

Biodegradable Cellulose-Based Materials for the Use in Food Packaging

Azza A. Al-Ghamdi, Abir S. Abdel-Naby

Abstract—Cellulose acetate (CA) is a natural biodegradable polymer. It forms transparent films by the casting technique. CA suffers from high degree of water permeability as well as the low thermal stability at high temperatures. To adjust the CA polymeric films to the manufacture of food packaging, its thermal and mechanical properties should be improved. The modification of CA by grafting it with N-Amino phenyl maleimide (N-APhM) led to the construction of hydrophobic branches throughout the polymeric matrix which reduced its wettability as compared to the parent CA. The branches built onto the polymeric chains had been characterized by UV/Vis, ^{13}C -NMR and ESEM. The improvement of the thermal properties was investigated and compared to the parent CA using thermal gravimetric analysis (TGA), differential scanning calorimetry (DSC), differential thermal analysis (DTA), contact angle and mechanical testing measurements. The results revealed that the water-uptake was reduced by increasing the graft percentage. The thermal and mechanical properties were also improved.

Keywords—Cellulose acetate, food packaging, graft copolymerization.

I. INTRODUCTION

SYNTHETIC polymer materials have been widely used in various field of human day activity. These synthesized materials are mostly prepared from petrochemicals, which are very limited [1]. Moreover, the extensive use of non-biodegradable polymers has caused serious environmental problems concerning accumulation of their waste products. In order to reduce these waste products, biodegradable polymers should displace the synthetic macromolecular materials in our daily life.

Biomaterials such as cellulose, starch-based compounds have the characteristics to be air permeable and to possess low temperature sealability, high productivity, and low cost [2], [3]. Bottle, disposable cups, packaging films, food containers, coating for all types of packaging are highly recommended to be manufactured using biodegradable polymers. The current trend in food packaging is the use of blends of different biopolymers [4]. However, the compatibility of the blend polymers in various compositions is a challenge problem facing this technique [5].

Cellulose is the most abundant natural biopolymer on earth. However, it suffers from being highly crystalline, infusible and insoluble in almost all organic solvents [6] due to its

Abdel-Naby is with the Department of Chemistry, Imam Abdulrahman Bin Faisal University, Dammam, Saudi Arabia (corresponding author, phone:0551385319, e-mail: aabdelnaby@iau.edu.sa).

A. Al-Ghamdi is with the Department of Chemistry, Imam Abdulrahman Bin Faisal University, Dammam, Saudi Arabia (e-mail: azaalghamdi@iau.edu.sa).

linearity and the presence of numerous hydroxyl groups which perform strongly hydrogen bonds throughout the polymeric chains. A number of cellulose derivatives are produced commercially. One of these derivatives is CA which possesses relatively low gas and moisture barrier properties but should be either plasticized or modified for film production [7]. Moreover, as biopolymer, CA suffers from hydrophilicity, which would limit its adjustment to food packaging application [8]. In our previous work, CA was chemically treated with N-amino phenyl maleimide (R-NAPhM) derivatives to improve its thermal and mechanical properties [8].

In the present work, graft copolymerization technique will be used to improve the thermal and mechanical properties of CA. R-NAPhM derivatives will be grafted onto the CA chains. R-NAPhM polymers are known to be of high thermal stability, which would enable the packaging films to resist environmental temperature changes.

II. EXPERIMENTAL

A. Materials

CA was purchased from (Aldrich) with average molecular weight 100,000 and acetyl content 39.8%. Benzoyl peroxide and phenyl hydrazine were obtained from (Aldrich). THF is used after distillation and all other reagents and solvents were used without any further distillation.

B. Synthesis of R-NAPhM

R-NAPhM derivatives were prepared according to the method described by Abdel-Naby from cyclocondensation of maleic anhydride and the phenyl hydrazine. The recorded melting point is 144 °C [9].

