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Conversion of Polyacrylonitrile to Poly amidoxime and Substitution with Maleic Anhydride, Itaconic Acid, Methyl Nadic Anhydride and Acetylchlorid

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ABSTRACT

The aim of this research is to modified and graft poly acrylonitrile to poly amidoxime [A_1] for dental fillers, because some of the prepared graft co polymers can be molded to a solid, such as maleicanhydride, itaconic acid, methyl nadic anhydride, acetylchloride. New properties of the substrate of useful derivatives as material were formed through chemical reactions. Due to their structural diversity and stability, onto backbone of polymers. The prepared polymers were characterized by Fourier Transforms Infra-Red (FTIR) spectroscopy and thermal analysis were considered. It was found the prepared graft co polymers can be changed to a white solid, to be suitable for dental fillers, which gave high thermal resistance with more stabilities, rhe degree of swelling was convenience for dental applications.

Keyword: Polyacrilonitrile, Poly amidoxime, Substitution with maleic anhydride, Itaconic acid, Methylnadic anhydride

INTRODUCTION

Copolymerization is used to change the some properties of known manufactured polymers to get high specific requires, and to reduce crystallinity, modify glass transition temperature or to enhance the mechanical or physical properties [1,2]. Graft copolymerization is a technique for modifying the chemical and physical properties of natural and synthetic copolymers such as alternating, periodic and block copolymers which generally linear chains. Some applications of graft copolymers include [3-5], membranes for the separation of gases or liquids compatibilizers for polymer blends [6-8], Impact resistant plastics. thermoplastic elastomers, hydrogels drug carrier polymers [9,10].

Polyacrilonitrile (PAN) nanofibers [11-13] were prepared by electro spinning and they were modified with hydroxylamine to synthesize Amidoxime Polyacrilonitrile (AOPAN) chelating nanofibers, which were applied to adsorb copper and iron ions. The conversion of the nitrile group in PAN was calculated by the gravimetric method. The structure and surface morphology of the AOPAN nanofiber were characterized [14,15]. Copolymerization is used to modify the some properties of known manufactured polymers to get specific requires, to reduce crystallinity, modify glass transition temperature or to improve solubility and to enhance the mechanical or physical properties [16], graft copolymerization is a technique for modifying the chemical and physical properties of natural [13] and synthetic copolymers [17] such as alternating, periodic, and block copolymers which generally linear chains. Some applications of graft copolymers include membranes for the separation of gases or liquids compatibilizers for polymer blends. Impact resistant plastics [18,19]. Thermoplastic elastomers, Hydrogels, Drug carrier polymers. The uranium concentration in seawater is 3 μg/l with an estimated 5×10^9 tons of uranium in the oceans, in solution as the tricarbonato complex. Any extraction process will encounter the problems attendant on this high dilution, the only possible techniques currently being ion exchange on chelating resins [20,21] or sorption onto inorganic materials [22-24]. Poly(amidoxime)/poly(hydroxamic acid) chelating resin has been produced with high uranium sorption from neutral solutions containing the metal as the tricarbonato complex, and the results of a study of the behavior of this resin towards seawater are given. High chemical and biochemical stability and fast sorption which can sorb 68 per cent of the uranium present using a 24 s resin to seawater contact time [25-29]. The main objective of the research is to synthesis and study of copolymers as fillers of dental or other uses by some synthetic and natural polymers.

MATERIALS AND METHODS

Polyacrilonitrile, maleicanhydride, itaconic acid, methylnadicanhydride were used from Fluka, and Hydroxyl ammonium chloride were purchased from BDH. Fourier Transform Infrared (FTIR) spectra were recorded by testing Shimadzu FTIR 8000 series spectrophotometer; Al-Thermal analyses were performed using Differential Scanning Calorimeter (DSC) and Thermogravimetry (TGA). Softening points were determined using Thermal Microscope (Kofler-method), and Reichert thermovar. SP.10/0.25, 160. The degree of swelling was calculated for each sample after 24 h, using the following Equation 1:

$$Vm = \frac{m_t - m_\circ}{m_\circ} \times 100 \qquad (1)$$

Where, m_0 is the weight of a dry polymer at t=0, m_t is the swallowed polymer after 24 h.

