

Synthesis and Characterization of New Polyamide Containing Triazine Ring As Central Core and Preparation of Its Reinforced Nanocomposites by Modified Graphene Oxide Nanoparticles with Chitosan

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Abstract

In this research work, first a newly synthesized diamine containing 1, 2 and 4 substituted of triazine (10) prepared by a seven steps reasonable synthetic route. Then aromatic polyamide (12) was prepared by direct polycondensation reaction of diamine (10) and commercial diacid such azelaic acid (11). Graphene oxide nanoparticles modified with chitosan (15) prepared by a two steps process by using the natural polymer chitosan; Polyamide films and nanocomposites films (PAN 16, 17) containing 3 and 5% weight percent of graphene oxide modified with chitosan were prepared through the solution method. Structure of resulting products was determined by FT-IR, ¹H-NMR spectroscopy and also structure, morphology, thermal and mechanical properties of resulting nanocomposite (PAN 16, 17) were characterized by FT-IR, X-ray diffraction (XRD), Energy dispersive X-ray spectroscopy (EDX), scanning electron microscopy (SEM), Thermo gravimetric analysis (TGA), differential thermal gravimetry (DTG) and UV-Vis spectroscopy.

Keywords: polyamide, triazine ring, thermal stability, graphene oxide nanoparticles, chitosan.

Introduction

In the recent years, nanocomposites reinforced with graphene nanoparticles have been widely studied by researchers, because graphene is two-dimensional nanoparticles of carbon atoms [1,2]. It has unique thermal, electrical and mechanical properties, and by using as a filler in different amounts can be greatly enhances the properties of nanocomposite. Previously, carbon nanotubes were used as polymer reinforcements, but their disadvantages, including lumpiness, limited access to high-quality nanotubes, and their high price, led to the use of graphene nanoparticles [3,4]. The advantages of graphene nanoparticles include

their abundance in nature, cheapness, favorable physical and mechanical properties, high transparency, specific surface graphene area, and the ease of creating functional groups on graphene sheets in order to prepare nanocomposites [5,6]. High-performance polymers have special properties such as thermal stability, flame retardancy, mechanical strength, high conductivity and non-transmission of heat, electricity or sound. These polymers are widely used in various industries such as telecommunication sciences, pharmaceuticals, aerospace and transportation. Many factors are responsible to show high performance ability of these type of polymers, includes: resonance stability, molecular symmetry, distribution and molecular weight, rigid chain structure and possibility to establish strong forces between polymeric chains and introducing additives such as mineral fillers, organoclays and metal particles [7,8]. The rapid development of high-performance polymers starts in 1950s, which was simultaneously with the development of the aerospace and electronics industries [9,10]. Polyamides and polyimides are the main part of high-performance polymers that have suitable options for using in advanced technologies due to special properties such as specific thermal and mechanical stability [11,12]. Polyamides as the first fully synthetic fibers was prepared and registered under the brand name Nylon in 1934 by W. H. Carruthers in Du Pont. Various applications of polyamides are suitable due to their properties, including excellent mechanical durability, thermal stability, resistance to solvents and chemical agents, and elasticity [13,14].

Nowadays, the most widely used method for the production of polymers is the Yamazaki method for condensation polymerization via phosphorylation. In this method, amino acids or aromatic diamines and aromatic dicarboxylic acids are reacted in the presence of an aryl phosphite (diphenyl and triaryl phosphites) and an organic base such as pyridine as condensing reagents in N-methyl-2-pyrrolidone (NMP) containing inorganic salt solvents, leading to the production of high molecular weight polymers [15,16 and 17].

Due to two important properties of nanoparticles, namely, increased surface area to volume ratio and different particle performance due to reduced dimensions, synthesized polymer can be loaded on the surface of nanoparticles [18,19]. Among nanoparticles, graphene is a suitable nanofiller in the field of polymers for the production of high-performance nanocomposites due to its good mechanical, electrical and thermal properties, and in this research work, synthesized polyamide was loaded on its surface [20,21].

Experimental

Materials

4-Nitrobenzoic acid ($\text{NO}_2\text{C}_6\text{H}_5\text{COOH}$), Thionyl chloride (SOCl_2), Ethanol ($\text{C}_2\text{H}_5\text{OH}$), Pyridine ($\text{C}_5\text{H}_5\text{N}$), Hydrazine monohydrate ($\text{N}_2\text{H}_4\cdot\text{H}_2\text{O}$), Ammonium acetate ($\text{NH}_4\text{CH}_3\text{CO}_2$), p-Toluene sulfonic acid (PTSA) ($\text{CH}_3\text{C}_6\text{H}_4\text{SO}_3\text{H}$), 3,5-Dinitrobenzoyl chloride ($\text{C}_3\text{H}_7\text{ClN}_2\text{O}_5$), N,N-Dimethylacetamide (DMAc) ($\text{CH}_3\text{CN}(\text{CH}_3)_2$), Triethylamine ($\text{N}(\text{CH}_2\text{CH}_3)_3$), Azelaic acid ($\text{HOOC}(\text{CH}_2)_7\text{COOH}$), Calcium chloride (CaCl_2), Triphenyl phosphate ($\text{OP}(\text{OC}_6\text{H}_5)_3$), N-Methyl-2-pyrrolidone ($\text{C}_5\text{H}_9\text{NO}$), Potassium permanganate (KMnO_4), Tetrahydrofuran (THF) ($(\text{CH}_2)_4\text{O}$), Chitosan, 4-Dimethylaminopyridine ($(\text{CH}_3)_2\text{NC}_5\text{H}_4\text{N}$), N,N'-Dicyclohexyl carbodiimide (DCC) were prepared by Sigma-Aldrich Chemical Co (USA) and Merck Chemical Co (Germany).

Devices and Equipment

^1H -NMR and ^{13}C -NMR spectra were recorded on a Bruker avance 300 MHz instrument (Germany). Fourier transform infrared (FTIR) spectra were recorded on Galaxy series FTIR 5000 spectrophotometer (England). Spectra of solids were performed using KBr pellets. Vibrational transition frequencies are reported in wave number and in the region of 400-4000 cm^{-1} . Band intensities are assigned as weak (w), medium (m), shoulder (sh), strong (s) and broad (br). Thermal Gravimetric Analysis (TGA) data of polymers were taken on a Mettler TA4000 System under N_2 atmosphere at a rate of 10 $^\circ\text{C}/\text{min}$. The progress of

the reaction was monitored by thin layer chromatography using a 60W UV-lamp. The X-ray diffraction (XRD) patterns were recorded using a Philips X-pert diffractometer (CuK α radiation, λ 0.15405 nm). A Memert 400 vacuum oven was used to drying samples and preparing nanocomposite films. UV-vis electron spectra were recorded using a Specord S600 single-beam spectrometer and a Perkinelmer Lambda 15 double-beam spectrometer. Scanning electron microscope (SEM) images were obtained using a KYKY-EM3200 device.

