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Surface Modification of Polypropylene by Grafting Films for Active Food Packaging

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Abstract

Polypropylene (PP) films were activated by corona discharge and then successfully chemically grafted with acrylonitrile monomer (AN). The grafted PP films were subsequently hydrolyzed in alkaline medium to introduce carboxyl and amide groups. The grafted PP films were characterized by infrared spectroscopy (FTIR), elemental analysis, thermal analysis (TGA), mechanical properties, x-ray diffraction analysis (XRD), density measurement, scanning electron microscopy (SEM), swelling characteristics, and permeability properties of oxygen and water vapor (OTR and WVTR). The hydrolyzed grafted PP was immersed in an acidic solution containing both chitosan and chitosan/thiourea. The chitosan and chitosan/thiouera immobilized grafted films were characterized by FTIR, XRD, SEM, swelling characteristics, and permeability properties of oxygen and water vapor. These films' were discovered to have improved antifungal and antibacterial properties over pristine PP film. A trial was conducted to illustrate the feasibility of using these modified films for active food packaging.

1. Introduction

Most of the polymers present in commerce especially polyolefin polymer have a hydrophobic and low activation surface energy nature; they are not wetted straightforwardly by polar materials, like adhesive, printing inks and paints. In order to overcome this obstacle, the hydrophobic surfaces need to be treated or modified to gain a hydrophilic character in order to generate polymers with desirable surface properties.

Polypropylene (PP) is one of the inactive synthetic polymer and the most important Polyolefin's in commercial application. It has been used extensively in plastic industry in different forms (fibers, fabrics, films.etc.). It has a vital position among thermoplastic polymers because it is cheap and has

good versatile properties, such as, good chemical stability, good mechanical, good thermal properties and good barrier properties. However, PP is hydrophobic in nature, and to overcome this disadvantage many studies and researches have proposed several methods and technologies for improving surface characteristics of the of PP [1–6], for example, corona discharge, flame [7], plasma [8, 9], UV irradiation [10], gamma-ray [11, 12], electron beam, ion beams [13], reactive extrusion, redox treatments [14, 15], to create active charged sites onto the outermost layer in order to improve the surface energy of the PP for the most important features that need to be enhanced, such as barrier properties, hydrophilicity, printability and adherence to other materials, while retaining the polymer's desirable

bulk properties without change to permit its use in a variety of industrial applications, on top of these applications and the most important and the focus of this study, such as food packaging application.

Grafting of polyolefin with functional monomers has proved to be a dramatic technique to impart several desirable properties to the inactive hydrophobic polymers. Grafting of PP was shown to improve its water contact angle, water absorption ability [16], medical applications [17], biocompatibility, anti-fouling [18], electrical properties, conductivity, the thermal stability [19], wettability, dyeability [20], antistatic, anti-scratch [21, 22], antibacterial activity [23], anti-fogging [24], rheological properties, adhesion properties, lubrication [25], and gas permeability [26].

The radiation induced grafting of methyl methacrylate (MMA) onto irradiated isotactic polypropylene film (IPP) by per-oxidation technique to prepared grafted (IPP-g-MMA) was reported [27].

To conquer the intrinsic weaknesses of low surface energy of polypropylene (PP) films was grafted with poly (methyl methacrylate) by blend surface modification [28]. The structure of grafted polypropylene films with acrylic acid at different degree of grafting was characterized by EDS, FTIR, TGA, DSC, SEM and, XRD [29].

Bi-axially oriented polypropylene commercial films (POPP) grafted with poly (acrylic acid) (PAA) the differences in surface roughness, elastic modulus, hardness, and resistance to permanent deformation caused by the chemical treatment were studied in terms of film orientation and surface modification [30, 31]. Polypropylene (PP) films were grafted with N-p-hydroxyl phenyl maleimide using γ-radiation. The effect of both monomer concentration and dose rate on the degree of grafting was evaluated [32].

Polypropylene (PP) was functionalized with maleic anhydride (MAH) in the presence of dicumyl peroxide (DCP) in a batch mixer using melt grafting with varying maleic anhydride and peroxide concentrations [33]. N-isopropylacrylamide (NIPAAm), 2-hydroxyethylmethacrylate (HEMA) and N-vinylimidazole (NVIm) were grafted separately onto polypropylene (PP) monofilament sutures. These grafted copolymers have properties with potential application in the synthesis of new biomedical devices [34].

Polypropylene (PP) films were grafted with a mixture of two (or more) monomers; with Butyl methacrylate and acrylamide (BMA/AAm) co-monomers using gamma radiation, the grafted films exhibit good thermal stability and hydrophilic characteristics, making them appropriate for heavy metal removal from wastewater [35]. Under UV – irradiation PP film was grafted by a mixture of monomer; N-Vinylpyrrolidone/Maleic anhydride. The binary monomers enhanced the hydrophilicity and the antimicrobial activity of the graft copolymer [36]. Polypropylene-graft-cardanol (CAPP) was prepared by reactive extrusion in the presence of three kinds of initiators: dicumyl peroxide (DCP), benzoyl peroxide (BPO) and di-tert-butyl peroxide (DTBP) to select the most efficient initiator on thegrafting degree [37]. A two-step reaction was used to prepare poly (3-hexylthiophene)-graft-polypropylene (P3HT-g-PP). PP was first functionalized with styrene giving polystyrene-graft-polypropylene (PS-g-PP) thereafter P3HT was polymerized on PS-g-PP via FeCl3 oxidative polymerization; the modification of the surface of PP with P3HT increased PP's thermal stability and conductivity [19].

Several set of monomer mixtures were grafted onto PP were grafted PP; acrylic acid (AAc)/styrene (S) [38], N, N' dimethyl acryl amide (DMAAM)/N-isopropyl acrylamide (NIPAAM) [39], acrylic acid (AAc)/N-isopropylacrylamide (NIPAAM) [40], acrylic acid (AAc)/Acrylonitrile (AN) [41], acrylonitrile (AN)/methacrylic acid (MAc), and acrylonitrile (AN)/glycidyl methacrylate (GMA) [42], vinylimidazole (VI) /acrylic acid (AAc) [43].

Polypropylene monofilaments are radiation-grafted with acrylonitrile (AN). The grafted PP monofilaments were then hydrolyzed to convert the nitrile groups into carboxyl groups to immobilize antimicrobial drugs [44, 45]. Radiation graft copolymerization of N-isopropyl acrylamide (NIPAAM) / acrylic acid (AAc) mixture was carried out on polypropylene (PP) nonwoven fabric to create a thermo-sensitive material, Temperature-triggered drug release was evident in the grafted membranes' immobilization and release behavior [46].

Chitosan alone or chitosan-based composite films with specific properties (Super-hydrophobicity excellent mechanical strength and acceptable barrier properties) [47], have been used as high-quality packaging materials for food preservation. Chitosan properties include also, biocompatibility, biodegradability, antimicrobial, antioxidant [48, 49],

and degradation products that are non-toxic, non-carcinogenic, and non-immunogenic. Furthermore, because it is derived from marine waste, it is a low-cost renewable material [50]. Huge numbers of chitosan derivatives have been reported in much literature [51, 52], among them, chitosan bearing S-linkage in its structure such as chitosan/thiourea have attracted attention due to its potent antifungal activity [53]. The experimental data showed that the antibacterial activities of the acyl thiourea derivatives are significantly greater than of the parent CS [54], and that they are a lot superior fungicidal agent (approximately 60 times more) than pure CS against the majority of the fungal strains tested [55].

To obtain an appropriate and durable packaging material, PP film was initially activated with plasma (corona discharge), which creates OH* or/and pO* active centers on the PP surface and then graft copolymerized with acrylonitrile monomer (AN) using benzoyl peroxide and then hydrolyzed with sodium hydroxyl to transform the nitrile groups into carboxyl and amide groups. The hydrolyzed grafted films were then treated with chitosan and chitosan/thiourea combinations.

The obtained final products were used for food preservation packaging, which is the primary goal of this work.