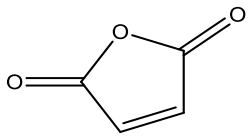
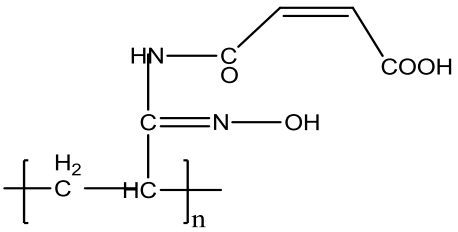
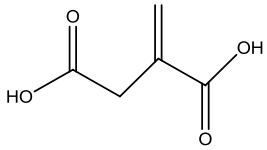
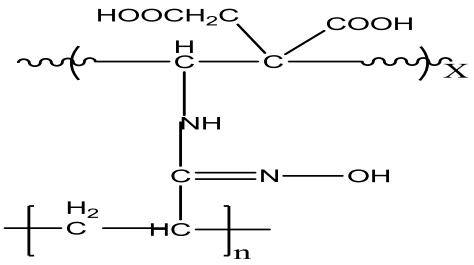
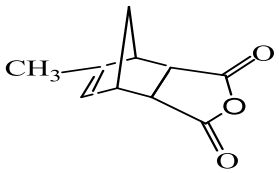
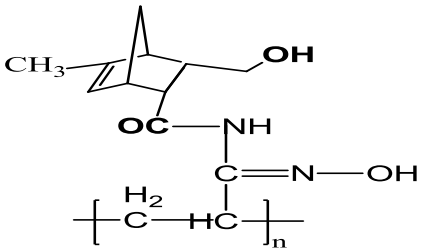
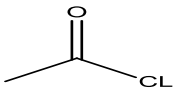
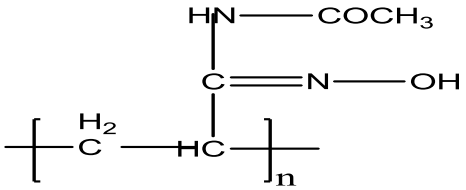
Conversion of PAN with hydroxyl ammonium chloride to (poly amidoxime) (A_1)

10 g of PAN dissolved in 20 ml of THF was placed into the flask and hydroxyl ammonium chloride solution was added to the flask, the reaction was carried out at 70°C for 2 h, shaking gradually, the product was separated from the solution by filtration and washed several times with deionized water until no further NH_2OH remained in the solution. It gave polyamidoxime A_1.

Substitution (A_1) with maleicanhydride, itaconic acid, methyl nadic anhydride, acetylchloride (A_2-A_5)

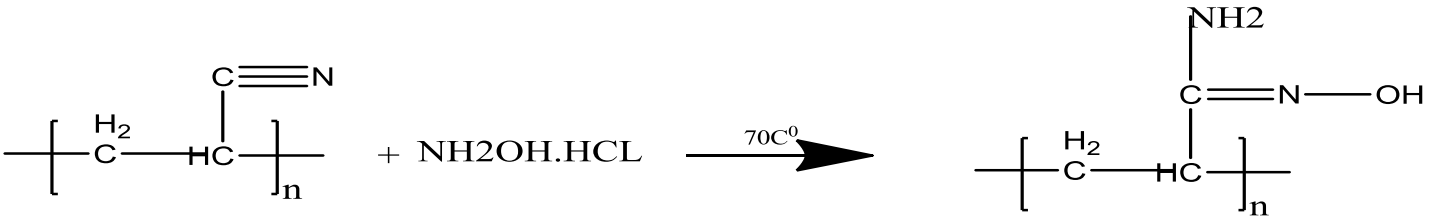
1 g polyamidoxime (A_1) dissolved in (5 ml) of acetone and few drops DMF. 1 g maleic anhydride dissolved in (5 ml) acetone, or itaconic acid or, methyl nadic anhydride or acetylchloride. The mixture was heated at 50°C using water bath for 1 h. The solvent was evaporated under vacuum; the product was washed three times with ether, dried in a vacuum oven at 50°C (Table 1).

Table 1: Physical properties of prepared polymers (A_2-A_5)

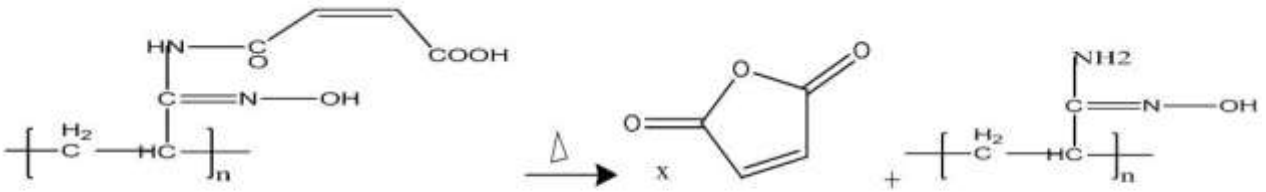
S. No.	Monomer M	Copolymer	Conversion (%)	μ in dl/g	Color	S.P (°C)
A_2			76	o.68	Brown	Viscous
A_3			80	o.64	Brown	=
A_4			77	0.55	Black	=
A_5			70	0.59	Black	=