Methods

Monomer Synthesis

Synthetic diamine (12) contains a triazine ring as central core was prepared from starting material 4-nitrobenzoic acid (1) according to a seven steps reasonable synthetic route as describing in following.

Preparation of 4-nitrobenzoyl chloride (2)

4-Nitrobenzoic acid (5.0 g, 30 mmol) (1), thionyl chloride (20 ml, 00 mol) were added into a 50 ml round-bottom flask equipped with a magnetic stirrer and reaction mixture was refluxed about 6 hours. Hydrochloric acid and sulfur dioxide gases bubbled out of the solution and then thionyl chloride was separated by vacuum distillation and a precipitate was formed and 4-nitro benzoyl chloride (2) was separated.....

FT-IR (KBr): $\bar{\nu}$ = 1344, 1520, 1686, 3100, 3400.

Preparation of ethyl-4-nitrobenzoate (3)

Ethyl-4-nitrobenzoate (3) was prepared by a simple esterification process. 4-Nitrobenzoyl chloride (2) (3.0 g, 16.2 mmol), 30 ml of absolute ethanol and (1.6 ml, 19.8 mmol) of pyridine were poured into a 100 ml round-bottom flask equipped with a magnetic stirrer and refluxed for 24 hours at 78 °C. Then the solvent was evaporated and the resulting precipitate was washed with distilled water. The yield was 92%.

FT-IR(KBr): $\bar{\nu}$ = 3119, 2991, 2906, 1718, 1525, 1350, 1278, 1103, 1012, 871, 841, 787, 713, 505 cm⁻¹.

2.3.1.3. Preparation of 4-nitrobenzohydrazide (4)

4-nitrobenzohydrazide was prepared by using following procedure. (1.50 g, 7.70 mmol) of ethyl-4-nitrobenzoate (3) and 20 ml of 99% ethanol and 2 ml of 99% monohydrate hydrazine were added and mixture refluxed for 24 hours at 78°C. The color of the mixture changed from white to yellow and then the reaction mixture was placed in an ice water bath and distilled water was added slowly to obtain 4-nitrobenzohydrazide (4). Then the resulting precipitates were filtered and a yield of 89% was obtained.

FT-IR (KBr): $\bar{\nu}$ = 3331, 3281, 3111, 3072, 1730, 1645, 1620, 1597, 1520, 1344, 1099, 1057, 937, 864, 731, 686, 609, 505, 459, 416 cm⁻¹.

Preparation of 3-(4-nitrophenyl) 5,6-diphenyl-1,2,4-triazine (6)

In this step, (0.09 g, 0.50 mmol) of 4-nitrobenzhydrazide and (0.10 g, 0.50 mmol) of benzyl were mixed with (0.21 g, 3 mmol) of ammonium acetate and 20 mol% of p-toluene sulfonic acid in a fine porcelain mortar and the homogenized mixture mixed in a test tube for 4 to 6 hours. It was placed in an oil bath with a temperature of 140°C. After the completion of the reaction, the contents of the test tube cooled to room temperature and washed with 10 ml of 99% ethanol for 1 hour at room temperature,

then the sediments were filtered and washed with hot ethanol and hot water and the product 3-(4-nitrophenyl)-5,6-diphenyl-1,2,4-triazine with an efficiency of 83%.

FT-IR (KBr): $\bar{\nu}$ = 3107, 3057, 1651, 1597, 1514, 1444, 1390, 1338, 1107, 1074, 1012, 864, 765, 698, 594 cm^{-1} .

Preparation of 3-(4-aminophenyl)-5,6-diphenyl 1, 2, 4-triazine (7)

(0.50 g, 1.41 mmol) of synthetic compound (6) along with 20 mL of 99% ethanol and (0.02 g) of Pd/C catalyst were poured into a 50-mL flask equipped with a magnetic stirrer and mixture was refluxed. Then 2 ml of 99% monohydrate hydrazine was added drop by drop and after 4 hours the mixture filtered to remove palladium. After distilled water was added to mixture until diamine 7 precipitated, filtered and washed with ethanol (yield of 90%).

FT-IR (KBr): $\bar{\nu}$ = 3379, 1616, 1494, 1446, 1394, 1307, 1172, 1080, 823, 773, 700, 530 cm^{-1} .

$^1\text{H-NMR}$ (300MHz, DMSO- d_6): δ = 8.26 (d, J = 8.40 Hz, 2H), 7.7-58.39 (m, 10H), 6.73 (d, J = 8.70 Hz, 2H), 5.92 (s, 2H).

$^{13}\text{C-NMR}$ (75 MHz, DMSO- d_6): δ = 161.4, 155.3, 154.3, 152.9, 136.4, 136.3, 130.7, 130.0, 129.6, 128.7, 121.3, 114.1 ppm.

Preparation 3[4-(3,5-dinitrobenzamide) phenyl] 5,6-diphenyl-1,2,4-triazine (9)

Into a 50 mL round bottom flask equipped with a magnetic stirrer (flask A), (0.65g, 2 mmol) of triazine (7), (0.69 g, 3 mmol) of 3,5-dinitrobenzoyl chloride (8), (20 ml, 215.1 mmol) of N, N-dimethylacetamide (DMAc) as solvent and 1 ml of triethyl amine as base was added and the mixture stirred at room temperature for 24 hours. Then distilled water was added to mixture to form sediment. Next, the precipitate was filtered, washed with hot distilled water and 96% ethanol respectively and dried under vacuum to form compound (yield of 82%)(9).

FT-IR (KBr): $\bar{\nu}$ = 3379, 1616, 1494, 1446, 1394, 1307, 1172, 1080, 823, 773, 700, 530 cm^{-1} .

$^1\text{H-NMR}$ (300 MHz, DMSO- d_6): δ = 11.06 (s, 1H), 9.18 (s, 2H), 8.97 (s, 1H), 8.53 (d, J = 7.65 Hz, 2H), 8.04 (d, J = 7.68 Hz, 2H), 7.7- 60.42(m, 10H).

Preparation 3-[4-(3,5-diaminobenzamide) phenyl] 5,6-diphenyl-1,2,4-triazine (10)

Into a 50 ml round bottom flask equipped with a magnetic stirrer, (0.50 g, 1 mmol) of synthetic compound (9), 20 ml of 99% ethanol, 0.05 grams of Pd/C catalyst were added. Then 2 ml of 99% monohydrate hydrazine gradually added until diamine (10) formed. After the completion of the reaction, palladium residues filtered and distilled water added to the solution under the filter to obtain a yellow precipitate (yield of 88%).

FT-IR (KBr): $\bar{\nu}$ = 3551, 3464, 3412, 3232, 2918, 2850, 1635, 1616, 1527, 1491, 1442, 1396, 1361, 1317, 1249, 1176, 823, 767, 696, 621, 478, 403 cm^{-1} .

$^1\text{H-NMR}$ (300 MHz, DMSO- d_6): δ = 10.26(s, 1H), 8.52(d, J = 6.00, 2H), 8.03(d, J = 9.00, 2H), 7.42-7.46 (m, 10H), 6.36 (s, 2H), 6.04 (s, 1H), 4.95 (s, 4H).