C. Graft Copolymerization

Graft copolymerization sample was prepared in a three-necked round bottom flask in a sonic water-bath. CA (0.049 mol) was dissolved in cyclohexanone under nitrogen atmosphere at 70 °C. R-NAPhM comonomer was then added to the reaction mixture and the system was heated for one hour to allow the reaction between monomer units and the acetate groups of glucopyranose rings. Afterwards, benzoyl peroxide (0.02 mol) was injected to the reaction medium to initiate the graft copolymerization.

The reaction was kept under nitrogen atmosphere in the sonic bath for 20 h. The graft copolymer was filtered, washed with hot methanol using Soxhlet system and then dried under vacuum. The percentage of graft was calculated using:

$$G\% = (W_g - W_o) / W_o \times 100.$$

where W_o and W_g are the weight of the CA before and after graft copolymerization, respectively.

D. Preparation of Grafted Polymeric Films

The grafted films were prepared by dissolving the copolymer solution in THF and then casting it into petri-dish. The film was dried in vacuum oven at 40 °C for 24 h. The thickness of grafted film was 0.7 ± 0.02 mm.

E. Characterization

1) UV/Vis Spectroscopy

UV spectra of grafted copolymer samples were recorded by Perkin-Elmer Lambda 4 UV/Vis spectrophotometer.

2) ^{13}C -NMR Analysis

The ^{13}C -NMR spectra of grafted samples were collected on Bruker Avanc-600 MHz spectrometer. All the chemical shifts were obtained in part per million (ppm) using tetramethylsilane (TMS) as the internal standard and DMSO or CDCl_3 are the solvents used.

3) Emission Scanning Electron Microscope (ESEM)

Morphology of grafted polymers were analyzed by (ESEM) using a FEG-SEM/EDS or LEO 440 Zeiss /LEICA model.

F. Thermal analysis

1) Thermogravimetry (TG) and DTA

TG and DTA of the grafted polymeric samples were characterized using a Perkin Elmer simultaneous thermal analyzer (TGA/DTA) under nitrogen gas, in the temperature range (50-600 °C) at heating rate ($10 \text{ }^\circ\text{C min}^{-1}$).

2) DSC

The glass transition temperature (T_g) of grafted copolymers was measured on a Perkin-Elmer differential scanning calorimeter (Moder DSC 2010, USA) by heating rate ($10 \text{ }^\circ\text{C/min}$) from 20 to 500 °C, under nitrogen atmosphere. The rate of gas flow was 20 ml/min.

G. Mechanical Properties

The plasticity of the film was measured by recording the rejuvenated temperature (T_r) using dynamic mechanical thermal analysis (DMTA) using a Rheometric Solid Analyzer II (Rheometric Scientific, Piscataway, NJ) under nitrogen atmosphere. The sample was subjected to a small axial force of 5 g and a modulating frequency of 16 Hz and heated at a rate of $5 \text{ }^\circ\text{C/min}$ until the length of the sample was stretched by 0.5 mm. The temperature at which the film was stretched by 0.5 mm was recorded as the rejuvenated temperature (T_r).

H. Wettability

This property was examined by measuring the contact angles of water droplets on the film with video contact angle (VCA 2000 Advanced surface technology, Bil-Lerica MA) at three different locations on the grafted CA film.

III. RESULTS AND DISCUSSION

A. Factors Affecting the Graft Copolymerization

To reach the optimum grafting conditions, the factors affecting the grafting process were studied.