RESULTS AND DIRCUSSION

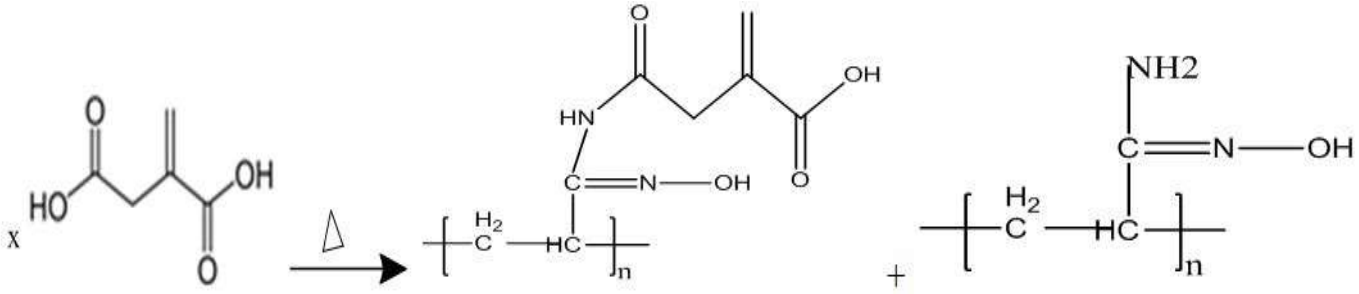
Conversion of polyacrilonitrile with hydroxyl ammonium chloride to (polyamidoxime) [A_1] and substitution [A_1] with maleicanhydride, itaconic acid, methyl nadic anhydride, acetylchloride [A_2-A_5] (Table 2 and Schemes 1-5). The amidoxime were obtained by treatment of nitrile groups with hydroxylamine at 70°C, giving rise to a selective functional group. The poly(amidoxime) was synthesized by conversion of the nitrile groups of PAN copolymers into amidoxime groups by a reaction with hydroxylamine. Four new polymers were prepared by substitution of [A_1] with different compounds, as shown below:



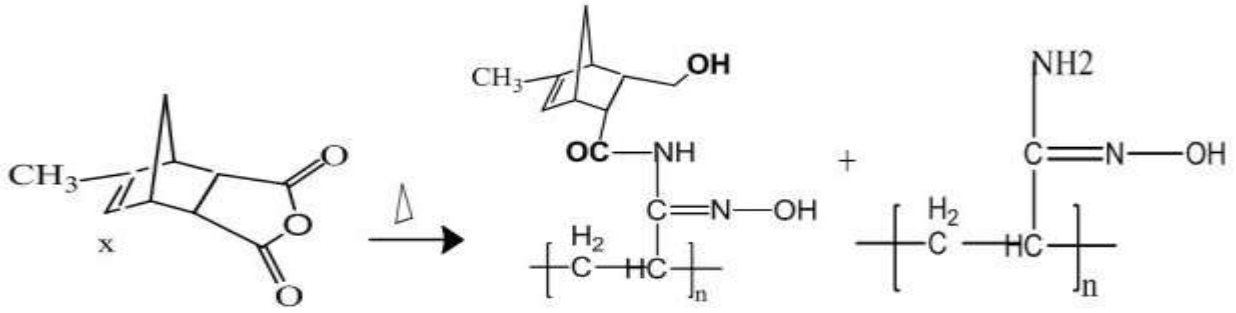
Scheme 1: Reaction polyacrilonitrile with hydroxyl ammonium chloride [A_1]



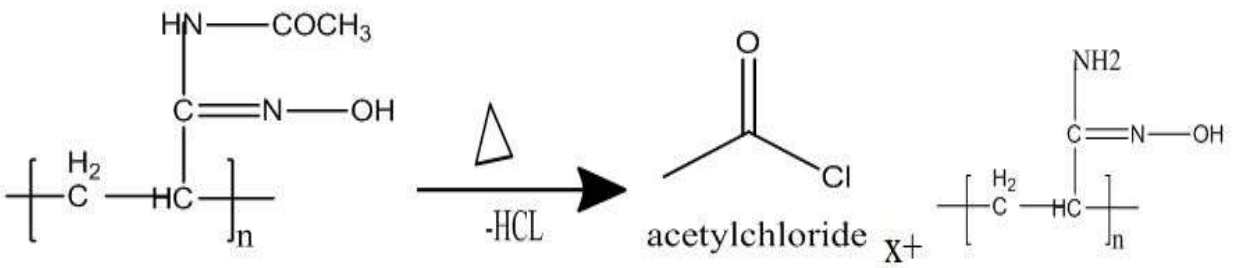
Scheme 2: Substitution [A_1] with maleicanhydride [A_2]