$^{13}\text{C-NMR}$ (75 MHz, DMSO- d_6): δ = 168.1, 160.1, 155.8, 155.6, 149.6, 143.4, 137.0, 136.1, 136.0, 131.0, 130.1, 129.7, 129.2, 128.9, 128.8, 120.4, 102.9 ppm.

Polymer Synthesis

Preparation of polyamide containing triazine ring (12)

Polyamide (12) was prepared by using following procedure. Into a 50 ml round bottom flask equipped with a magnetic stirrer, (0.13 g, 0.30 mmol) of diamine (10), (0.05 g, 0.30 mmol) of azelaic acid (11), (0.10g, 0.90 mmol) of calcium chloride, (0.80 mL, 3.05 mmol) of triphenyl phosphite and (1.50 mL, 15.43 mmol) of N-methyl-2-pyrrolidone (NMP) were added and the reaction mixture refluxed at 120°C for 8 hours. The reaction mixture was cooled to room temperature and then 25 ml of methanol added to the mixture to form polyamide (12), washed several times with hot methanol and kept overnight at room temperature and 12 hours at 80-90°C under vacuum oven and yield of polyamide (12) was obtained 87%.

FT-IR (KBr): $\bar{\nu}$ = 3506, 3435, 3335, 1674, 1602, 1529, 1444, 1394, 1319, 1244, 1174, 1076, 871, 821, 765, 727, 694, 590, 526, 445, 416 cm^{-1} .

$^1\text{H-NMR}$ (300 MHz, DMSO- d_6): δ = 10.59 (s, 1H), 10.05 (s, 2H), 8.53 (d, J = 9.00, 2H), 8.18 (s, 1H), 8.01 (d, J = 9.00, 2H), 7.8 (s, 2H), 7.7-6.042 (m, 10H), 2.3 (s, 4H), 1.60 (s, 4H), 1.3 (s, 8H).

Preparation of Polyamide/Nanocomposite [16, 17]

Preparation of Graphene Oxide Nanoparticles [13]

First, (1.50 g) of graphite was added to a mixture containing 90 ml of concentrated sulfuric acid and 10 ml of concentrated phosphoric acid, then (6.00 g) of potassium permanganate was slowly added to the reaction mixture and heated for 12 hours at 50°C. Some ice with hydrogen peroxide was added to the reaction container and the resulting mixture was centrifuged. Finally, the precipitate was washed with hydrochloric acid, water and ethanol and the obtained product was dried [22].

FT-IR (KBr): $\bar{\nu}$ = 3396, 1734, 1622, 1153, 1055, 596, 434 cm^{-1} .

Preparation of Graphene Oxide Nanoparticles Modified With Chitosan (15)

(100 mg) of graphene oxide (13) was poured into 250 ml of tetrahydrofuran and placed in an ultrasonic bath for one hour. Then (0.34 mmol) chitosan (14), (100 mg, 1 mmol) 4-dimethyl amino pyridine and (1.00 g, 5 mmol) N, N-dicyclohexyl carbodi-imide were added to mixture. Then, it was stirred by a magnetic stirrer for 6 hours and the black solid was collected, washed with tetrahydrofuran and dried at vacuum oven [23].

FT-IR (KBr): $\bar{\nu}$ = 3437, 2924, 2879, 1645, 1562, 1437, 1394, 1329, 1211, 1095, 615, 513 cm^{-1} .

Preparation Of 3% And 5% Polyamide/Nanocomposite Films [16, 17]

Nanocomposites of 3 and 5% by weight percent were prepared through the solution method. First, poured (0.25 g) of polyamide (12) as a polymer matrix in two test tubes and dissolve it in 15 ml of N, N-dimethyl acetamide and mixed for 6 hours to form a completely uniform solution. Then, in two separate test tubes, two different amounts of graphene oxide modified with chitosan (15) (0.007 g) and (0.013 g) and (15 ml, 186 mmol) of N, N-dimethyl acetamide was added and mixed for 2 hours. The samples were placed in an ultrasonic bath at room temperature to disperse homogenously the chitosan-modified graphene oxide into solvent. Then, each of the mixtures containing graphene oxide nanoparticles was added to the polymer solutions while stirring in an ultrasonic bath, and the mixtures were stirred for one hour at 40°C under ultrasonic waves. In the next step, the mixtures were transferred into the petri dish and placed into a vacuum oven at 90°C for 12 hours until the solvent evaporates and nanocomposite films were formed.

FT-IR (KBr) (16): $\bar{\nu}$ = 3284, 3246, 3088, 2926, 2854, 1755, 1653, 1529, 1442, 1392, 1321, 1244, 1176, 1076, 1008, 933, 854, 823,

765, 692, 588, 526 cm⁻¹.

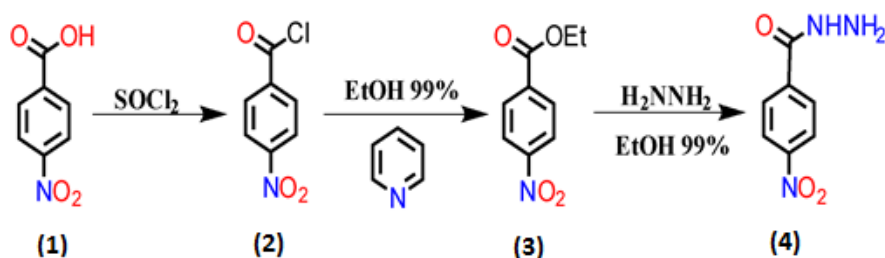
FT-IR (KBr) (17): $\bar{\nu}$ = 3269, 3065, 2928, 2856, 1755, 1676, 1628, 1601, 1531, 1496, 1442, 1394, 1317, 1248, 1176, 1076, 1012, 933, 856, 821, 765, 694, 590, 528 cm⁻¹.

Results and Discussion

The new synthetic diamine (10) contains a triazine ring as main core, which was prepared from 4-nitrobenzoic acid (1) as a starting material by using a seven-steps synthetic route. The special properties of triazine rings have many applications for these compounds in the fields of agriculture, medicine and pharmaceuticals, such as blood pressure regulation, neuron protection, anticancer, antiviral, antifungal properties. Solid-phase reaction (solvent-free) is one of the new methods used for the synthesis of triazine rings [24, 25].

Studying the Structure of Monomers

Final synthetic compound (10) as a diamine monomer containing a triazine ring that used to prepare polyamide (12) was initially prepared from the reaction of 4-nitrobenzoic acid (1) in seven consecutive reaction steps (Scheme 1). First 4-nitro benzoyl hydrazide (4) prepared by a three steps reaction by reaction of 4-nitrobenzoic acid (1) with thionyl chloride at refluxing solution. Resulting 4-nitrobenzoyl chloride (2) converted to its ethyl ester by reaction with ethanol 99% in presence of pyridine as base and then resulting ethyl ester (3) was converted to benzoyl hydrazide (4) by using a mixture of hydrazine and ethanol 99% (Scheme 1).



