

# Graft Copolymerization of Cellulose Acetate with Nitro-N-Amino Phenyl Maleimides

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**Abstract**—The construction of Nitro -N-amino phenyl maleimide branches onto Cellulose acetate (CA) substrate by free radical graft copolymerization using benzoyl peroxide as initiator led to formation of highly thermal stable copolymers as shown from the results of gravimetric analysis (TGA). CA-g-2,4-dinitro amino phenyl maleimide exhibited higher thermal stability than the CA-g-4-nitro amino phenyl maleimide as shown from the initial decomposition temperature ( $T_0$ ). This is due to the ability of nitro group to form hydrogen bonding with hydroxyl group of the glucopyranose ring which increases the crystallinity of polymeric matrix. The crystalline shapes representing the graft part are clearly distinct in the Emission scanning electron microscope (ESEM) morphology of the copolymer. A suggested reaction mechanism for the grafting process was also discussed.

**Keywords**—Cellulose acetate, crystallinity, graft copolymerization, thermal properties.

## I. INTRODUCTION

THE extensive use of biodegradable polymers in various applications, rather than the synthetic macromolecular materials increased in our daily life as a great demand of the environment. Some of these applications are fiber applications [1], [2].

Biomaterials such as cellulose based polymers suffer from poor heat stability as well as high water permeability [3], [4].

To adjust the biopolymeric materials to fiber applications, various techniques were used to achieve this goal. Blending technique is the simplest one [5]. However, the compatibility of the blend polymers in various compositions is a serious challenge facing this technique. Graft copolymerization of the biomacromolecules is the most chemical modification technique used for the improvement of thermal and mechanical properties of these biodegradable polymers [6].

Cellulose acetate is a semicrystalline biodegradable polymers. It is widely used in plastic applications. However, the low thermal stability of high temperature limits the use of such biodegradable polymer in fiber applications.

The maleimide derivatives are known to be highly thermal stable compounds [7], [8] and are widely used in chemical modification of polyvinyl chloride and cellulose acetate for plastic applications.

In the present work, graft copolymerization of cellulose acetate by thermal stable monomer moieties, mono and di-

nitro aminophenyl maleimide will be synthesized. The thermal property of various graft copolymers will be investigated.

## II. EXPERIMENTAL

### A. Materials

Cellulose acetate (CA) was purchased from (Aldrich) with average molecular weight 100,000 and acetyl content 39.8 %. Benzoyl peroxide, 4- nitrophenyl hydrazine and 2,4-dinitro phenyl hydrazine were obtained from (Aldrich). Sodium acetate anhydrous and Acetic anhydride were obtained from (BDH). Maleic anhydride was purchased from (Acros).

Tetrahydrofuran (THF) is used after distillation and all other reagents and solvents were used without any further distillation. The other reagents were used as received without further purification.

### B. Synthesis of N-(Amino Phenyl) Maleimide

N-(Amino phenyl) maleimides derivatives were prepared according to the method described by Abdel-Naby from cyclocondensation of maleic anhydride and the phenyl hydrazine. The recorded melting point are (254 °C) for 4-(NO<sub>2</sub>) APhM and (175 °C) for 2,4-di (NO<sub>2</sub>) APhM [8], [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). N-(Amino phenyl) maleimide derivative 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 [8].

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 the following relation:

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

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

### D. Preparation of Graft Copolymer Films

The grafted films were prepared by dissolving the copolymer 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).

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### E. Characterization

#### 1. $^{13}\text{C}$ -NMR Analysis

The  $^{13}\text{C}$ -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  $\text{CDCl}_3$  are the solvents used.

#### 2. Emission Scanning Electron Microscope (ESEM)

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

#### 3. Thermal Analysis

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

## III. RESULTS AND DISCUSSION

To reach the optimum grafting conditions, the factors affecting the graft copolymerization were studied. The suitable initiator percentage does not exceed (0.02%) to avoid termination of growing radicals by excess free radicals produced from decomposition of the initiator molecules. The temperature was adjusted at (70  $^{\circ}\text{C}$ ) to prevent the ceiling temperature of the branch formed to be reached. Moreover, the comonomer concentration was chosen to be (0.02 mol.  $\text{l}^{-1}$ ). High concentration of comonomer might led to the formation of high percentage of homopolymers.