2. Experimental

2.1. Materials and Reagents

polypropylene film (pp) (35 μm thickness) industrial grade of (melting index (MFI) = 2.9 g/l0 min; ρ= 0.905g/cm³) was cut into a size of (40x40 mm²) and then rinsed with acetone for about 24 hours and dried in oven at (55 °C). Acrylonitrile monomer (AN) (purity>98%) was provided by Merck (Darmstadt, Germany). Benzoyl peroxide (Darmstadt, Germany). Benzene, N, N-dimethylformamide (DMF), isopropanol, ethanol, petroleum ether, diethyleneglycol, acetic acid, hydrochloric acid, sulfuric acid as analytical reagent (purity > 98%), Mohr's salt {NH4)₂Fe(SO4)₂·6H₂O} and KCl was used as analytical reagent (purity > 98%) and acetone were from (El- Gomhouria Co. Egypt). Sodium hydroxide was received from Merck (Darmstadt, Germany). Thiourea was from (Merck, Germany), and for all experiments, distilled water was used. Chitosan was produced through the alkaline deacetylation of chitin derived from shrimp [56]. The deacetylation level is about 72.74%.

2.2. Preparation

2.2.1. Corona treated PP films and Purification

Locally purchased polypropylene film were treated with corona discharge station model (MR/b 40K-IGBT), with power of about 15 kW and voltage of $3\times400V$.

2.2.2. Graft copolymerization procedure

The grafting process was performed by weighing (approximately 0.25 g) of PP film cut into strips (4 x 4 cm) and immersed in benzene solution containing acrylonitrile different concentrations (10: 100 v/v %). Benzoyl peroxide [BPO] was added as an initiator in different concentrations (0.03, 0.04, 0.05 and 0.06 mol % of AN), followed by ammonium ferrous sulphate (Moher's salt) (1.0 x10⁻³ M), sulphuric acid (H2SO4, 0.1 M) and purged with nitrogen gas for 10 minutes, and then immersed in a water bath at various temperatures range (70, 80, 90, and 100 °C) for various times (3, 4, 5, 6, and 7 hrs). Following the grafting reactions, the samples were soaked in a Soxhlet with DMF for 24 hours to eliminate the excess of monomer and the formed homopolymer.

The degree of grafting of the PP film was calculated using the following equation:

$$\text{Degree of grafting (G\%)} = \frac{Wg - Wo}{Wo} \times 100 \qquad (1)$$

Where Wg and Wo are the weights of the AN-grafted PP film and the pristine PP, respectively.

2.2.3. Alkaline treatment of grafted PP film (hydrolysis)

The PP-g-PAN film was placed in a glass tube containing the required amount of sodium hydroxide solution (10 %). The tube was then placed in a water bath that was kept at a constant temperature of 90-100 °C for 24 hours. Following hydrolysis, samples were placed in 2 % hydrochloric acid for 2 h to transform carboxyl groups into the proton form. Finally, washed with deionized water and dried in a vacuum oven set to 50 °C. According to [44], as shown in (Fig. 1).
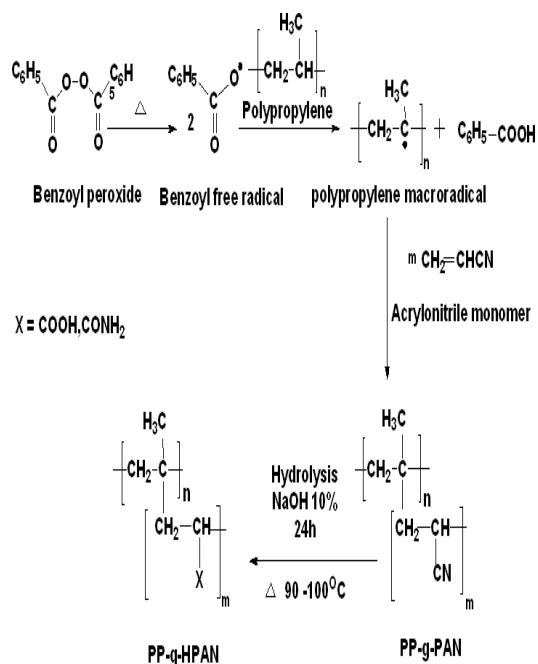
Fig. 2. Synthesis of chitosan/thiourea (CT)

Fig. 1. Graphically procedure of the chemical graft of AN monomer onto the PP film and method of hydrolysis.

2.2.4. Extraction of Chitin and its conversion to Chitosan.

Chitin and Chitosan have been extracted and processed as in reference [57].

2.2.5. The synthesis of Chitosan - Thiourea (CT) Polymer

Chitosan/Thiourea (CT) was made by dissolving (5g) of chitosan powder in 500 ml of 1% (v/v) acetic acid (CH₃COOH) solution with continual stirring process. To produce chitosan/thiourea (CT), the chitosan solution was mixed with 500 ml of 0.2 M ammonium thiocyanate with a continual stirring for 5 hours at ambient temperature, the precipitate was obtained by adding 250 ml of NaOH (20 %, w/v). According to [58, 59], the participant was removed through filtration, cleaned with a water/ethanol solution, and dried to produce a chitosan/thiourea (CT), in which –CSHN₂ (thiourea) replaced one hydrogen atom of NH₂ group of chitosan and was easy to be dissolved into acetic acid solution to the next application (Fig. 2).
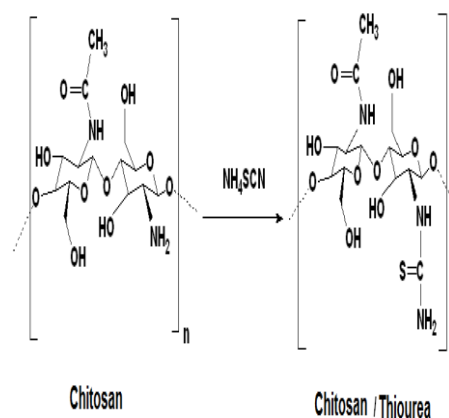
2.2.6. Chitosan and Chitosan / Thiourea complex immobilization on modified PP films.

Immobilization of chitosan on the hydrolysis PP-grafted film (PP-g-HPAN) was carried out by the dip-coating method, as described by [60]. PP-g-HPAN was immersed in an acidic CS solution, obtained by dissolving about 5g of chitosan, was slowly added to 500 ml of 2.5% (v/v) acetic acid (CH₃COOH) solution with constant stirring for 24 hrs at room temperature. The CS was coated onto the grafted PP film (PP-g-HPAN/CS). The film was removed from the vessel and washed with deionize water at room temperature to eliminate the un reacted chitosan and dried according to [61].

The hydrolysis PP-grafted film (PP-g-HPAN) was immersed in acidic CT solution prepared by dissolving 3g of chitosan /thiourea into 500 ml of 2.5 percent (v/v) acetic acid solution under constant stirring. The grafted PP film (PP-g-HPAN/CT) coating was removed from the vessel and allowed to dry. The amount of CS and CT (G %) was calculated gravimetrically and was approximately 7.7 % and 7.6 %, respectively. calculated as follows:

$$\text{Degree of Substitution (S \%)} = \frac{Wg - Wo}{Wo} \times 100 \quad (2)$$

Where, Wg and Wo are the weights of the PP-g-HPAN/CS or PP-g-HPAN/CT and PP-g-HPAN, respectively.

2.3. Instrumentation

2.3.1 Infrared (IR) Spectroscopy

FTIR spectra were measured using Tescan Shimadzu FTIR spectroscopy (Model 8000, Japan) in the range 500- 4000 cm^{-1} at the Micro analytical Center, Cairo University (Egypt).

2.3.2. Nuclear magnetic resonance NMR

^{1}H NMR spectra was carried out on Varian Mercury 300 BB (NMR 300) (Mercury, USA). in mixed solvent of trifluoroacetic acid (TFA) & deuterated dimethyl sulfoxide (DMSO-d^6) solvent at 30 °C and chemical shifts were expressed as part per million; (δ values, ppm).