Scheme 1: preparation of 4-nitro Benz hydrazide (4)

In the infrared spectrum of compound [4], the asymmetric and symmetric stretching absorptions of the nitro group (NO₂) in the areas 1520 and 1344 cm⁻¹ and the absorption of the carbonyl group in the region 1686-1 cm and also absorptions related to -NH groups and -NH₂ in the regions 3100-3400 cm⁻¹ confirmed formation of the desired structure (Figure 1).

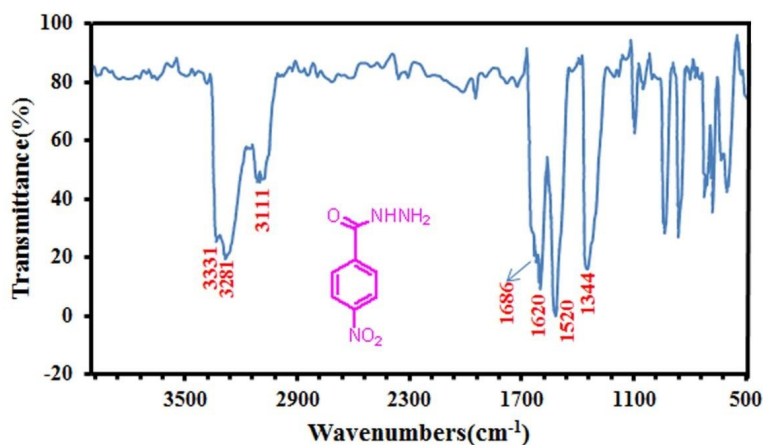
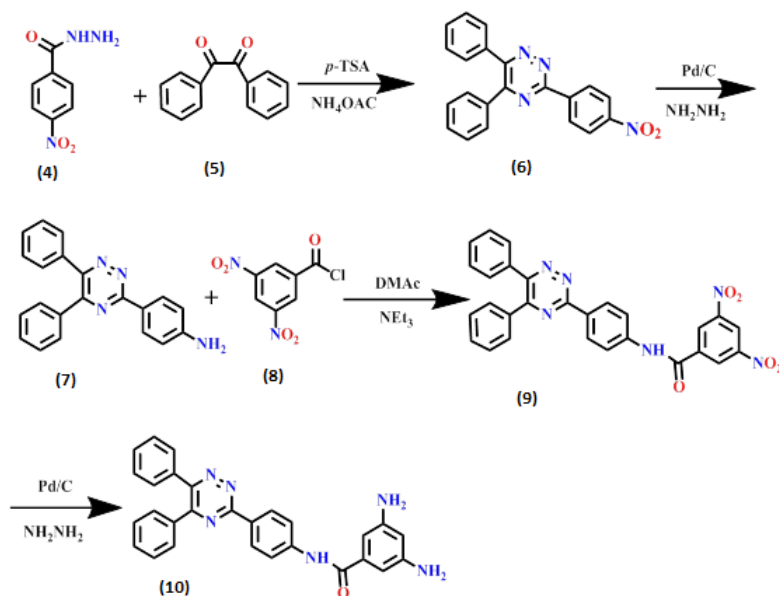


Figure 1: Infrared spectrum of 4-nitro Benz hydrazide (4)

To preparation of diamine (10), first hydrazide (4) was condensed along with benzyl (5) by using 4-tolune sulfonic acid in the presence of ammonium acetate, then nitro compound (6) was reduced by Pd/C in hydrazine and amine (7) was converted to dinitro benzoyl amide derivative (9) by reaction with 3,5-dinitrobenzoyl chloride (8). Finally, new synthetic diamine (10) was prepare by reduction of dinitro benzoyl amide derivative (9) by using Pd/C in hydrazine as reducing agent (Scheme 2).



Scheme 2: Synthetic route for preparation of diamine (10)

The structure of compound (6) was confirmed through the infrared spectrum (Figure2). Removal of carbonyl amide adsorption in the region 1686 cm^{-1} and absorptions related to $-\text{NH}$ and $-\text{NH}_2$ groups between $3400\text{--}3100\text{ cm}^{-1}$ and also formation of $\text{C}=\text{N}$ peak at 1651 cm^{-1} confirms the construction of compound (6).

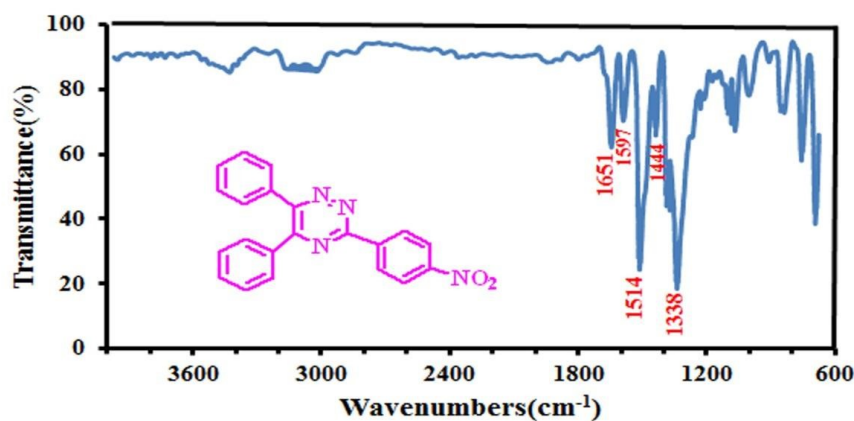


Figure 2: Infrared spectrum of 3-[4-nitrophenyl] 5,6-diphenyl-1,2,4-triazine (6)

Also, in the ^1H -NMR spectrum absorption in the region of 8.76 ppm showed a double peak related to aromatic hydrogens in the ortho position relative to the nitro group, which confirms the structure of compound (6) (Figure 6).

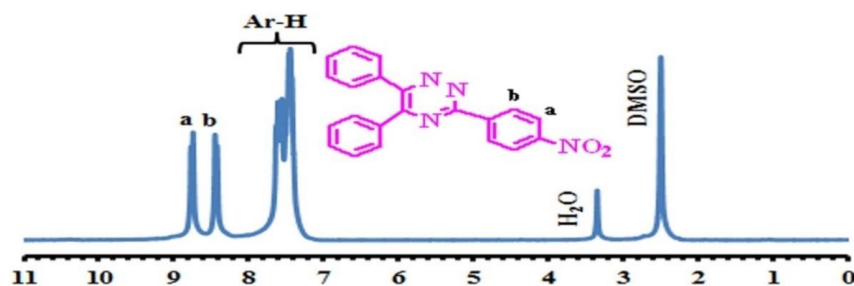


Figure 3: ^1H -NMR spectrum 3-[4-nitrophenyl] 5,6-diphenyl-1,2,4-triazine [6]

In the ^{13}C -NMR spectrum of compound (7), the peak in the region of 161.43 ppm corresponds to the carbon attached to the two nitrogen atoms of the triazine ring (a) and the peak in the region of 152.98 ppm corresponds to the carbon attached to the amine group (c) (Figure 4).