B. Effect of Monomer Concentration

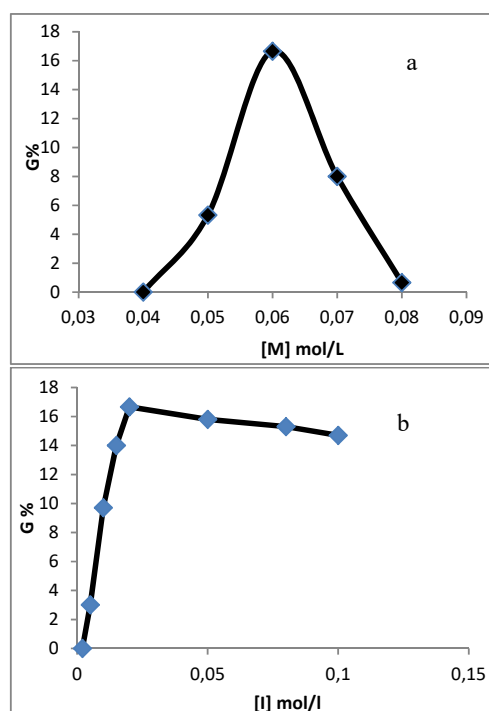
Fig. 1 (a) showed the effect of the monomer concentration on the percentage of grafting at constant temperature (70 °C), initiator (0.02%) for 20 h. The results revealed that the percentage of grafting increased from 0.02% (0.04 mol l^{-1} monomer concentration) to 16.66% (0.06 mol. l^{-1}) followed by a remarkable decrease in the percentage of graft with the further increase in monomer concentration, which might be attributed to homopolymer formation.

C. Effect of Initiator Concentration

It is observed from Fig. 1 (b) that the percentage of graft increased with increasing the initiator concentration up to 0.02 mol. l^{-1} followed by a gradual reduce in %G. This might be due to termination of growing radicals by excess free radicals produced from the decomposition of the initiator molecules.

D. Effect of Temperature

The results shown in Fig. 1 (c) revealed that the increase in temperature up to 70 °C led to a gradual increase in the percentage of graft followed by a gradual decrease in the %G at higher temperature, which indicates that the ceiling temperature of the branch formed was reached.



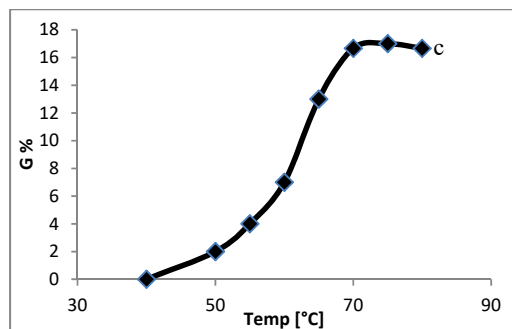


Fig. 1 Factors affecting percentage of graft of APhM onto CA, (a) Effect of APhM concentration [M], [initiator concentration (0.02 mol/l) for 20 h, at 70 °C], (b) Effect of initiator concentration [I], [monomer concentration 0.06 mol/l for 20 h, at 70 °C] and (c) Effect of temperature, [monomer concentration 0.06 mol/l, initiator concentration 0.02 mol/l for 20 h]

E. UV/Vis Spectroscopic Analysis

Investigation of CA-g-APhM in THF by UV/Vis spectroscopy showed a new broad peak at 350- 400 nm as

compared to ungrafted CA. This new peak was attributed to the APhM moieties. Moreover, the increase in the intensity of this peak was found to be proportional to the increase in the graft percentage.

F. ^{13}C -NMR Spectroscopy

^{13}C -NMR spectrum of CA-g-APhM was studied as shown in Fig. 2 and Table I. The spectrum showed the following additional peaks as compared to that of CA.

1. A new peak at 58 ppm indicating the formation of a new bond between nitrogen atom of (-NH) group of APhM and carbon atom (7) of CA.
2. Disappearance of the (C=C) peak at 140 ppm and appearance of the (C-C) peak at 41 ppm indicating the polymerization of APhM comonomers.
3. The peak at (125 ppm) is related to monosubstituted carbon of benzene ring (8).

According to the above-mentioned data, a reaction mechanism for the grafting process was suggested.