2.3.3. Elemental analysis

Elemental analyses were performed in Perkin Elmer (Model 2410 series II) C, H, N, S Analyzer (USA) at the Micro analytical Center, Cairo University (Egypt).

2.3.4. Potentiometric Titration

In 25 ml of standard (0.1 M) HCl solution, 0.5 gm of chitosan was dissolved. The solution was then topped up to 100 ml with distilled water, and 0.1g of KCl was added to bring the ionic strength down to 0.1. The standard titrant of (0.05 M) NaOH solution was added to the chitosan solution gradually. The pH meter model (HANNA H19025) was used for continuous pH measurements.

2.3.5. Thermal analysis

The thermo-gravimetric analysis (TGA) and differential thermo-gravimetric analysis (DTGA) were used to investigate the sample's thermal stability. A precise weight of the sample in an aluminum pan was measured using Shimadzu TGA-50H (Japan), from 25 °C – 600 °C temperature range at a heating rate of 10 °C/min under nitrogen.

2.3.6. Mechanical properties

The stress-strain curves were measured using a Zwick Tensile Testing Machine (German) 2012/GmbH +G. At 500 N, the load cell was used. ASTM D882-18 [62], was the test standard. The values reported are the average of five measurements.

2.3.7. Density measurement

Density measurements were performed by immersing films in a solution made of isopropanol (d, 0.79 g/cm^3) and diethyleneglycol (d, 1.115 g/cm^3) and using a Densitometer - K20 by KRUSS - GmbH (Germany) as a density solution adjustment device.

2.3.8. X-ray diffraction analysis

The X-ray diffraction (XRD) patterns of films were recorded in the 2θ range of 10-35º using Brukur D-8 Advance (Germany). The power was set at (40 kV, 30 mA). The X-ray source was CuKα radiation (wavelength, 1.540 A°).

2.3.9. Scanning electron microscopy

A Hitachi Model S-4700 Scanning Electron Microscope (SEM was used to examine the surface morphological characteristics) of the obtained films. The samples were loaded on the surface of an aluminum SEM specimen holder and coated with gold before observation to avoid charging under an electron beam. The accelerating voltage was 20 kV.

2.3.10. Swelling Characteristics

The swelling characteristics obtained films were investigated as a function of time in distilled water at room temperature 25 ºC according to [63].

2.3.11. Permeability properties of oxygen and water vapour

Oxygen and Water vapor transmission rates through the film samples were determined using a Systech Illinois Instruments, Inc (U.S.). By the model 8501 oxygen permeation Analyzer and 7001 water vapor permeation analyzer. Testing was carried out at 25 °C in an arid atmosphere (0 % RH) for oxygen transmission rate according to the test standard ASTM D3985 - 17 [64], and at 38 °C in moisture content (80- 90 % RH) for water vapor transmission rate according to the test standard ASTM F1249 - 20 [65].

We start with an overview, which is depicted in the following figure and will be explored in the results and discussion section (Fig. 3).
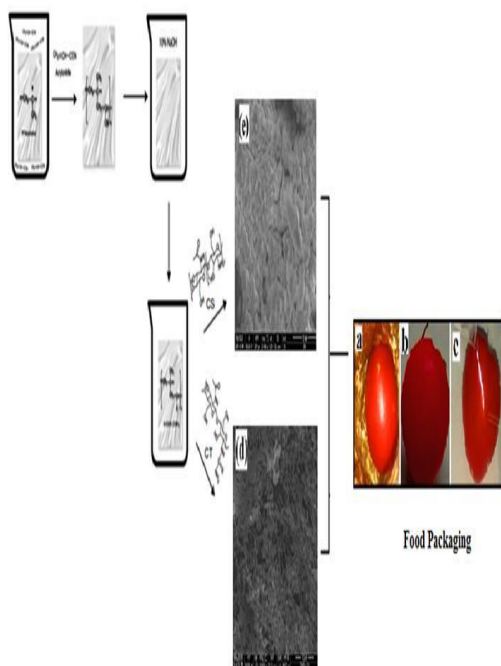
Fig.3. Schematic illustration of the preparation of PP graft and its food packaging applications.

3.   Results and discussions

3.1. Characterization of the structure of the grafted PP films

   The film development was made by graft polymerization of acrylonitrile (AN) on PP film. The percentage of grafting depends on a variety of reaction parameters, such as monomer concentration, reaction temperature, reaction time, and initiator concentrations are described in Figs. 4(a), (b), (c) and (d).

3.1.1.   Effect of monomer concentration.

   Fig. 4(a) shows the effect of monomer concentration on the grafting percentage (G %) onto PP film. It can be observed that the grafting of AN increases initially with increasing monomer concentration giving maximum percentage (115%) at a monomer concentration of 80% (V/V) and then decreases on further increasing the concentration of AN because, initially, the number of monomer molecules diffusing through the reaction medium is large and reaching the free radical sites on the PP

backbone increasing the grafting extent. The G % decreases with further increasing monomer concentration, which may be due to the formation of more homopolymer in the medium leading to increased viscosity. As a result, the viscosity hinders the monomer diffusion and acrylonitrile monomer acts as a non-solvent for PAN in the viscous medium and competes with the graft copolymerization [66– 68].

3.1.2.   Effect of Temperature

   Fig. 4(b) shows the effect of temperature from 70 ºC to 100 ºC on the percent grafting. Generally, with increasing temperature, grafting percentage increases giving a maximum percentage at 115 % grafting percentage at 90 ºC due to increase in the decomposition of initiator leading to formation of more free radicals and the generation of active side on polymeric backbone. This leads to a higher degree of grafting. However, as the temperature rises above 90 ºC, the grafting rate decreases. This is probably because at higher temperatures, a higher combination rate of monomers is obtained through increasing homopolymerization reaction, which increases the viscosity and hinders the monomer diffusion, resulting in insufficient monomer concentration to react with the active radicals, which results in a decreased grafting rate [63, 67].

3.1.3.   Effect of reaction time

   Fig. 4(c) shows the effect of reaction time on the percent grafting of AN onto PP film at different time intervals (2, 3, 4, 5, 6, 7 hrs). It was observed that the grafting level increases initially with an increase in reaction time from 2 hr to 5 hr and reached a maximum value of 115% grafting after 5hrs, then level of. This behavior may be attributed to the fact that in the beginning, with an increase in reaction time, the free radicals have more time to generate. Leading to higher level of grafting. However, on further time, increases the free radicals number level of, and thus no further change in grafting level was observed [63].

3.1.4.   The effect of initiatorconcentration

   Fig. 4(d) shows the influence of initiator [BPO] concentration on the rate of grafting. It was observed that the percentage of grafting increases up to a certain level and reaches a maximum value

of 115% grafting at a concentration of [0.05 M] of the initiator. It gradually decreases after that. The initial increase in the percent grafting is caused by an increase in the concentration of radicals formed through the decomposition of the initiator. The availability of the free radicals generated enhances the graft percentage. When the concentration of the initiator exceeds a certain value, it causes an increase in the rate of mutual termination of chain Reactions and increases the homopolymerization [63].
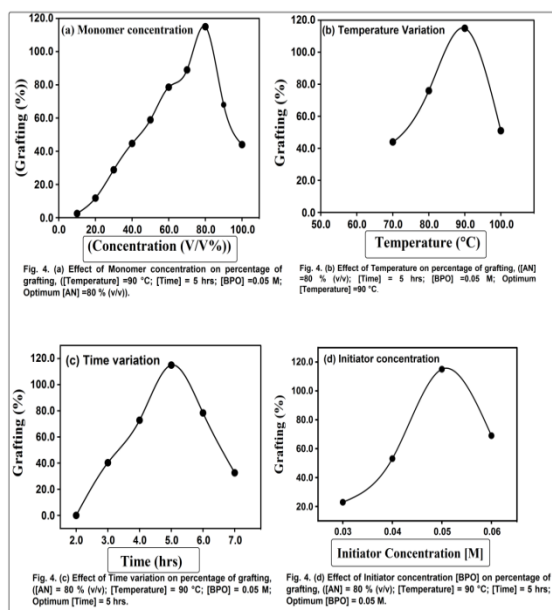

Fig. 4. (a- d). Illustrate the effect of monomer concentration, temperature, time variation, and initiator concentration on PP grafting.