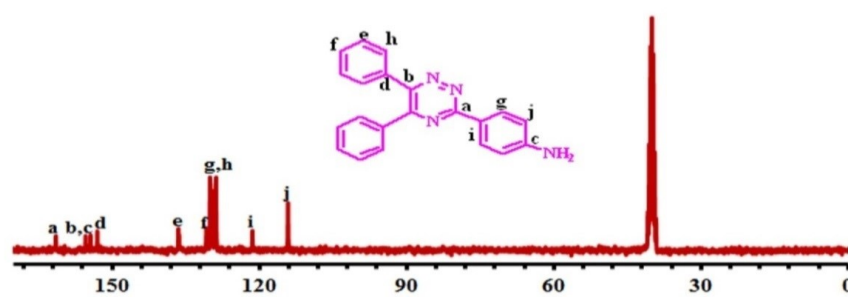


Figure 4: ^{13}C -NMR spectrum of 3-[4-aminophenyl]5,6-diphenyl-1,2,4-triazine [7]

The reaction of 3,5-dinitrobenzoyl chloride (8) with compound (7) prepared 3-[4-(3,5-dinitrobenzamide) phenyl]5,6-diphenyl-1,2,4-triazine (9). In the infrared spectrum of this compound (Figure 5), absorptions related to nitro groups are shown in the regions of 1344 and 1543 cm^{-1} and absorption related to the carbonyl of the amide group shown in 1683 cm^{-1} .

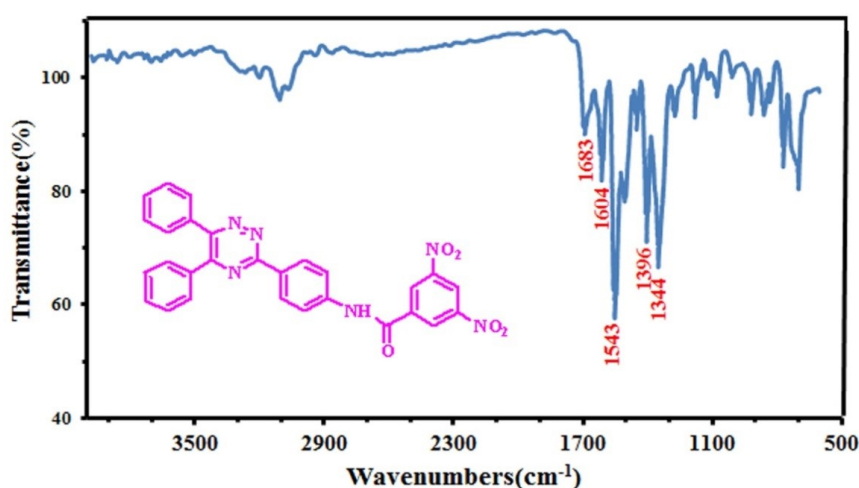


Figure 5: Infrared spectrum of 3-[4-(3,5-dinitrobenzamide) phenyl]5,6-diphenyl-1,2,4-triazine (9)

In the ^1H -NMR spectrum of the above compound, a single peak related to the amide group appears in the region of 11.06 ppm,

as well as two single peaks related to the hydrogens between the two nitro groups at aromatic ring appeared at 8.97 ppm (Figure 6).

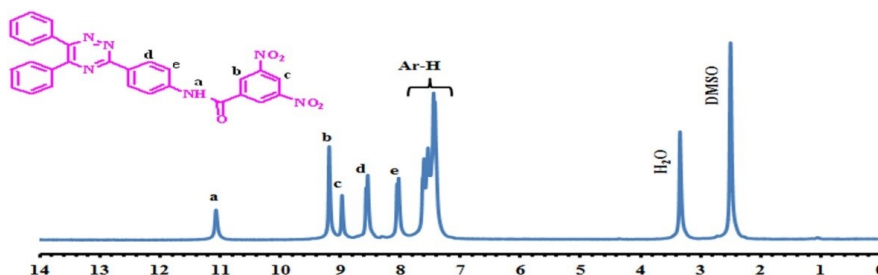


Figure 6: ^1H -NMR spectrum of 3-[4-(3,5-dinitrobenzamide)phenyl]5,6-diphenyl-1,2,4-triazine (9)

The dinitro compound (9) was reduced to diamine (10) by using palladium on carbon catalyst in the presence of hydrazine. Chemical structure of diamine (10) was confirmed through FT-IR, ^1H -NMR and ^{13}C -NMR spectroscopic data. The infrared spectrum of diamine (10) shows strong peaks between 3553–3412 cm^{-1} , which indicates the presence of amino groups. Also, the complete removal of the dinitro absorptions and the appearance of the peaks related to the amine groups show the complete conversion of the dinitro compound to diamine.

In the ^1H -NMR spectrum of diamine (10), a single peak at 6.04 ppm corresponds to the hydrogen between the two amine groups, and a single peak at 4.95 ppm represents the hydrogens of the two amine groups. Other aromatic hydrogens are shown as Ar-H in Figure 7.

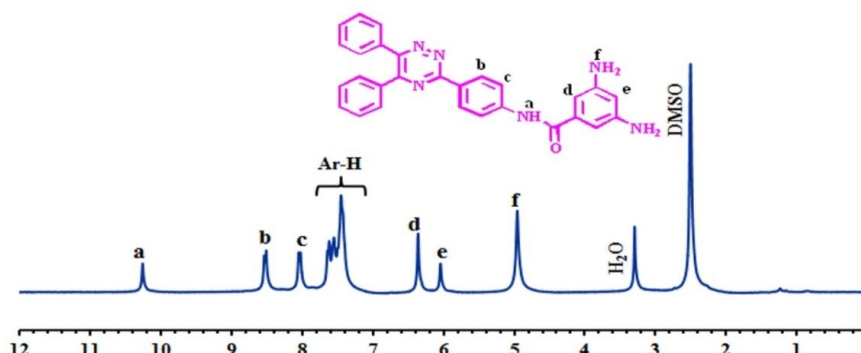


Figure 7: ^1H -NMR spectrum of 3-[4-(3,5-diaminobenzamide)phenyl]5,6-diphenyl-1,2,4-triazine (10)

In the ^{13}C -NMR spectrum of diamine (10), the peak at 168.07 ppm corresponds to the carbonyl group, shown by (a), and the peaks at 155.68–160.79 ppm correspond to the carbons of the triazine ring shown by (b, c and d). The aromatic ring carbons appear at 128.01–131.86 ppm, as well as the carbon between the two amino groups at 120.41 ppm (Figure 8).