Scheme 3: Substitution of [A_1] with itaconic acid [A_3]



Scheme 4: Subsistitution of [A_1] with methyl nadic anhydride [A4]



Scheme 5: Subsistitution of [A_1] with acetylchloride [A_5]

Polyamidoxime

The structures of polymers [A_1-A_5] were confirmed by FTIR (Figures 1-5).

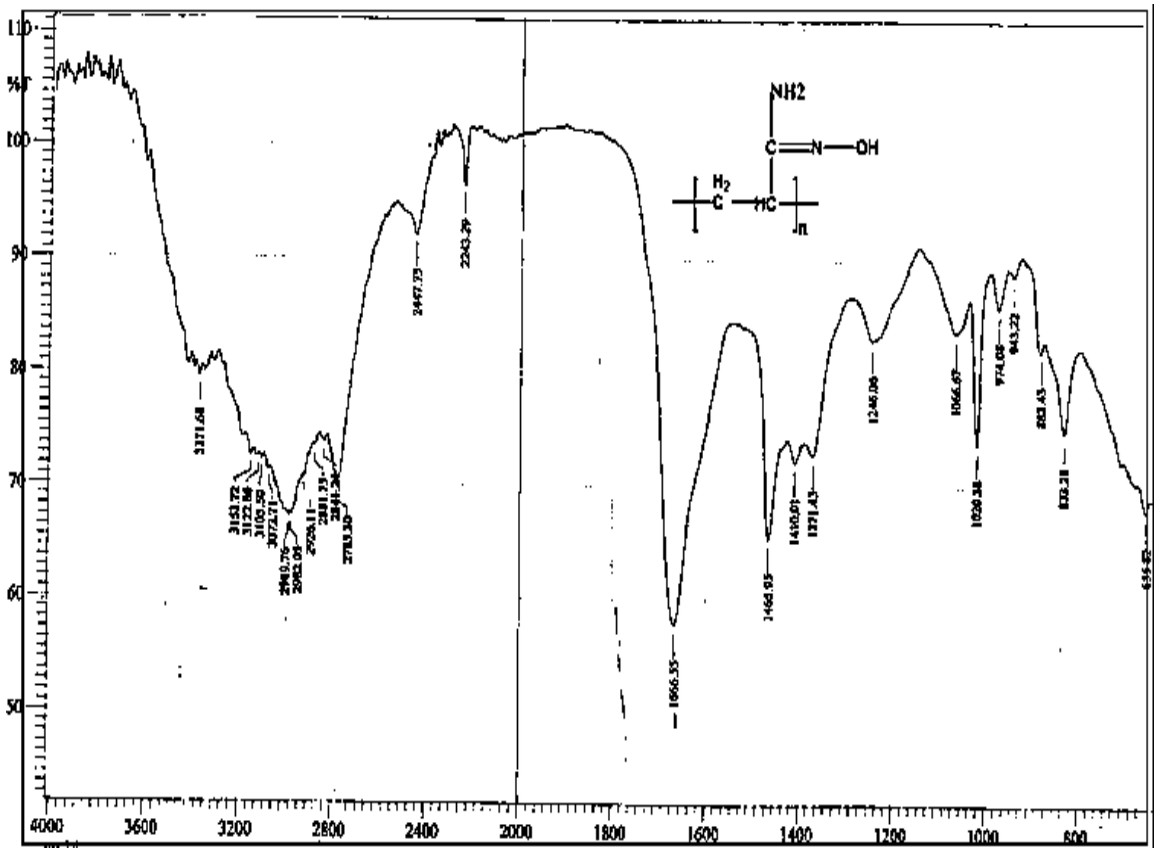


Figure 1: FTIR spectrum of polymer A_1 showed absorption peaks at 2970 cm^{-1} of υ_{CH2} aliph. 3105 cm^{-1} of (N-H), υ(OH) 3400-3500 cm^{-1} stretch and 1666 cm^{-1} (strong), υ(C=N) of (polyamidoxime)