3.2. Infrared Spectroscopy (IR)

The FTIR spectra of pristine PP, PP-g-PAN and PP-g-HPAN films are shown in Fig.5 [(a), (b) and (c)]. The IR spectrum of the PP-g- PAN (Fig.5 (b)) shows a characteristic sharp peak at 2242 cm^{-1} (strong) for stretching band of nitrile $-C \equiv N$group and 1670 cm^{-1} (medium) for the stretching of the $-C=N-$ group. The intensity of the 2242 cm^{-1} increases with the degree of grafting. The prominent bands in the PP film appear in the region 2800–3000 cm^{-1}, which correspond to C–H stretching vibrations for $-CH_2 -$ groups, in addition to the absorption peak at 1458 and 1377cm^{-1} which is assigned to $-CH_3$ bending vibrations (Fig.5 (a)). The IR spectrum of the PP-g-HPAN (Fig.5 (c)) shows a new absorption peak at 1666 cm^{-1} for (C=O) of the amide ($-CONH_2$) band, 1558 cm^{-1} for

(C=O) for the carboxylate group (–COOH) and a broad band at 3200 -3500 cm^{-1} due to the overlap of the stretching vibration –NH and –OH of the amide and carboxylic group. This is an indication that the nitrile groups are transformed into other functional groups (carboxyl and amide) groups during hydrolysis. It is noticeable that the persistence of the peak at 2242 cm^{-1} in the IR spectra of PP-g-HPAN is due to the presence of a trace of the cyano groups of PAN that that was not completely hydrolyzed to carboxyl and amide groups.
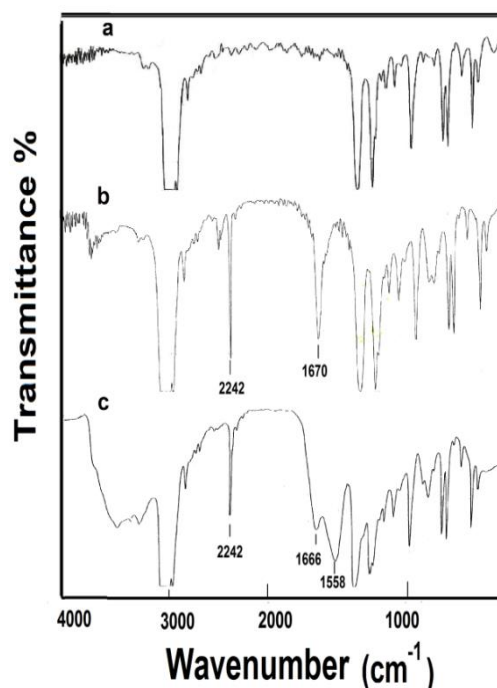

Fig. 5. FTIR spectra of (a) pristine PP, (b) PP-g-PAN and, (c) PP-g-HPAN films.

3.3. Elemental analysis

The grafted and the hydrolyzed films were analyzed for the elements(C, H and N) content. The data are shown in Table 1. It could be seen that PP-g-PAN, and the hydrolyzed PP-g-PAN films contain nitrogen, while the pristine PP does not have any nitrogen. A slight decrease in the nitrogen content in the hydrolyzed polymer is observed due to the conversion of some amide groups into carboxyl groups.

Table 1. Elemental analysis of pristine PP, PP-g-PAN and hydrolyzed PP-g-PAN films.

Sample	Elemental analysis, %		
	C [%]	H [%]	N [%]
Pristine PP	72.3	9.83	-
PP-g-PAN	70.82	8.58	12.87
PP-g-HPAN	68.42	7.97	11.68

3.4. Thermal properties behaviour for the obtained products (TGA and DTGA).

Fig. 6[(a), (b) and (c)] show the TGA and DTG thermograms of pristine PP, PP-g-PAN and PP-g-HPNA films. As demonstrated, grafting caused a significant change in the thermal behavior of the PP film. In the case of pristine PP film there is only one main degradation step at around (390 °C) as the initial decomposition temperature (IDT) and complete degradation occurs near (480 °C) as a final decomposition temperature (FDT), giving no residue at about (600 °C) and according to the DTG curve, the highest rates of decomposition occur at (480 °C) as shown in Fig. 6 (a). In case of the TGA analysis of the grafted PP films (PP-g-PAN) shows an irregular weight loss with further increase in temperature via two main degradation steps. In the first step weight loss was observed at an initial decomposition temperature (IDT) of (241 °C) and a final decomposition temperature (FDT) at(467 °C) with weight loss of (-≈ 56.86 %), which corresponds to the degradation of the grafted chain on the surface of polypropylene. In second step, the weight loss was observed at an initial decomposition temperature (IDT) about of (503 °C) and a final decomposition temperature (FDT) at 621 °C with weight loss of (-≈31.4 %) which might correspond to the thermal decomposition of polypropylene chain degradation. However, a final residue of about (≈11.72 %) at (600 °C) and according to the DTG curve, the highest rates of decomposition occur at (441 °C and 592 °C). As illustrated in Fig. 6 (b). While in the case of PP-g-

HPAN, the thermal degradation occurs at three-steps. In the first step weight loss was observed in the range of (34 °C -111 °C) with (-≈7.17 %) weight loss corresponding to the dehydration process of moisture during hydrolysis. In the second step, the weight loss was observed at the initial decomposition temperature (IDT) at (179 °C) and was reached to final decomposition temperature (FDT) at 444 °C with (-≈57.18%) weight loss. The irregular weight loss with further increase in temperature is due to the presence of several decomposition groups' (acid –COOH–, amide –$CONH_2$ and few traces of –C≡N groups of (PAN)) that did not convert completely in the hydrolysis step. In the third step, the weight loss occurred at initial decomposition temperature (IDT) at (498 °C) and was reached to final decomposition temperature (FDT) at (652 °C) with weight loss (-≈25 %), with a residue remaining approximate (≈10.7 %) above (600 °C), and according to the DTG curve, the highest rates of decomposition occur at (62 °C, 287 °C, 418 °C, and 588 °C), as shown in Fig. 6 (c). A small inflexion that appears in PP-g-PAN could be due to weight loss of moisture in region (50-100 °C) corresponded to the dehydration.
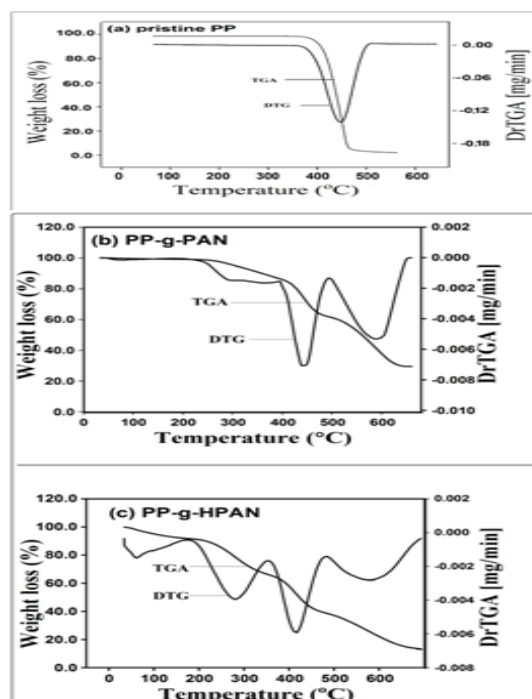
Fig. 6. The TGA and DTGA curve of (a) pristine PP film, (b) PP-g-PAN and(c) of PP-g-HPAN films.