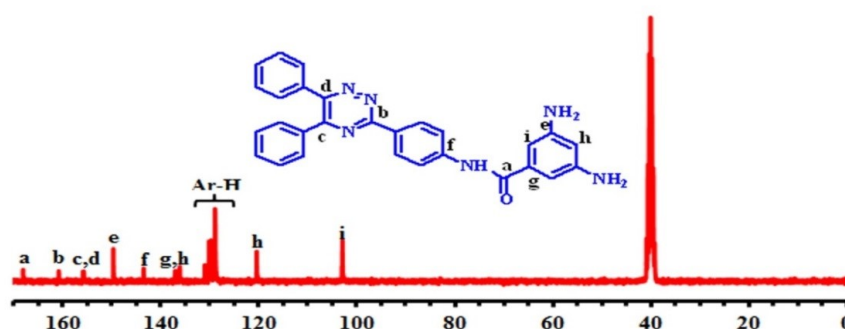
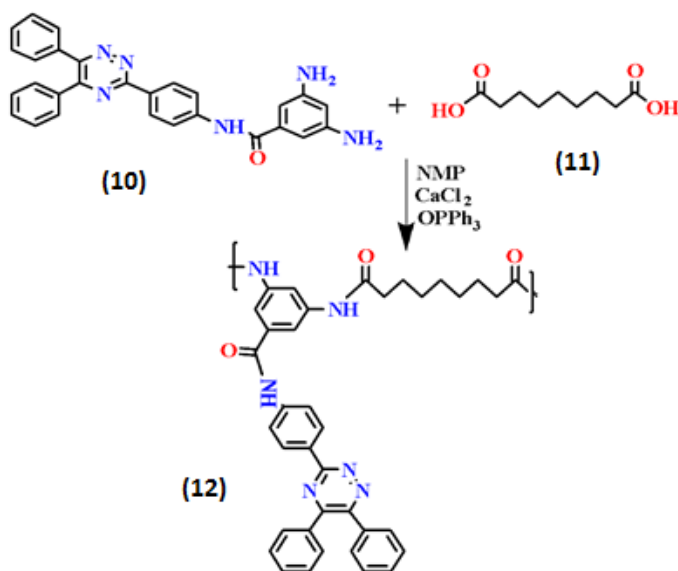


Figure 8: ^{13}C -NMR spectrum of 3-[4-(3,5-diaminobenzamide)phenyl]5,6-diphenyl-1,2,4-triazine (10)

Studying the structure of polyamide (12)

Polyamide (12) was prepared by the Yamazaki method. In this method, amino acids or aromatic diamines and dicarboxylic acids are reacted in the presence of an aryl phosphite and an organic base such pyridine in N-methyl-2-pyrrolidone as solvent containing calcium chloride to produce high molecular weight polymer. The reaction between diamine (10) and azelaic acid (11) was carried out in N, N-dimethyl acetamide as solvent, in the presence of pyridine and triphenyl phosphite resulted polyamide (12) (scheme3).



Scheme 3: preparation of polyamide (12)

The structure and properties of polyamide (12) were investigated by infrared spectroscopy (FT-IR), nuclear magnetic resonance (¹H-NMR), X-ray diffraction (XRD), ultraviolet-visible spectroscopy (UV-vis), thermo gravimetric analysis (TGA), and differential thermo gravimetry (DTG) techniques.

In the infrared spectrum of polyamide (12), the main absorptions such as 3335 cm⁻¹ (stretching vibrations of the amide N-H group), 3061 cm⁻¹ (aromatic C-H stretching vibrations), 1674 cm⁻¹ (stretching vibrations of the carbonyl group), 1394 cm⁻¹ (tensile vibrations -CH₂) confirms formation of the resulting polyamide figure 9.

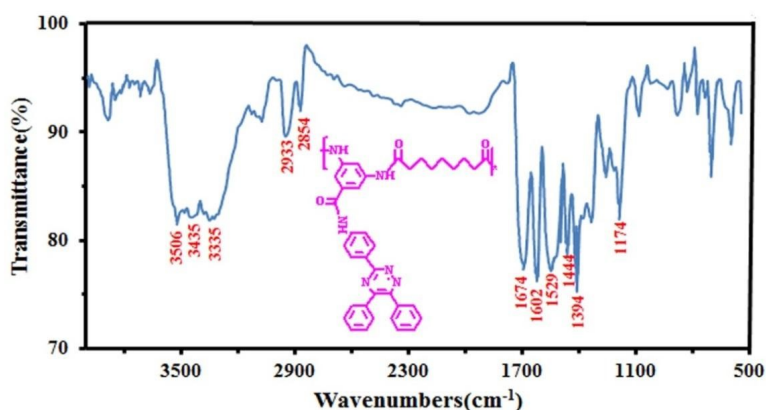


Figure 9: Infrared spectrum of polyamide (12)

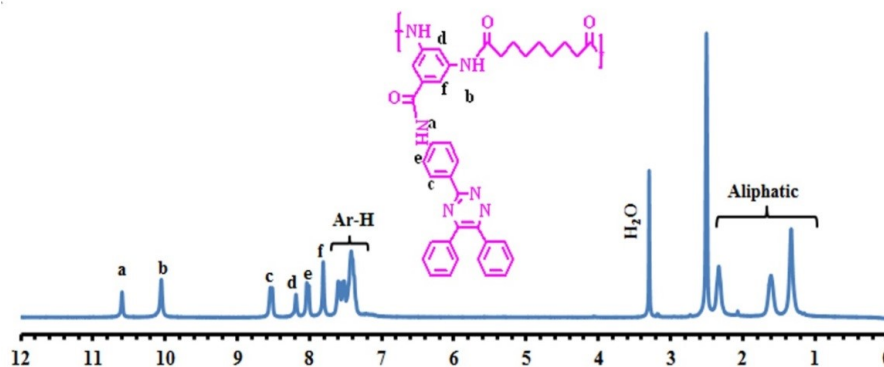


Figure 10: ^1H -NMR spectrum of polyamide (12)

Preparation of Graphene Oxide Nanoparticles Functionalized With Chitosan

In the aim of preparation of graphene oxide nanoparticles first natural graphite was oxidized by the Hammer method and then functionalized using chitosan. The $-\text{NH}_2$ groups in chitosan can react with oxygen-containing functional groups on the surface of graphene oxide and bind to its surface. The structure of the functionalized graphene oxide was confirmed by infrared spectroscopy via the absorption at 3396 cm^{-1} related to the stretching vibrations of the hydroxyl group and the absorption at 1734 cm^{-1} related to the stretching vibrations of the carbonyl group. Also, the absorption at 1622 cm^{-1} related to the aromatic rings and the absorption at 1153 cm^{-1} related to the stretching vibrations of the C-O bond [26] (figure 11 Part A).

Following standard procedure as wish to formation of graphene oxide functionalized by chitosan, dicyclohexyl carbimide (DC-C) was used to activated the carboxyl group into graphene oxide and also 4-dimethyl amino pyridine (DMAP) was used to activated the nucleophilic strength of functional groups into chitosan. It cased the formation of a new covalent bond with chitosan. In the infrared spectrum of functionalized graphene oxide, carbonyl amide absorption appeared at a lower frequency expected than graphene oxide (1645 cm^{-1}) which indicates the creation of amide linkage between chitosan groups (NH_2) and carboxyl groups of graphene oxide. Also, a peak at 1095 cm^{-1} corresponding to C-O and broad absorption in the region of 3437 cm^{-1} is related to amide groups (Figure 11b).