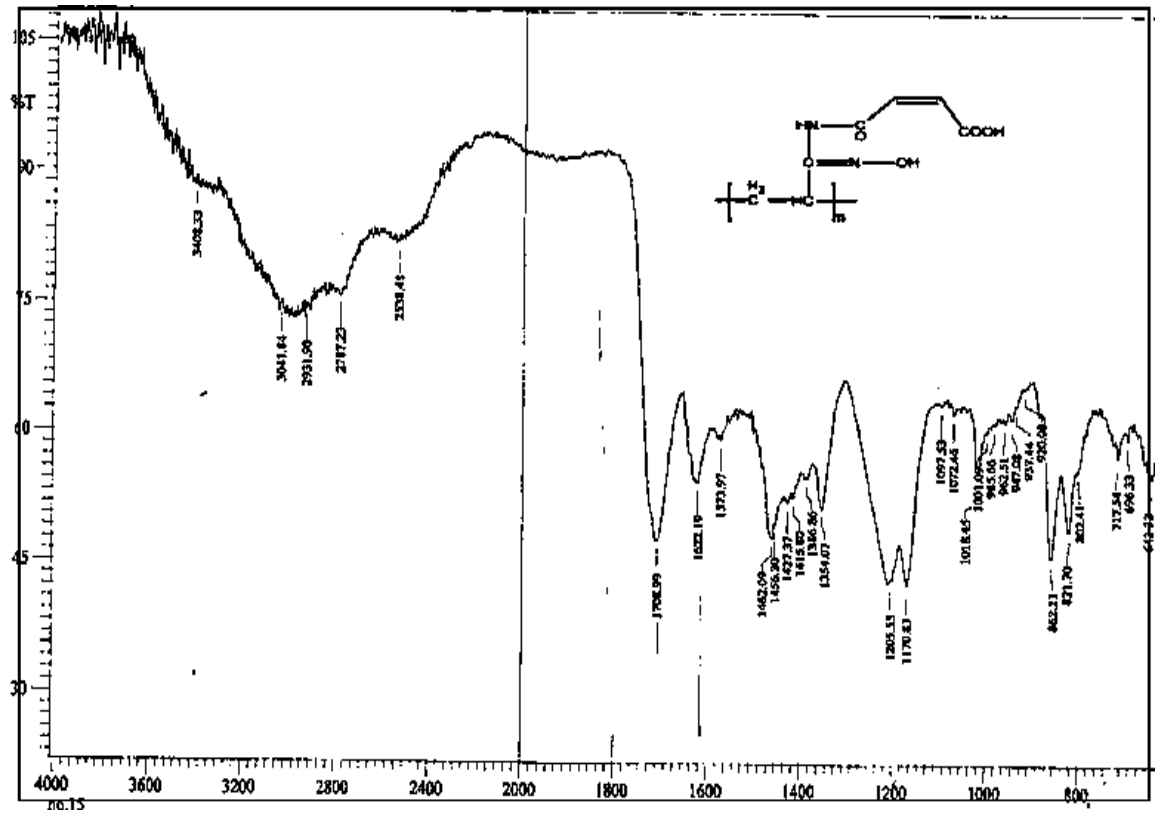


Figure 2: FTIR spectrum of polymer A_2, absorptions appeared at 1728, 1670 cm^{-1} (C=O) (strong) of maleamic acid, 1070 cm^{-1} (C-O) stretch and 1354 cm^{-1} of (C-N), 1728, 1670 (C=O) (strong) maleamic acid