3.5. Swelling behaviour

Fig.7 shows the swelling behavior of pristine PP, PP-g-PAN and PP-g-HPAN films. It can be seen that the pristine PP shows very small water uptake, while a slight increase in swelling degree is observed with the grafted polymer. A much pronounced swelling is observed for the hydrolyzed graft copolymer which is due to the presence of hydrophilic groups resulting from the conversion of the –CN groups into –COOH and –CONH$_2$.
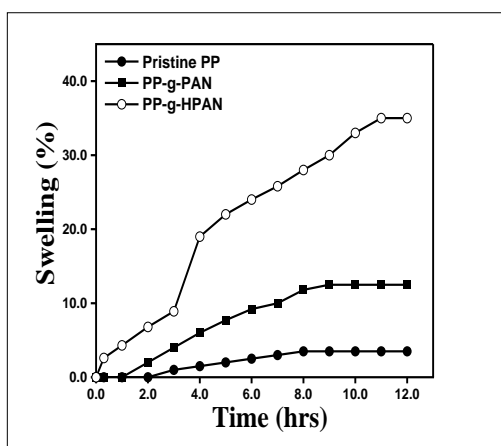

Fig. 7. Swelling behavior of pristine PP, PP-g-PAN and PP-g-HPAN film.

3.6. Mechanical properties

Tensile and Elongation at break values of pristine PP film are 125 MPa and 152 %, respectively. In case of PP-g-PAN and PP-g-HPAN the tensile strength and elongation are significantly affected; however, the tensile strength improves slightly with increasing grafting level up to about (≈58.9%), above this level, a large deterioration of polymer tacks place. It could be because at lower graft levels, the formed PAN acts as filler and exerts a reinforcing effect on the system.

The short PAN chains may be incorporated within the voids in the amorphous region of the PP backbone causing a reinforcement effect, thereby increasing the tensile strength of the film. However, with further grafting, the uniformity of the chains was affected and the longer PAN chains disturb the molecular chains of the pp matrix, thus lowering the tensile strength.

The elongation of the grafted chains, on the other hand, decreases with increasing graft level, which may be explained by the fact that the grafted chains are linked to the PP backbone, reducing chain mobility and lowering elongation. Several cases of grafted polypropylene - monomer systems have yielded similar results [44, 69].
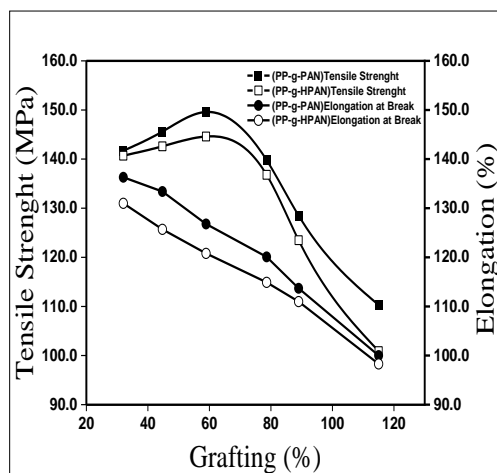

Fig.8. Shows the variation of tensile strength and elongation for both PP-g-PAN and PP-g-HPAN films with grafting (%).

3.7. Density measurement

Fig.9. shows the density of pristine PP, PP-g-PAN and PP-g-HPAN films as a function of the degree of grafting. The density of pristine PP was measured to be (d, 0.905 g/cm^3), which rises to 0.967 g/cm^3 for a graft level of 115 %.

The density increases continuously as the amount of grafting increases, the increase in density may be attributed to the higher density of grafted PAN moiety (d, 1.184 g/cm^3) that is incorporated into the PP film, the increase in density at low graft levels is due to the free incorporation of a large fraction of PAN within the voids in the amorphous region of polypropylene backbone.

With increased grafting, more PAN appears to be incorporated into the polymer's interlamellar regions, where chains are pushed apart to accommodate these large grafted [70].
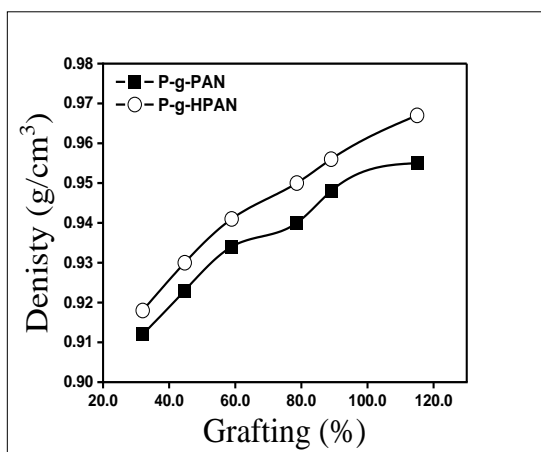
Fig.9. Variation of density with the degree of grafting in PP-g-PAN and PP-g-HPAN film.

3.8. X-ray analysis

Fig.10 [(a), (b) and (c)] show the X-ray patterns of pristine PP, PP-g-PAN and hydrolyzed PP-g-PAN films. The crystalline reflections of the unmodified, grafted PP and hydrolyzed PP films occur at identical angles and no additional peak was observed in the range of 10–35°. The PP film shows a crystalline diffraction pattern that suggests the semi-crystalline nature of the film. However, the intensity and shape of the peaks show slight decreases in the grafted samples [Fig. 10 (b) and (c)], leading to the conclusion that the innate crystallinity of PP film decreases due to acrylonitrile grafting. Similar observations have been made [44, 71].
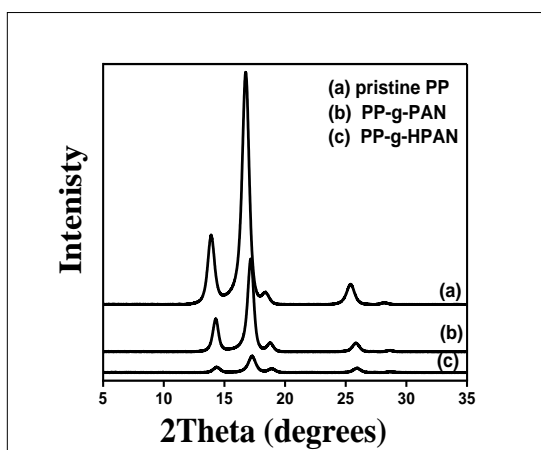

Fig.10. X-ray diffraction patterns of (a) virgin PP, (b) PE-g-PAN, and (c) hydrolysis PP-g-PAN films.

3.9. Permeability properties of different gases (Oxygen and Water vapor).

3.9.1. Oxygen permeability

The improvement of the oxygen barrier property of a film is of great importance because oxygen promotes many degradation mechanisms of food, such as corrosive phenomena, oxidations, and great modification of the demolition of organoleptic properties and flavor exchange, especially of fresh products (e.g., fruits, salads, and vegetables (ready-to-eat) [72]. According to [64], the oxygen transmission rate (OTR) of Pristine PP film is (1090 cc/m2/day), and the ORT should not exceed 1300 cc/m2/day. The mean oxygen permeability of PP-g-PAN and PP-g-HPAN was found to be (634.8 cc/m2/day) and (437.7 cc/m2/day), respectively (Fig 11(a)). These values illustrate a great improvement hydrolysis. This important result is a further indication of the validity of this modified PP for packaging applications.