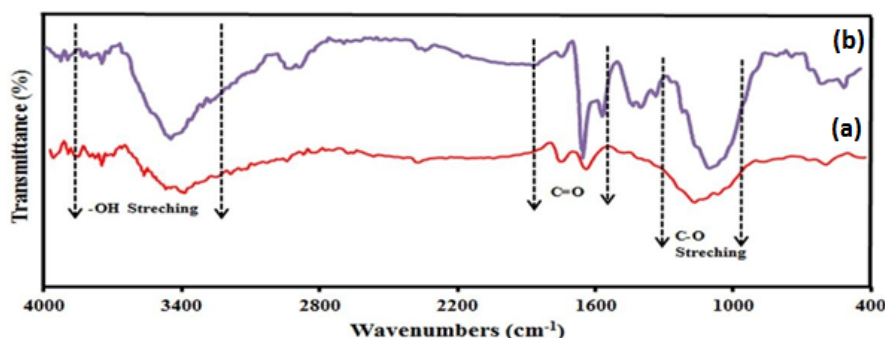


Figure 11: Infrared spectrum. a) graphene oxide. b) graphene oxide functionalized with chitosan

Study of Polyamide And Nanocomposites Films Behaviors

The structure, optical and thermal behaviors of the resulting polyamide films and nanocomposites were investigated and characterized using X-ray diffraction (XRD), ultraviolet-visible spectroscopy (UV-vis), scanning electron microscopy (SEM), thermogravimetric analysis (TGA) and differential thermal gravity (DTG).

X-ray Diffraction (XRD)

X-ray diffraction of graphene oxide functionalized by chitosan & pristine polyamide (12), related nanocomposite at 3 and 5% weight percent & that prepared by using the convenient amounts of graphene oxide functionalized by chitosan, are shown in figure (1-10). In the case of graphene oxide functionalized by chitosan, peaks at the regions of 21.53° and $2\theta = 19.85^\circ$ are characteristic peaks of graphene oxide functionalized with chitosan. The position and intensity of the peaks into nanocomposites as well as the removal nanoparticles peaks show graphene oxide nanoparticles functionalized with chitosan well covered and dispersed into polymer matrix [27].

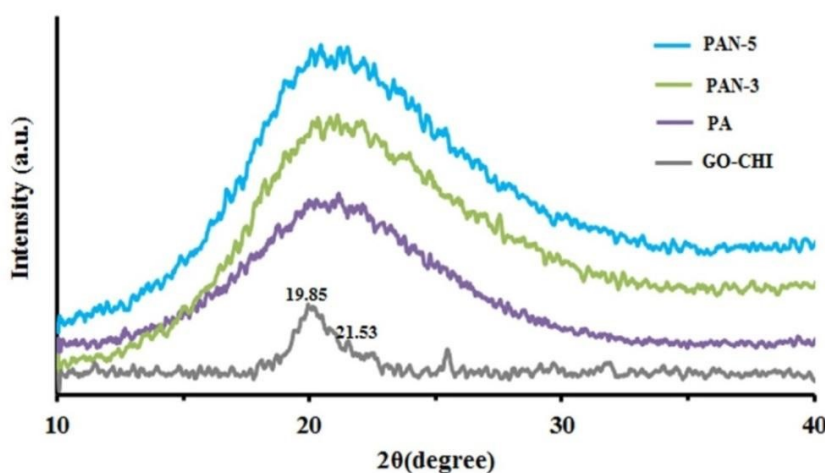


Figure 12: X-ray diffraction of nanoparticles, polymers, and nanocomposites

Thermal Gravimetric Analysis (TGA) and Differential Thermo Gravimetric Analysis (DTG) Of Polyamide (12) and Prepared Nanocomposites

The thermal decomposition of polyamide (12) and nanocomposites of 3% (16) and 5% (17) have been investigated by using the TGA technique (Figure 12). In this method, the amounts of sample mass reduction are measured as a function of temperature with time. The lower of weight losses of the samples show the higher of thermal stability. Decomposition temperature of 5% of weight loss (T5) of polyamide appear at 158°C and decomposition temperature of 10% of weight loss (T10) appear at 211°C . The char yields related to polyamide (12) at 800°C , it around 21%. On the other hand, 5% of weight loss (T5) of 3% (PAN-3) showed at 207°C and also 10% of weight loss (T5) of 3% (PAN-3) showed at 292°C , which has increased notably in compared to the polyamide pristine. Also, the char yields related to 3% (PAN-3) at 800°C is around 31%, so showed a massive increase in compared to the polyamide pristine. Data related to 5% nanocomposite (PAN-5), showed another increase in thermal stability compared to the polyamide pristine. The decomposition temperature of 5% of weight loss (T5) at 370°C and the decomposition temperature of 10% of weight losses (T10) at 411°C showed greater increase at resulting data compare to polyamide pristine and also 3% (PAN-5). Notably the char yields related to 5% (PAN-5) around 38% at 800°C was another sign to higher thermal stability of resulting nanocomposite.

As we seen, by the increase of nanoparticles into the polymer matrix, its thermal stability increased and this increase can be due to the fact that modified graphene nanoparticles causes the high thermal stability by nature and its modification by chitosan has caused it to interact well with the polymer matrix in nanocomposites. By creating a hydrogen bond with the polymer matrix, the thermal stability of the nanocomposite has heightened.

Oxygen limitation index (LOI), is the minimum amount of oxygen in a mixture of oxygen and nitrogen that a polymer sample needs to start burning and catch fire. The index of oxygen limitation can be based on the equation of van Krieuilen-Haftezer (Relation 1) and estimated by using char yields of polymers and nanocomposites.

Relationship (1) $LOI = 5.17 + 0.4 CR$ CR: Char yield

In general, the polymer compounds whose LOI value is more than 26 are known as flame retardant compounds and shown fire resistance. This value (LOI) calculated for polyamide (12) and nanocomposites (PAN-3, PAN-5) and shown in table (1).

Table 1: Thermal Properties of Polyamide and Prepared Nanocomposites.

Oxygen limitation index	Char Yield (%)	Maximum decomposition temperature (C°)	Decomposition temperature of 10% by weight (C°)	Decomposition temperature of 5% by weight (C°)	samples
25.9	21	390	211	158	Polyamide (PA)
29.9	31	389	294	207	Nano composite 3% (PAN-3)
32.7	38	394	411	370	5% nano composite (PAN-5)

According to results table (1), the decomposition temperatures for 5% and 10% weight percent in nanocomposites have favorably increased in compared to pristine polyamide and show higher thermal stability. Also, according to the values related to the oxygen limitation index, resulting nanocomposites show better flame retardancy in compare to pristine polyamide.