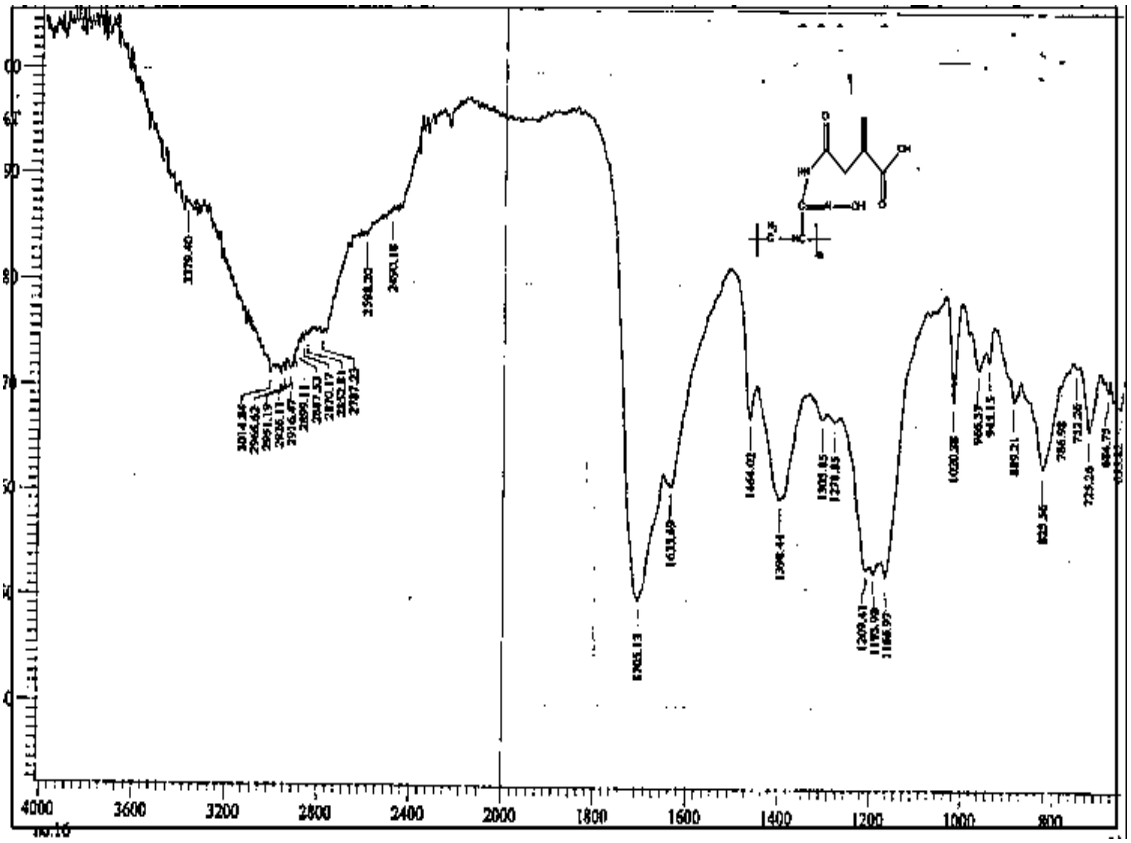


Figure 3: FTIR spectrum of polymer A_3 showed absorption peaks at (1166) cm^{-1} (C-O) stretch of itaconic acid, 1398 cm^{-1} (C-N, (3450, 2900) (OH), 1705 (C=O) itaconic acid