### A. Characterization of the Graft Copolymers

$^{13}\text{C}$ -NMR spectroscopy was the main tool used to characterize the structure of the synthesized copolymer of CA modified by 4-( $\text{NO}_2$ ) APhM (Fig. 1 and Table I) [7].

TABLE I

$^{13}\text{C}$ -NMR SPECTRAL CHARACTERISTIC DATA OF CA- 4-( $\text{NO}_2$ ) APhM MODIFIED POLYMER [7]

Structure	Carbon atom	$^{13}\text{C}$ -NMR ( $\delta$ ppm)
	1	141
	2	168
	3	150
	4	113
	5	126
	6	144
	7	52.1

The presence of nitro group in phenyl ring enhanced the ionization of imine group (as shown in Fig. 3).

The  $^{13}\text{C}$ -NMR spectral data confirm illustrated suggested sites for the reaction of 4- $\text{NO}_2$  (APhM) and acetate group of glucopyranose ring (as shown in Fig. 3).

The results showed the following:

1. A new peak at (52.1 ppm) confirming the bond formation between nitrogen atom of the imino (-NH) of comonomer and carbon (C7) of glucopyranose of cellulose acetate

after losing the acetate group.

2. The ethylenic bond ( $\text{C}=\text{C}$ ) of maleimide moiety is kept unchanged during the chemical modification at (141ppm) [7]. This enhanced the grafting process (Fig. 3).
3. Appearance of peak in the aromatic region (146.9 ppm) confirming the presence of aromatic ring of aminophenyl maleimide moieties.

The confirmation of the grafting copolymerization was indicated by disappearance of peak corresponding to ethylenic double bond as shown in Fig. 3 and Table II.

It is well known that the acetylation of cellulose to form cellulose acetate occurs at position C2 and C6 of glucopyranose ring.

The results of C-g-4-( $\text{NO}_2$ )APhM revealed that the monomer moiety replaced the acetate group at position 2 of the glucopyranose ring of cellulose acetate (Fig. 3), unlike modification of CA by the 4-( $\text{NO}_2$ )APhM, the CA-g-2,4-di( $\text{NO}_2$ )APhM showed replacement of acetate group in both position C2 and C6 of glucopyranose ring (Figs. 4 and 5, Tables II and III).

### B. Morphology

The examination of the products of both the modified and grafted products by ESEM are shown in Fig. 6. The difference between chemical modification product (Fig. 2) and that of graft copolymer (Fig. 4) is clearly distinct.

The modified surface morphology (Fig. 6 (b)) [7] shows crystal formation which confirm the ability of nitro groups in the comonomer moieties to perform hydrogen bonding with hydroxyl groups of glucopyranose rings (Fig. 7) [7].

TABLE II  
 $^{13}\text{C}$ -NMR CHEMICAL SHIFTS ( $\Delta$  PPM) CHARACTERISTICS OF [CA-G-4-( $\text{NO}_2$ ) APhM] SAMPLE

Structure	Carbon atom	$^{13}\text{C}$ -NMR ( $\delta$ ppm)
	1	41.7
	2	169.4
	3	149.4
	4	108.0
	5	125.4
	6	140.7
	7	56.9
	8	146.9