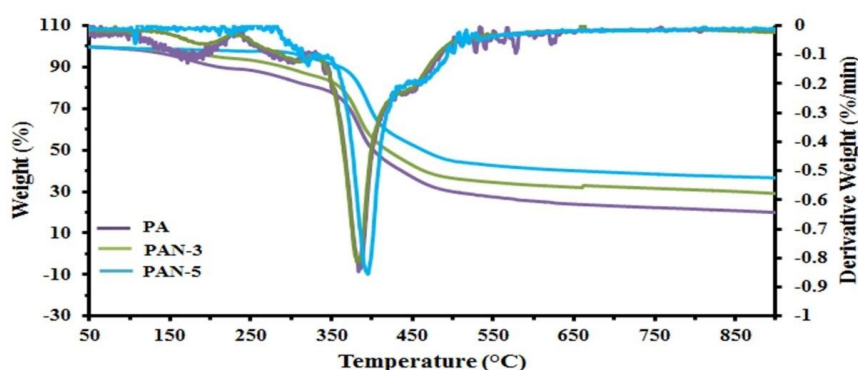


Figure 13: Thermal gravimetric analysis (TGA) and differential thermo gravimetric test (DTG) of prepared polyamide and their nanocomposites.

Differential thermogravimetric (DTG) analysis data also shown in figure 13. In this method, the ratio of mass change to temperature or time change is plotted. By means of this curve, the resulting maximum decomposition temperature (TMax) related to polyamide and their nanocomposites. are about 390oC for pure polymer and about 389oC and 394oC for 3% and 5% nanocomposites, respectively (Table 1).

Scanning Electron Microscope (SEM) Images

Scanning electron microscope (SEM) characterize the quality surface of nanoparticles and finding useful information about the shape and size of nanoparticles dispersed into polyamide matrix. According to figure 14, there are holes in the structure of graphene oxide that are uniformed and connected, and the dark streaks in it are related to the structure of graphite. In the case of graphene oxide functionalized by chitosan, it is observed that the rough surface is covered with shiny and hard polar groups, which shows that chitosan interacts well with graphene oxide layers [28].

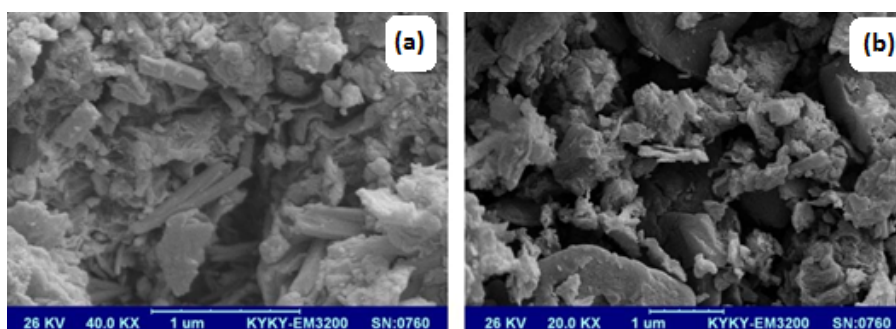


Figure 14: Scanning electron microscope images a) graphene oxide b) graphene oxide functionalized with chitosan

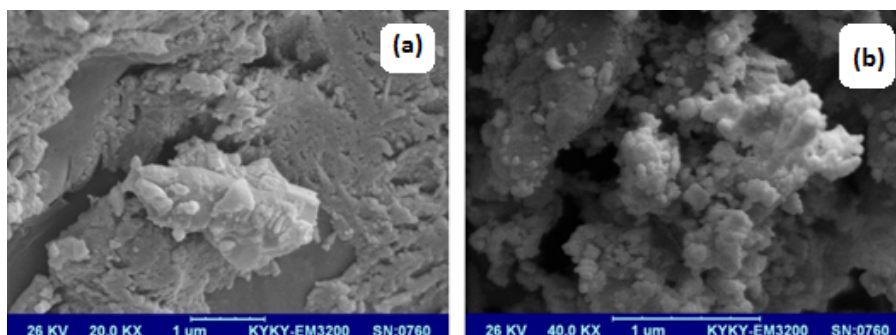


Figure15: Scanning Electron Microscope Images. a)3% Nano Composite Film. b) 5% Nano Composite Film

Figure 15 shows the scanning electron microscope images of 3% and 5% nanocomposite films. As seen in the pictures, the nanoparticles are well dispersed in the polymer matrix.

Ultraviolet-Visible Spectroscopy (UV-vis)

The optical behavior of polyamide (12) and 3 and 5% nanocomposites (PAN-3 and PAN- 5) were studied by ultraviolet-visible spectroscopy. Polyamide solution in N, N-dimethyl formamide has the highest absorption in the region of $\lambda_{\text{max}} = 320 \text{ nm}$ that it is related to $\pi-\pi^*$ transitions. In the case of nanocomposites, this absorption has moved to the 315 nm region. Examining these spectra show that graphene oxide nanoparticles functionalized by chitosan, interlayered between polymer chains caused to a visible increasing energy gap between HOMO and LUMO orbitals, and show a blue transition, which indicates strong interaction between nanoparticle and polyamide (Figure16).

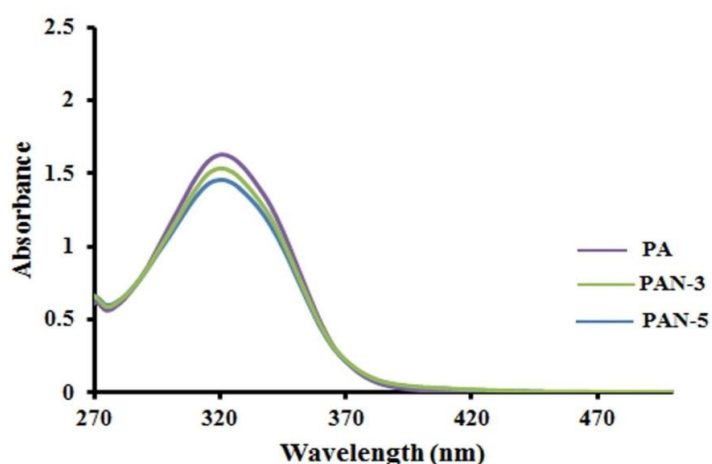


Figure 16: Ultraviolet-Visible Spectroscopy of Polyamide (12) and PAN-3 and PAN- 5

Conclusion

In this project, a new synthetic diamine containing a triazine ring as a central core (10) was successfully prepared and its structure was confirmed by infrared spectroscopy, hydrogen nuclear magnetic resonance, and carbon nuclear magnetic resonance. In the following, the desired polyamide (12) was prepared by direct polycondensation reaction of resulting diamide (12) and azalaic acid (11) through the modified Yamazaki method. Polyamide and nanocomposites films containing 3 and 5% weight percent of graphene oxide modified with chitosan were prepared through the solution and structure, properties of them were study by using FTIR infrared spectroscopy, HNMR techniques, X-ray diffraction (XRD), Energy dispersive X-ray spectroscopy (EDX), scanning electron microscopy (SEM), Thermo gravimetric analysis (TGA), differential thermal gravimetry (DTG) and UV-Vis spectroscopy. Due to the fact the prepared polyamide contains a triazine ring and its nanocomposites can be considered as promising materials in different industries such as pharmaceutical, agricultural and water treatment industries.

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