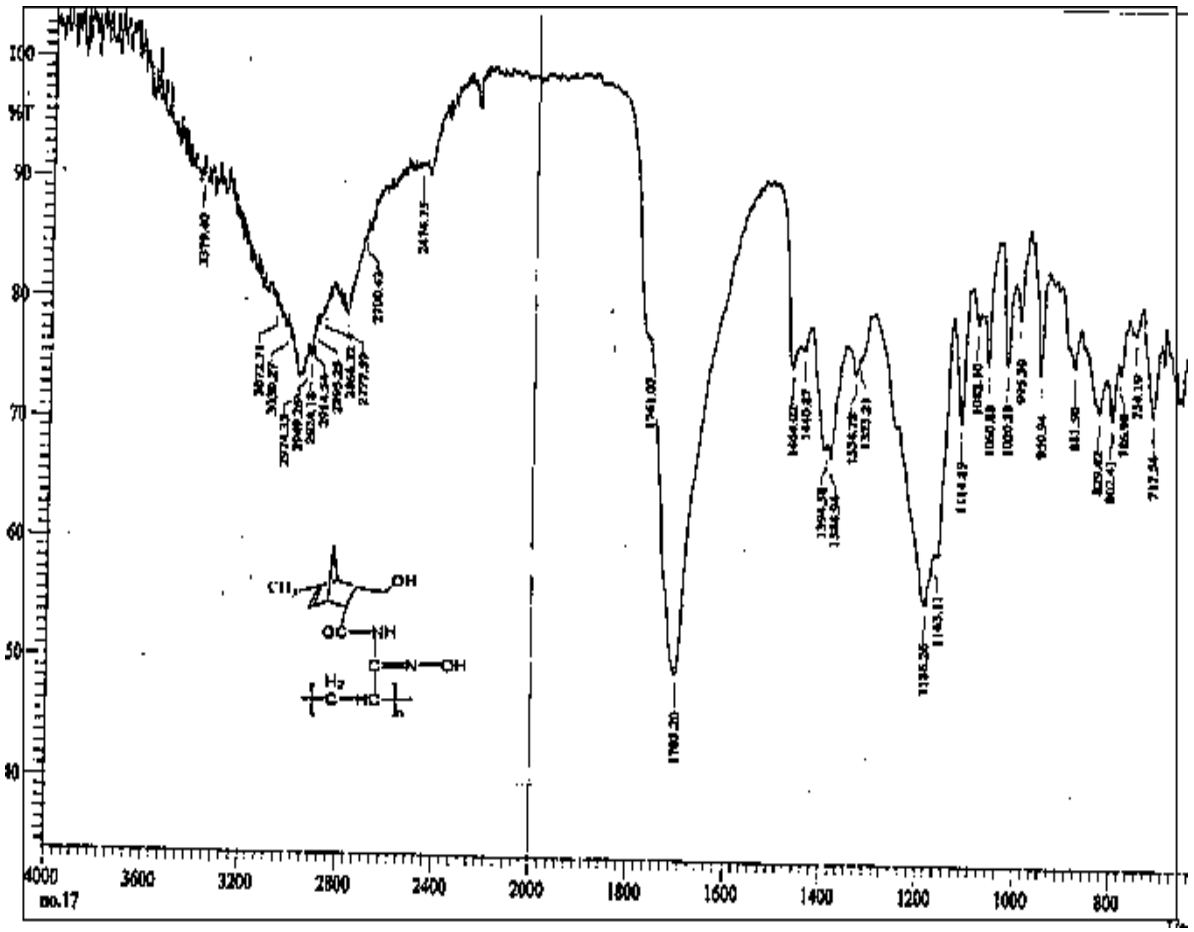


Figure 4: FTIR spectrum of polymer A_4 showed absorption peaks at 1384 cm^{-1} (C-N), 1761, 1680 (C=O) methyl nadamic acid