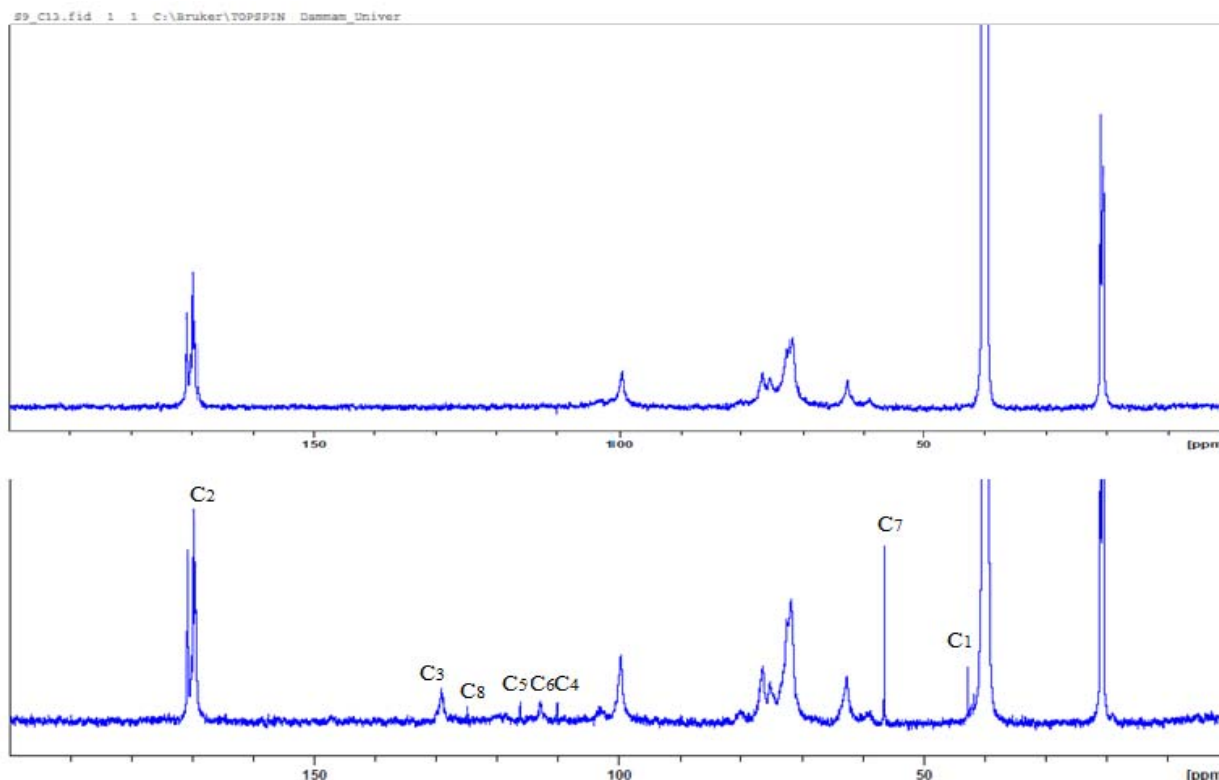


Fig. 2 ^{13}C NMR spectrum of (a) CA and (b) CA-g-APhM (16.66%)

G. Thermal Gravimetry (TG)

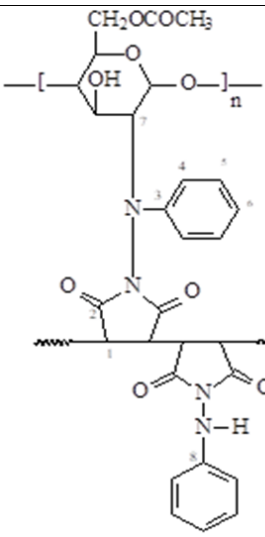
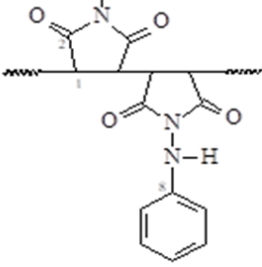
The aim of this work is to produce food packaging CA films able to resist thermal degradation. To reach this goal, the polymer was copolymerized with APhM derivatives.

The thermal stability was investigated using TG. The initial decomposition temperature and total weight loss (wt. loss %)

values of the copolymer samples are shown in Table II. The data revealed that the thermal stability of samples with low percentage of graft (0.02 and 0.66%) exhibited high value of initial decomposition temperature (T_0) (300 and 310 °C) and total weight loss % equal to 83.9 and 83.5% respectively. Conversely, it was found that increasing the percentage of grafting up to 5.33% and 16.66% led to remarkable decrease

in the total weight loss (78.1% and 79.7%, respectively) as compared to CA (89.3%), although these samples exhibited lower (T_o) values as compared to CA.