3.9.2. Water vapor permeability

The water vapor barrier property is important in food preservation and extending shelf life by reducing physical and chemical deterioration caused by moisture content. Maintaining the flavor, texture, and overall quality of packaged food products depends on managing moisture migration. Bakery, delicatessen, dairy, meat, pet food products, gourmet snacks, coffee, grains, and non-food products require a moisture-free environment to avoid undesirable changes in texture, taste, and microbial stability. The water vapor transmission rate (WVTR) of virgin PP, PP-g-PAN and PP-g-HPAN polymers is displayed in (Fig. 11(b)) WVTR is expressed in (g/m2/day). The WVTR value of virgin PP film is found to be (4.3 g/m2/day), which is below the maximum acceptable value of (4.7 g/m2/day), according to [65]. The WVTR values of PP-g-PAN (3.6 g/m2/day) and PP-g-HPAN (2.96 g/m2/day) are lower than those of pristine PP, indicating that grafting of the surface of PP provides a dramatic improvement in the barrier properties. The decrease in oxygen and water vapor permeability may be due to decreases in the free volume available (amorphous regions) and to the presence of grafted side chains of the PAN. In addition, the increased polarity of PAN and the formed polar groups after hydrolysis (COOH and

CONH₂) may lead to the formation of tight intermolecular hydrogen bonds, reducing the free volume of the polymer. As a result, gas transport must be reduced [73].
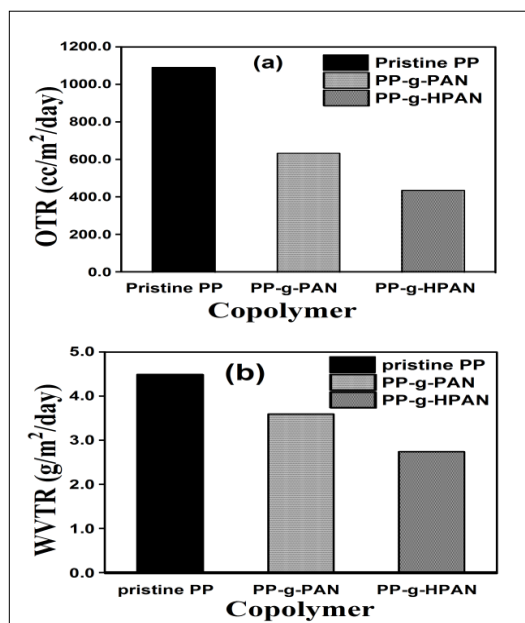

Fig.11. (a) OTR and (b) WVTR values of pristine PP, PP-g-PAN and hydrolysis PP-g-PAN films.

4. Characterization of chitosan (CS) and chitosan/thiourea (CT)

4.1. IR spectroscopy Technique (IR)

FT-IR spectroscopy was used to confirm the chemical structure of CS and CT are given in Fig.12.

The pristine CS shows the characteristic broad bands around 3341 cm⁻¹ assigned to the overlapping –OH , –NH and –NH₂ stretching vibrations, 2916 cm⁻¹ and 2877 cm⁻¹ assigned to asymmetric and symmetric vibrations of –CH₃ groups, 1643 cm⁻¹ and 1586 cm⁻¹ assigned to (C=O stretching in O=C-NH of amide I) and (–NH bending vibrations in O=C-NH of amide II), respectively.

1419- 1388 cm⁻¹ assigned to asymmetric C–H stretching bending of CH₂ group, 1062 cm⁻¹ assigned to C–O stretching vibrations of the glucosamine ring. In the spectra of CT the disappearance of the peak at 1586 cm⁻¹ (vibrations of primary amino groups) and

the appearance of a new peak at 1531 cm⁻¹ is the vibration adsorption peak of the thiourea moiety group. The C=S group is visible in the CT spectrum and its intensity became weak as result of the amino group of chitosan being substituted. In addition, a new peak at 1411cm⁻¹ was assigned to the N-C=S group, according to [58, 74–76], which is characteristic of thiourea groups.

This demonstrates that thiourea groups were successfully grafted onto the CS backbone. The band at 2060 cm⁻¹ indicates the existence of a certain amount of ionically bound SCN–ions.
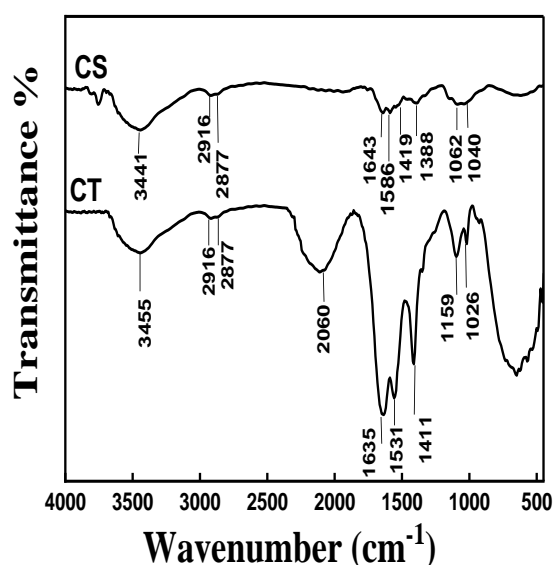

Fig.12. FTIR spectra of pristine CS and CT

4.2. Nuclear magnetic resonance ¹HNMR

Figs. 13(a) and (b) show the ¹H NMR spectroscopy of CS and CT sample, respectively.

By comparing the results of Fig.12 (a), to that of Fig 12 (b), one can see the same identical peaks and shape of the peaks (all found from 1.9 ppm to 8.3 ppm), as was given in many previous references [54, 56], for both native CS and CT with a slight decreases in the intensity and shape of the peaks at the case of CT sample than CS which, conform the attached of thiourea group to the proton of free amino group NH₂ in chitosan.
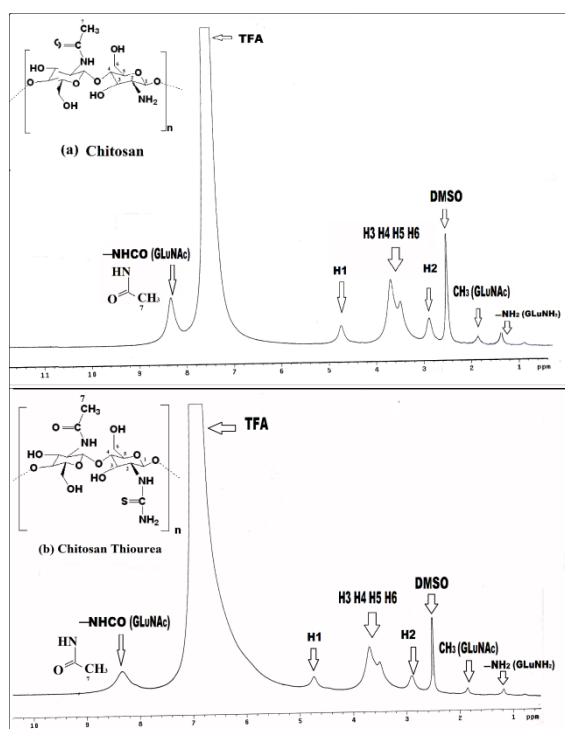
Fig.13. ¹H NMR spectra of (a) CS, (b) CT in mixed solvent of TFA & DMSO-d⁶ at 30 °C.

4.3. Elemental analysis

The Elemental analysis of obtained CS and CT are analyzed for its elements as shows in (Table 2).

Table 2: Elemental analysis of chitosan and chitosan/thiourea.

sample	Elemental analysis, %			
	C [%]	H [%]	N [%]	S [%]
Chitosan (CS)	41.8	8.07	7.44	-
Chitosan/thioura (CT)	37.1	7.93	11.22	2.75

5. Properties of the PP grafted films with attached chitosan (CS) and chitosan/thiourea (CT).

5.1. IR spectroscopy Technique (IR)

The FTIR spectra of PP-g-HPAN/CS and PP-g-

HPAN/CT are shown in [Fig.14 (a) and (b)]. In the IR spectrum of the PP-g-HPAN/CS Fig.14 (a), for the CS immobilized surface shows , a new broad band appeared in the range of 3000 - 3600 cm⁻¹, which is due to the stretching vibration of N-H and the O-H peaks, and show significant variation between regions 1550- 1700 cm⁻¹, where this regions are the characteristic of the carbonyl groups of CS , 1635 cm⁻¹ for amide I and 1573 cm⁻¹ for amide II, which overlap with the IR absorbance of residual carbonyl groups of carboxylic acid during hydrolysis and the formation of amide bond with deacetylation sites of CS, in lower intensity than IR spectra of PP-g-HPAN and parent CS. This could be an indication of the loss of some free carboxyl groups as a result of the formation of an amide bond with deacetylated CS molecules. The IR spectra of PP-g-HPAN/CT Fig.14 (b) shows a new two additional peaks at 1527cm⁻¹ and 2060 cm⁻¹ ,which, characteristic to thiourea
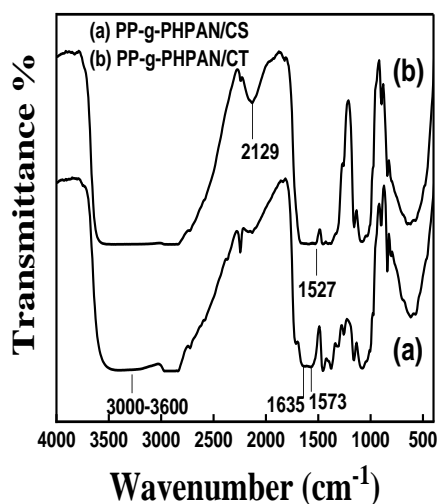

Fig. 14. FTIR spectra of (a) PP-g-HPAN/CS and (c) PP-g-HPAN/CT films.

