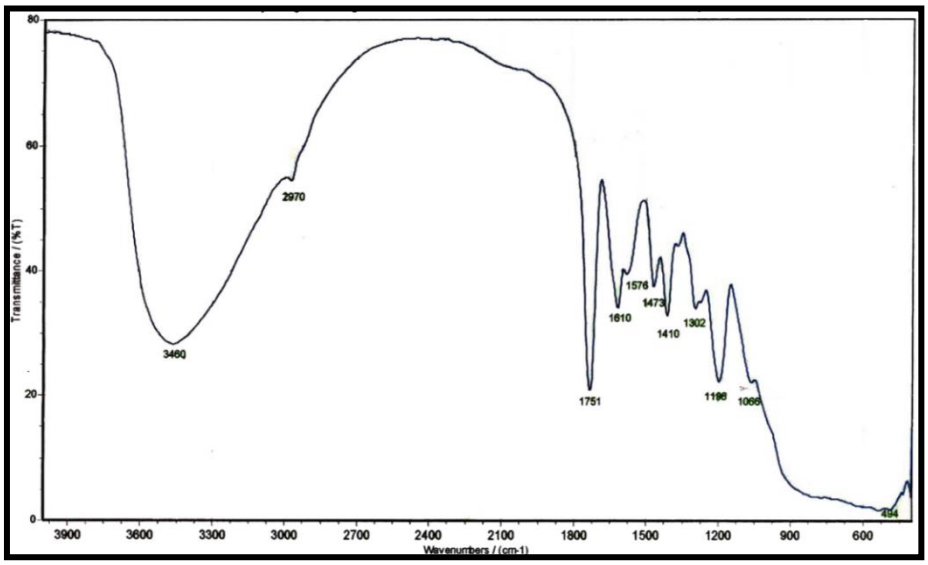

Figure (6): FTIR for alumina grafted acrylic acid.

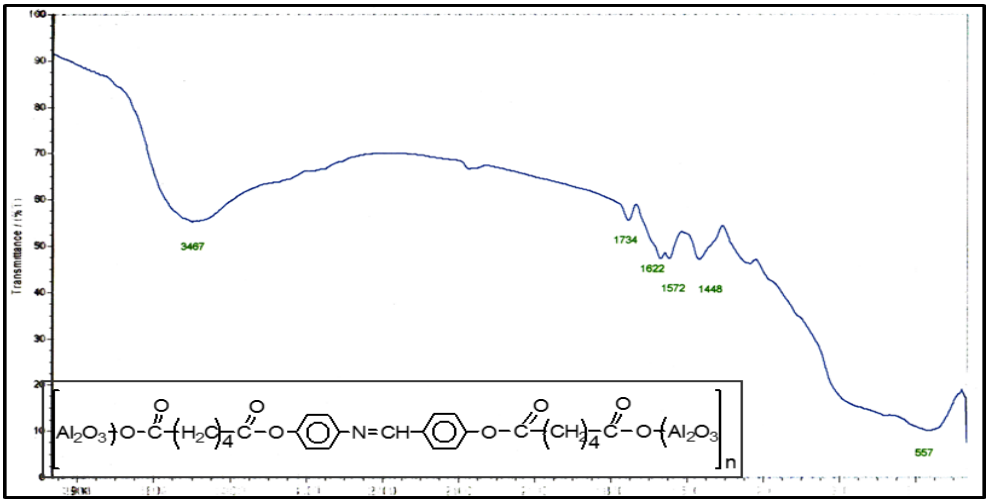

Figure (7): FTIR for N P_1.

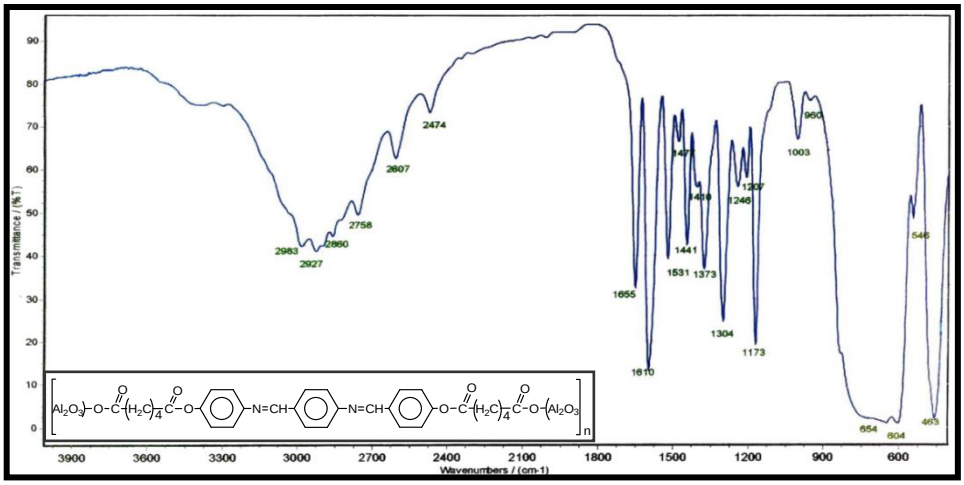

Figure (8): FTIR for NP_2.

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