TABLE I
 ^{13}C NMR CHEMICAL SHIFTS (Δ PPM) CHARACTERISTICS OF (CA-G-APhM) SAMPLE

Structure	Carbon atom	^{13}C -NMR (δ ppm)
	1	41
	2	170
	3	130
	4	110
	5	116
	6	114
	7	58
	8	125

The decrease in the total weight loss % of the grafted samples is attributed to the thermal stability of the Amino phenyl maleimide branches [9], [10] which might wrap around the backbone of CA, supporting it at high temperatures. On other hand, the increase in the length of APhM branches

increases the amorphous regions percentage of the copolymer matrix, thus decreasing the initial decomposition temperature (T_o) from 250 °C for CA to 200 and 210 °C for 5.33 and 16.66% of grafted samples, respectively (Fig. 3).

H.DTA

The DTA curves of CA and its graft copolymer are given in Fig. 4. The results showed that the exothermic peak (T_p) at 388 °C, corresponding to the crystalline region of CA, is shifted to the lowest temperature with the increase in % of graft. High grafting percentage sample (16.6%) showed shift of this peak to lower temperature, (279 °C) while samples with (0.02%) graft exhibited (T_p) value equal to (389 °C) comparable to that of CA (388 °C). Thus, increasing graft percentage would decrease the secondary interaction force between chains leading to amorphous polymer matrix.

I. Dynamic Thermomechanical Properties

It is well known that CA should be plasticized prior to its adjustment to plastic applications [11], otherwise, the mechanical properties of the products will be reduced. T_o investigates the mechanical properties of the grafted samples, the dynamic thermomechanical properties technique was used. The film was exposed to a load of 5 gm and frequency 16 Hz and then heated (rate of 5 °C/ min) until elongation equal to 0.5 mm, this temperature is known as (T_r) rejuvenated temperature. The results in Table II revealed that the value (T_r) decreased with the increase in the percentage of graft to reach 99 °C for CA-g-N-(APhM) maleimides (16.66%) as compared to CA (210 °C) and plasticized CA (198 °C). Thus, the branch built by the grafting process acted also as a plasticizer for the copolymer film.

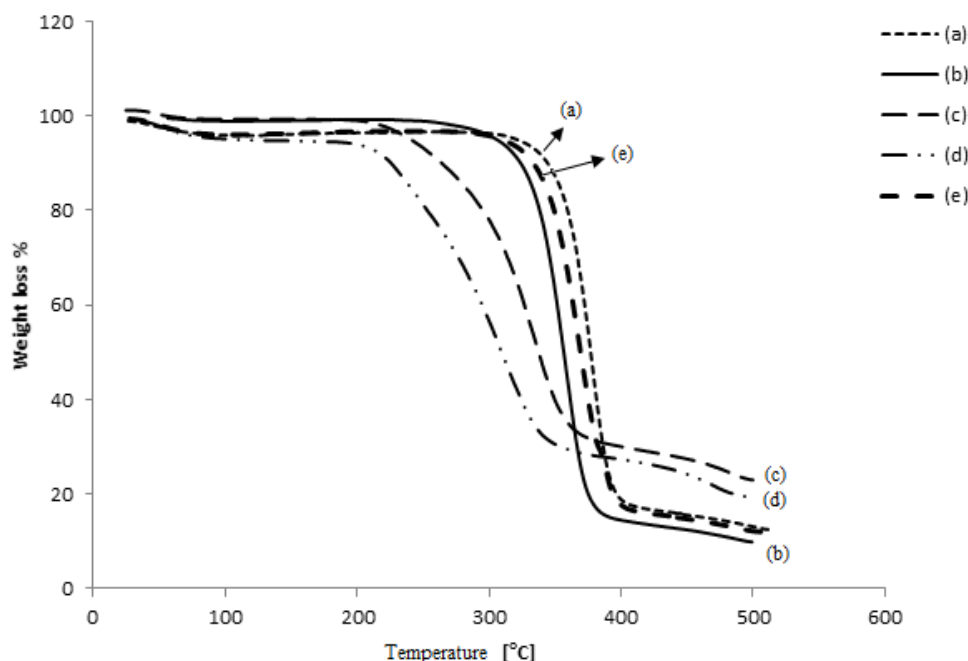


Fig. 3 TG of CA samples grafted with various percentage of APhM (a) 0.66%, (c) 5.33%, (d) 16.66%, (e) 0.02% as compared to that of CA (b)