5.2. X-ray diffraction analysis

The X-ray patterns of hydrolyzed PP-g-PAN, PP-g-HPAN/CS and PP-g-HPAN/CT films are presented in [Fig.15 ((a), (b) and (c)], respectively. Fig.15. (b) shows a new peak at $2\theta = 22.1°$ which is relevant to the crystal form of chitosan which is further prove of the attachment of chitosan to the PP film. While, in Fig.15 (c), this small peak vanishes, indicating that the addition of the thiourea group to the chitosan chain altered its crystalline structure slightly [77].
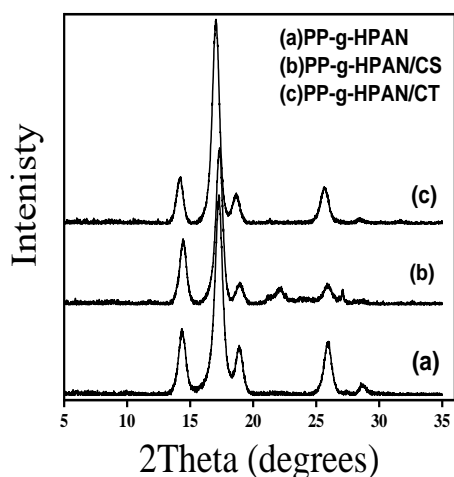
Fig. 15. X-ray diffraction patterns of (a) hydrolysis PP-g-PAN, (b) PP-g-HPAN/CS, and (c) PP-g-HPAN/CT films.

Fig.16. TGA and DTGA (a) hydrolysis PP-g-HPAN film attached with CS, (b) hydrolysis PP-g-HPAN film attached with CT.

5.3. Thermal properties, TGA and DTG

The TGA and DTG thermograms of the hydrolyzed grafted PP film (PP-g-HPNA) attached with (CS) and (CT) are shown in [Fig. 16 (a) and (b)]. The TGA of the grafted PP films with (CS) and (CT) exhibits similar profiles.

Thermal degradation occurs in three steps. In the first step, weight loss corresponding to the dehydration of water (36-110 °C). In the second step; the weight loss between (250 and 350 °C), due to the decomposition of the grafted chain of acid (–COOH–) and amide (–CONH2) (181- 449 °C), and a final step (500-700 °C) due to the degradation of PP.

The water loss (- ≈ 9.38 % and - ≈ 8.81 %) in the grafted PP with CS and CT is higher than that of the PP-g-HPNA (- ≈7.28 %) which is due to the more hydrophilic nature of the attached chains [78].

It is observed from DTG the maximum rates of decomposition of PP-g-HPAN/CS at 112 °C, 261 °C and 425 °C, whereas of PP-g-HPAN/CT the maximum rates of decomposition at 72 °C, 289 °C and 410 °C.
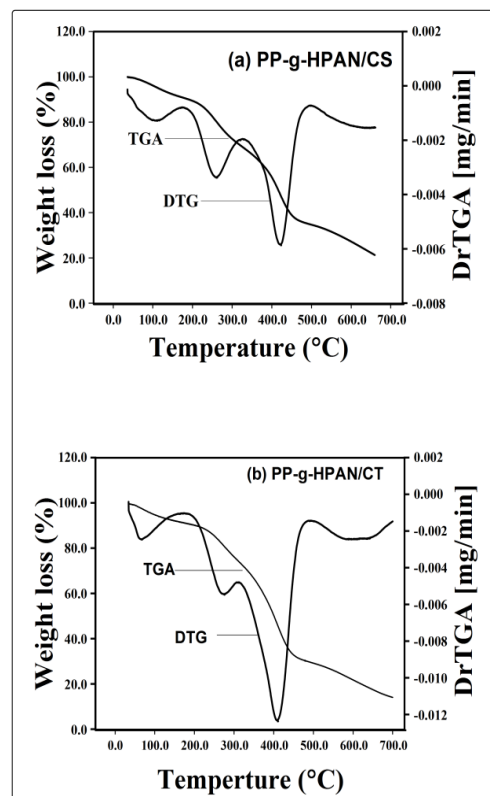
5.4. Permeability properties of the prepared polymers

5.4.1. Oxygen permeability

Fig.17 (a) shows a significant improvement in the oxygen barrier property of the hydrolyzed grafted PP film when attached with CS and CT compared to the hydrolyzed film alone. One can see a significant improvement in oxygen permeability between the original PP and the hydrolyzed grafted PP films. The mean oxygen transmission rate (OTR) of PP-g-HPAN/CS and PP-g-HPAN/CT is (67.29 cc/m^2/day) and (58 cc/m^2/day), respectively. According to this observation, CS and CT coated grafted PP were classified as excellent oxygen barriers, which consequentially qualifies this system for active food backing applications.

5.4.2. Water vapor permeability

Fig.17 (b) shows the WVTR of the grafted PP film when attached with CS and CT. The coated layer has a slight influence on the water vapor barrier than a hydrolyzed grafted PP without attached with CS

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and CT. When the results arecompared, one can see that the grafted PP, the PP-g-HPAN/CS and PP-g-HPAN/CT films generally, have a significant improvement in water vapor permeability over the origin PP. The mean water vapor transmission rate (WVTR) of PP-g-HPAN/CS and PP-g-HPAN/CT were found to be (2.99 g/m^2/day) and (3.12 g/m^2/day), respectively. The presence of the bio-coating did not lead to a significant improvement in WVTR than the PP-g-HPAN. This could be due to the chitosan hydrophilicity. The chitosan layer can act as a water reservoir on the PP surface. As a result, chitosan absorbs water from the humid air. The chitosan/water interaction, in particular, causes increased mobility in the hydrophilic macromolecule chains as well as swelling of the polysaccharide network. They are at the root of the gas diffusivity and gas solubility phenomena [79].
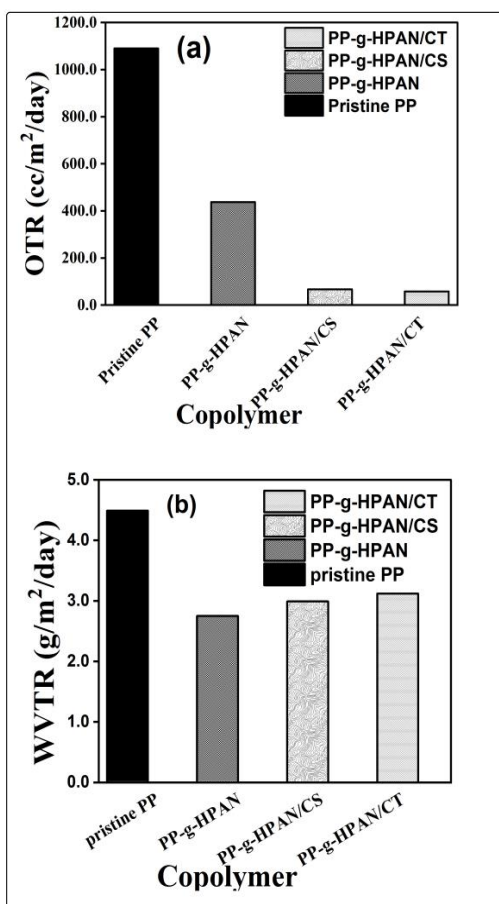

Fig.17. (a) OTR and (b) WVTR values pristine PP, PP-g-HPAN, PP-g-HPAN/CS and PP-g-HPAN/CT.