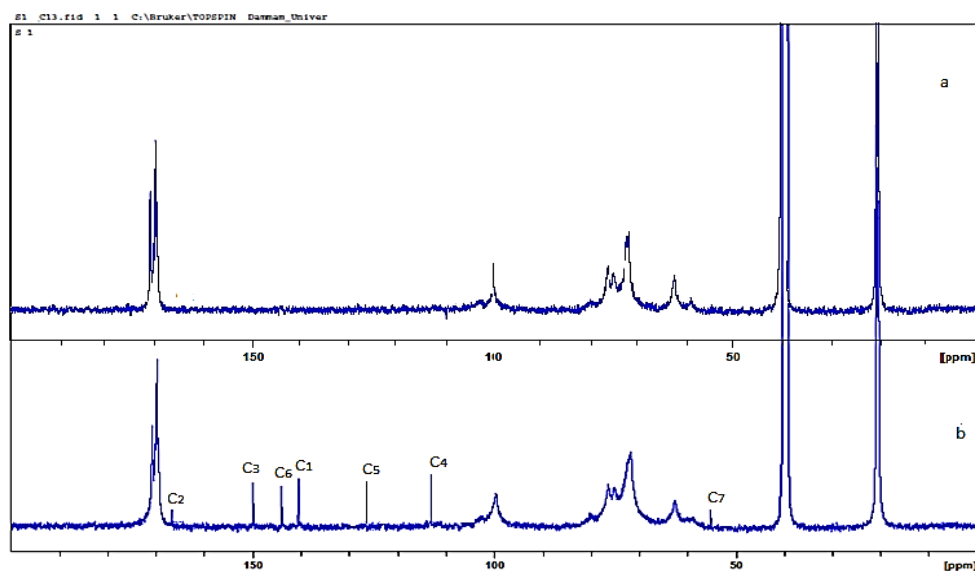


Fig. 1  $^{13}\text{C}$ -NMR spectral characteristics of (a) CA and (b) CA modified by 4-(NO<sub>2</sub>) PhAM [7]

Dr. Azza Abdullah Alghamdi  
 Sample: 65 DMSO:CDCL<sub>3</sub> Dammam Uni.  
 @C13\_NS256\_KAAU DMSO (D:\outside) jaber 5