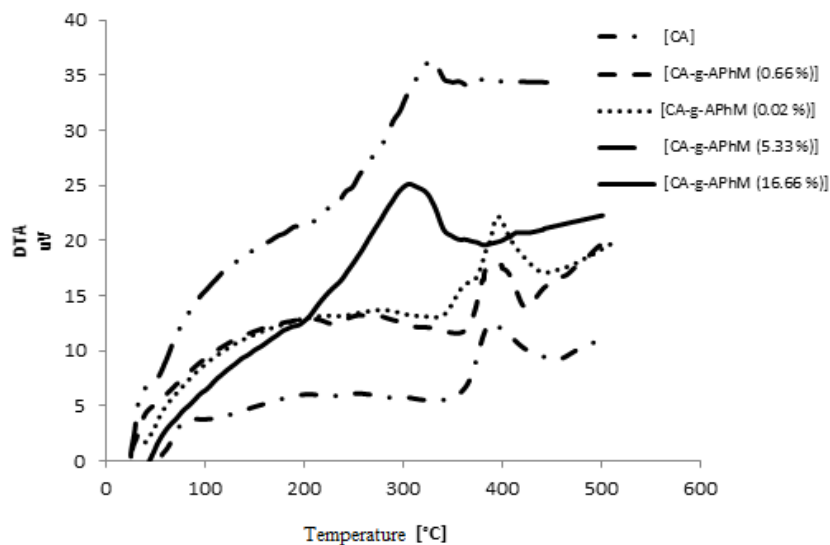


Fig. 4 Effect of percentage of grafting of APhM onto CA on (DTA) as compared to that of CA

TABLE II
EFFECT OF PERCENTAGE OF GRAFT ON THE THERMAL, WETTABILITY AND MECHANICAL PROPERTIES OF CA-G-APhM

Grafted polymer	% of graft	T_o (°C)	Wt. loss (%) at 500°C	T_g (°C)	Contact angle (°)	Rejuvenated temperature (C°) (T_r)
CA	0.00	250	89.3	189.49	64.0	210
	0.02	300	83.92	189.41	62.4	207
CA-g-APhM	0.66	310	83.55	190.1	75.3	220
	5.33	210	78.15	186.2	78.9	127
	16.66	200	79.75	184.1	84.5	99

J. DSC

The data in Table II showed that each graft sample exhibited single (T_g) value different from that of CA. This indicates that a new graft copolymer was formed. Moreover, it was found that (T_g) value decreased with the increase in the percentage of graft. This is attributed to the effect of graft copolymerization on reducing the crystallinity of the polymeric matrix, as increasing the length of APhM branches reduced the intermolecular forces between CA chains.

K. Wettability

The wettability of various samples of (CA-g-APhM) films was examined by measuring the contact angle of water droplets on each film (Table II). The results indicated that the CA graft copolymer films exhibited higher contact angles than ungrafted CA film. This might be attributed to the presence of organic branches of poly (APhM) through the backbone of CA. Moreover, increasing the percentage of graft leading to high contact angle value. The maximum value of contact angle (84.5°) corresponds to the highest percentage of graft samples (16.66%).

L. Morphological Characterization

Examination of the morphology of CA (a) and CA grafted with APhM (16.66%) sample (b) by ESEM showed the grafted regions well distinct over the semicrystalline matrix of CA (Fig. 5).