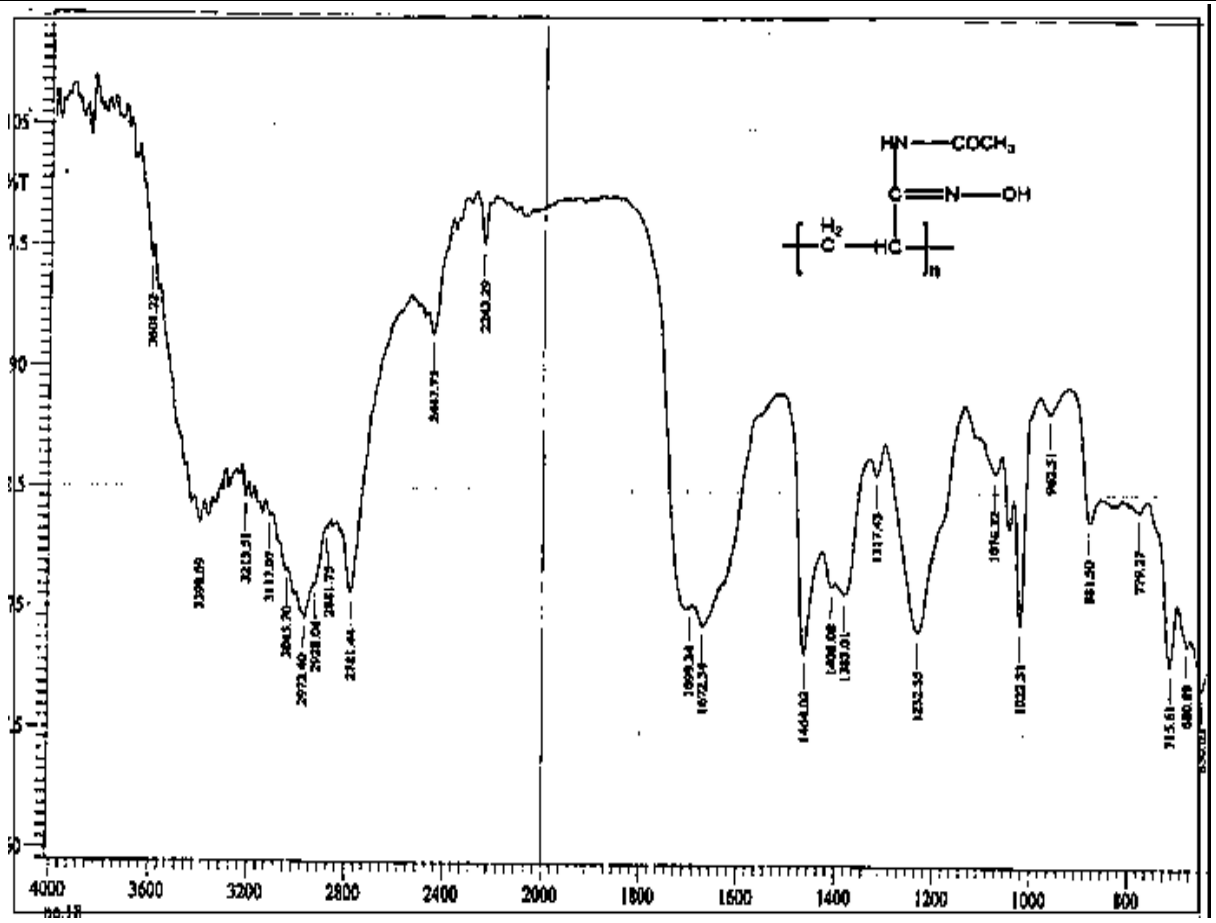


Figure 5: FTIR spectrum of polymer A_{18} showed absorption peaks at 1383 cm^{-1} (C-N), 1670 (C=O) ester

Table 2: FTIR Spectral data for compounds [A_1-A_5]

Compound No.	υ(N-O) (cm^{-1}) (Polyamidoxime)	υ(OH) (cm^{-1}) stretch (Polyamidoxime)	υ (C=N) (cm^{-1}) (Polyamidoxime)	υ other (cm^{-1})
A_1	974	3400-3500	1666 (strong)	---------
A_2	962	3408	1622	1728, 1670 (C=O) (strong) maleamic acid
A_3	966	3380	1635	(3450, 2900) (OH), 1705 (C=O)itaconic acid
A_4	950	3380	1700	1761, 1680 (C=O) methyl nadamic acid
A_5	962	3600	1672	1670 (C=O) ester

The thermal stability study

The thermal stability of some selective prepared co polymers were investigated technique is based on measuring the weight loss as a function of time at constant temperature or as a function of temperature at constant rate of heating by measuring the sample weight, and the change at a programmed rate of heating. The change in weight was measured as a function of temperature which gave valuable information about the thermal stability of the prepared polymers such as (A3-A4) was taken 10-20 mg from the prepared polymers use Helium as inert gas in rat 20 ml/min). The thermo-grams were recorded and analyzed, as shown in Tables 3-8 which indicated the high thermal resistance and showed the steps of weight loss-temperature. This high thermal resistance indicated the high interaction between hydrogen bonding of polar groups through the co polymer chains.

Table 3: DSC of polymer (A_3) first stage

Sample	Onset point	offset point	Point of reaction	Peak maximum	Enthalpy
A_3	163.4°C (13 min)	212.9°C (18 min)	-19.937 mw at 164.2°C (13 min)	-26.019 mw at 196.9°C (16 min)	-31.93 J/g

Table 4: DSC of polymer (A_3) second stage

Sample	Onset point	offset point	Point of reaction	Peak maximum	Enthalpy
A_{24}	276. 4°C (25 min)	310.0°C (28 min)	-31.049 mw at 295.7 °C (27 min)	-32.565 mw at 300.5 °C (27 min)	-78.06 J/g

Table 5: DSC of polymer (A_3) third stage

Sample	Onset point	offset point	Point of reaction	Peak maximum	Enthalpy
A_{24}	312.0°C (28 min)	330.7°C (30 min)	-26.475 mw at 313.6°C (29 min)	-31.801 mw at 321.0°C (29 min)	-46.25 J/g

Table 6: DSC of polymer (A_4) first stage

Sample	Onset point	offset point	Point of reaction	Peak maximum	Enthalpy
A_4	100.3°C (7 min)	131.3°C (9 min)	-24.942 mw at 107.0°C (7 min)	-26.029 mw at 117.9°C (8 min)	-7.12 J/g

Table 7: DSC of polymer (A_4) second stage

Sample	Onset point	offset point	Point of reaction	Peak maximum	Enthalpy
A_4	143.7°C (10 min)	156.3°C (11 min)	-25.220 mw at138.6°C (10 min)	-25.821 mw at144.5°C (10 min)	-6.27 J/g

Table 8: DSC of polymer (A_4) third stage

Sample	Onset point	Offset point	Point of reaction	Peak maximum	Enthalpy
A_4	198.5°C (16 min)	223.9°C (18 min)	-35.774 mw at 201.8°C (16 min)	-40.151 mw at 207.6°C (16 min)	-41.67 J/g

CONCLUSION

It was concluded that the prepared graft co polymers can be molded and then changed to a white solid, to be convenience for dental, with a suitable cost, beneficial thermal safety, extended life of useful as dental fillers, because the preparing conditions which gave high thermal resistance with more stabilities The degree of swelling was calculated for each sample after 24 h=zero, was convenience for dental uses.The best one was A_3 as a dental filler.

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