5.5. Water uptake properties

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The water uptake of PP-g-HPAN/CS and PP-g-HPAN/CT with time is greater than that of PP-g-HPAN (Fig.18) which confirms the successful immobilization of CS and CT on the grafted film and does not show any tangible difference to the addition of the thiourea group to the chitosan chain, and depend mainly on the hydrophilic nature of chitosan [79].
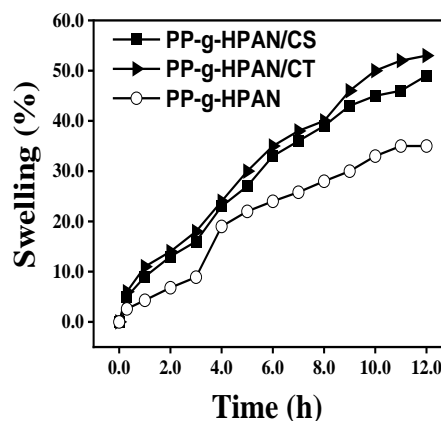

Fig. 18. Swelling behavior of PP-g-HPAN, PP-g-HPAN/CS and PP-g-HPAN/CT.

5.6. Scanning electron microscope (SEM)

Scanning electron microscopy (SEM) for pristine PP, PP-g-PAN, PP-g-HPAN, PP-g-HPAN/CS, and PP-g-HPAN/CT is shown in Fig. [19 (a)-(e)]. By comparing the surface morphology, it was observed that the surface of the pristine PP film was smooth and there were no wrinkles on the surface [Fig. 19 (a)]. However, in case of grafted polypropylene and (PP-g-PAN) and (PP-g-HPAN), the surface is not smooth and many wrinkles are observed due to the chemical grafting of acrylonitrile monomer (AN) and incompatibility of the hydrophilic group's formation (COOH and CONH$_2$) with the hydrophobic PP film [Fig. 19 (b)- (c)]. On the other hand, it can be seen that the grafted chains with attached CS and CT drastically change the morphology of the surface of PP. As shown in the figure [Fig. 19 (d- e)]. The structure is completely different from the original's smoother surface. The observed wrinkles on the surface indicate that the grafting and immobilization of CS and CT occur on the activated surface.
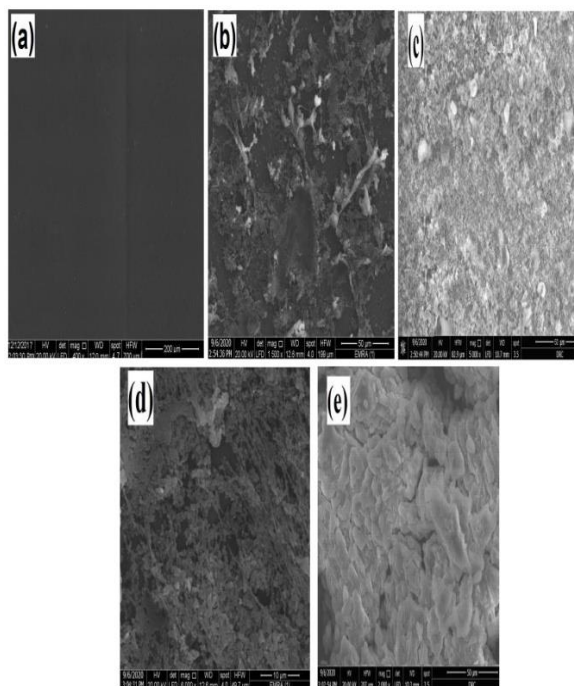
Fig. 19. SEM images of (a) pristine PP, (b) PP-g-PAN, (c) hydrolysis PP-g-PAN, (d) PP-g-HPAN/CS, and (e) PP-g-HPAN/CT films.

6. Packaging application

Microbial contamination decreases food shelf life and increases the risk of food borne illness. The traditional and decontamination methods of food preservation [80], are still in use such as, drying, heating, freezing, refrigeration, fermentation, ultrasound [81], and irradiation [82], modified atmosphere packaging, and adding antimicrobial agents or salts. Unfortunately, some of these techniques cannot be applied to some food products, such as fresh meats and ready-to-eat products; it is not consummate especially to inhibit the growth of pathogenic microorganisms that may endanger consumers' health [83].

Food quality may change during storage, packaging, and shipping, resulting in spoilage and the growth of pathogenic microorganisms, taking into consideration that traditional methods may not be sufficient as a fundamental method of food preservation. It has become clear in recent years that the use of performing antimicrobial packaging is required for the preservation process, and that relying solely on traditional preservation methods is insufficient to minimize pathogenic microorganism's transfers between the food and storage medium. A novel development concept that appears to overcome the disadvantages of traditional methods by incorporating antimicrobial packaging techniques [84], with non-biodegradable plastic-based packaging materials [85], before extrusion, or with polymer as edible coating thin layer [86], these packaging technologies could play a role in extending shelf-life of foods and reduce, inhibit, or delay the activities of targeted microorganisms growth on the surface of food and extending food shelf life [87].

7. Shelf life of foods

Food packaging not only provides a way to transport food safely, but also provides extended shelf life, protection from harmful bacteria, contamination and spoilage. Chitosan has shown its application prospects in food preservation, and has great potential to play an effective role as antimicrobial agent carriers in active packaging systems for the quality preservation of a variety of foods In order to achieve a suitable and dependable packaging material. In order to test the prepared grafted PP film attached with chitosan as a packaging for storage and extending the shelf-life time of foods, such as, tomato as an example. A bag was fabricated 12×12 cm, a fresh tomato of a regular size (45 g) of tomato, was collected and cleaned and stored in this bag (PP-g-HPAN/CS). Another similar two fruits were stored in air (b) and a third one was kept in unmodified PP bag (c) the samples were examined at intervals and compared to each other and the experiment was carried out in triplicate, Fig 20 shows the current state of the three samples. Samples B and C completely deteriorated after 7 days Fig 21 and after 20 days Fig 22, whereas the samples in the treated bags were nearly intact with no obvious spoilage infection. This offers a non-harmful, environmentally friendly method to prevent post-harvest fruit rot during storage and postpone the onset of infection.

Fig.20. Effect of keeping tomato fruit at zero-time (a) modified PP bag, (b) air (c) and unmodified PP bag.

Fig.21. Effect of keeping tomato fruit at 7 days (a) modified PP bag, (b) air (c) and unmodified PP bag.

Fig.22. Effect of keeping tomato fruit at 20 days (a) modified PP bag, (b) air and (c) unmodified PP bag.

8. Conclusions

Acrylonitrile was successfully grafted on polypropylene films by chemical grafting method. Different monomer concentrations, effect of temperature, effect of reaction time and the effect of initiator concentration have been examined. The degree of grafting increased with increase in monomer concentration, temperature, reaction time and initiator concentration. Maximum value of grafting can reach115% at 80 v/v% AN concentration, 80 ºC of temperature, 5 hrs reaction time and [0.05] initiator concentration. The subsequent alkaline hydrolysis of PAN formed carboxylic and amide groups onto the film surface. The grafting of acrylonitrile followed by hydrolysis leads to significant changes in physical structure and was proven by using different physicochemical techniques FTIR spectra, X-ray diffraction, Thermal analysis (TGA and DTGA), Mechanical properties, scanning electron microscopy, Density measurement, Swelling characteristics and Permeability properties of oxygen and water vapor. Followed by immobilization with chitosan and chitosan / thiourea layer onto the grafted PP film. The modified films showed excellent antimicrobial properties. These films may have improved antifungal and antibacterial properties over pristine PP film.

9. Statistics

All measurements are the mean of three replicates; the results obtained were processed by analysis of variance and the significant difference (LSD) Levels of 1% and 5% [88].

10. Author statement

The authors confirm contribution to the paper. All authors reviewed the results and approved the final version of the manuscript.

11. Declaration of competing interest

The authors declare that they have no competing interests.

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