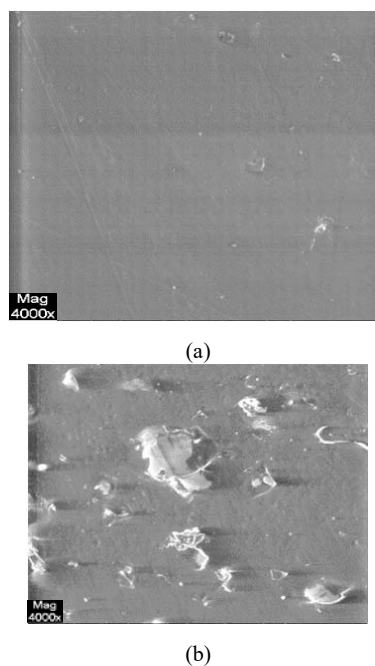


Fig. 5 ESEM morphology of polymeric film (a) CA and (b) CA-g-APhM (16.66%)

IV. CONCLUSION

Graft copolymerization of APhM onto CA showed an

effective role in reducing the wettability of CA to permit the adjustment of the resulting copolymer to food packaging industry. The effect of reaction parameters, such as monomer concentration, initiator concentration and temperature on the percentage of graft were studied.

The structure of the graft copolymer was confirmed by ^{13}C -NMR spectroscopy. Moreover, the presence of the comonomer moieties led to a remarkable improvement in the thermal stability of the graft copolymer as compared to undrafted CA. Furthermore, the graft copolymer films exhibited lower Tg value as compared to CA film which improved its stretching ability.

REFERENCES

- [1] A. K. Mohanty, A. Wibowo, M. Misra and L. T. Drzal, "Development of renewable resource-based cellulose acetate bioplastic: Effect of process engineering on the performance of cellulosic plastics," *Polym. Eng. & sci.*, Vol. 43 (5), pp. 1151-1161, 2003.
- [2] V. Thakur and S. Voicu, "Recent advances in cellulose and chitosan based membranes for water purification: A concise review," *Carbohydr. Polym.*, Vol. 146, pp. 148-165, 2016.
- [3] L. S. Nair and C. T. Laurencin, "Biodegradable polymers as biomaterials," *Prog. Polym. Sci.*, Vol. 32 (8-9), pp.762-798, 2007.
- [4] D. Briassoulis, "An Overview on the Mechanical Behaviour of Biodegradable Agricultural Films," *J. Polym. Env. Vol. 12 (2)*, 65-81, 2004.
- [5] H. Kamal and F.M. Abd-Elrahimb and S. Lotfy, "Characterization and some properties of cellulose acetate-co-polyethylene oxide blends prepared by the use of gamma irradiation," *J. Rad. Res. Appl. Sci.*, Vol.7 (2), pp.146-153, 2014.
- [6] R. Chandra and R. Rustgi, *Biodegradable polymers. Progress in Polymer Science*, 23 (7), pp. 1273-1335, 1998.
- [7] A. S. Abdel-Naby and S. A. Aboubshait, "Cellulose acetate blends with acrylonitrile/N-phenyl maleimide copolymers morphological and thermal properties". *J. Therm. Anal. Calor.*, Vol. 114 (3), pp. 1279–1286, 2013.
- [8] A. S. Abdel-Naby and A. A. Al-Ghamdi, "Chemical modification of cellulose acetate by N-(phenyl amino) maleimides: Characterization and properties," *Int. J. Biol. Macromol.*, Vol. 68, pp. 21–27, 2014.
- [9] A. S. Abdel-Naby and A. O. Al-Dossary, Use of N-(N0-Arylamino) maleimides to Improve theThermal Properties of Poly (vinyl chloride) Through Chemical Modification and Graft Copolymerization. *J. Vinyl. Addit. Technol.* Vol. 14 (4), pp. 167-174, 2008.
- [10] Abdel-Naby, A. S. and A. O. Al-Dossary, Stabilization of poly (vinyl chloride) against photo-degradation using dienophilic compounds. *J. Appl. Polym. Sci.* Vol. 114, pp. 3218–3228, 2009.
- [11] O. A. Fridman and A. V. Sorokina. Criteria of efficiency of cellulose acetate plasticization. *Polym. Sci. ser. B.* Vol. 48 (9-10), pp. 233-236, 2006.