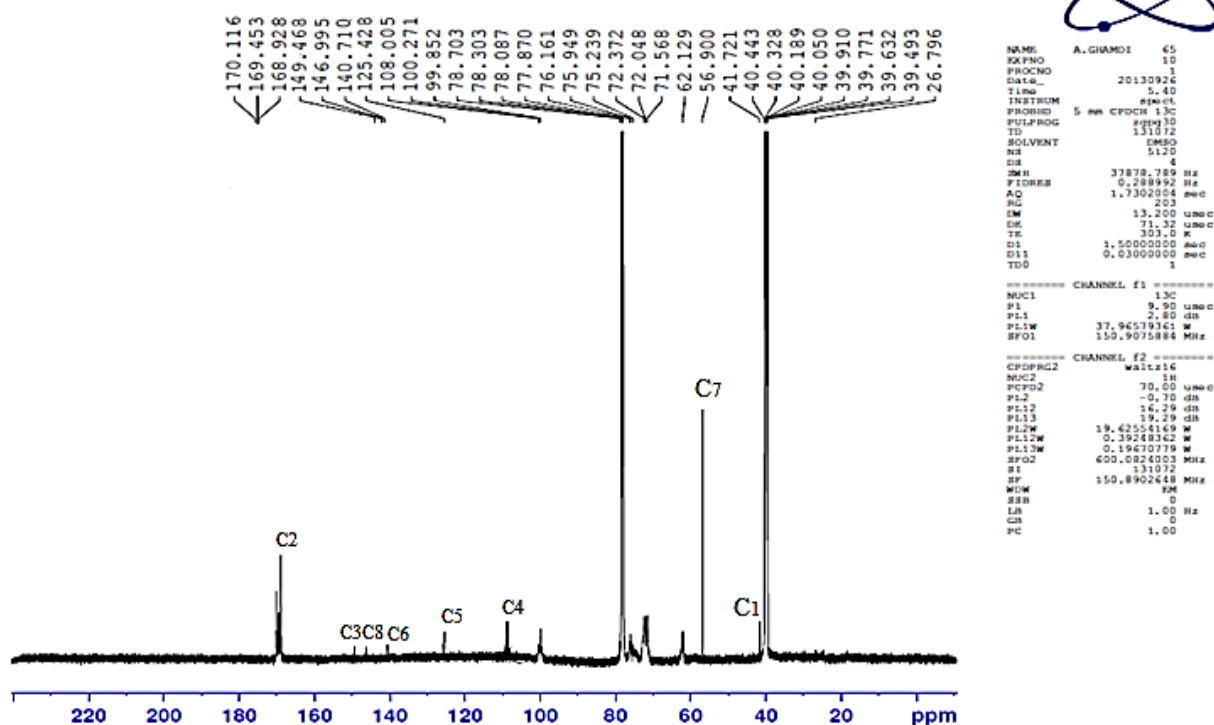


Fig. 2  $^{13}\text{C}$ -NMR spectrum of CA-g-4-(NO<sub>2</sub>) APHM

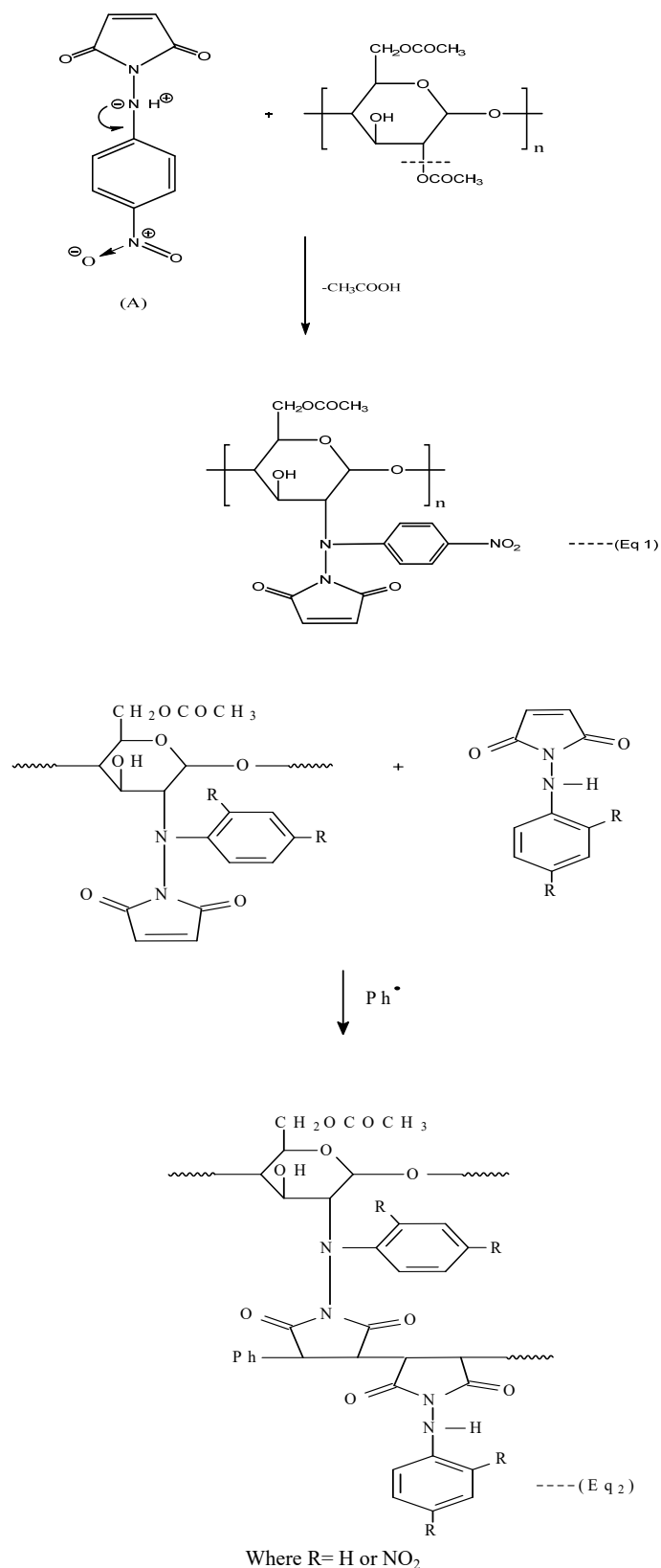
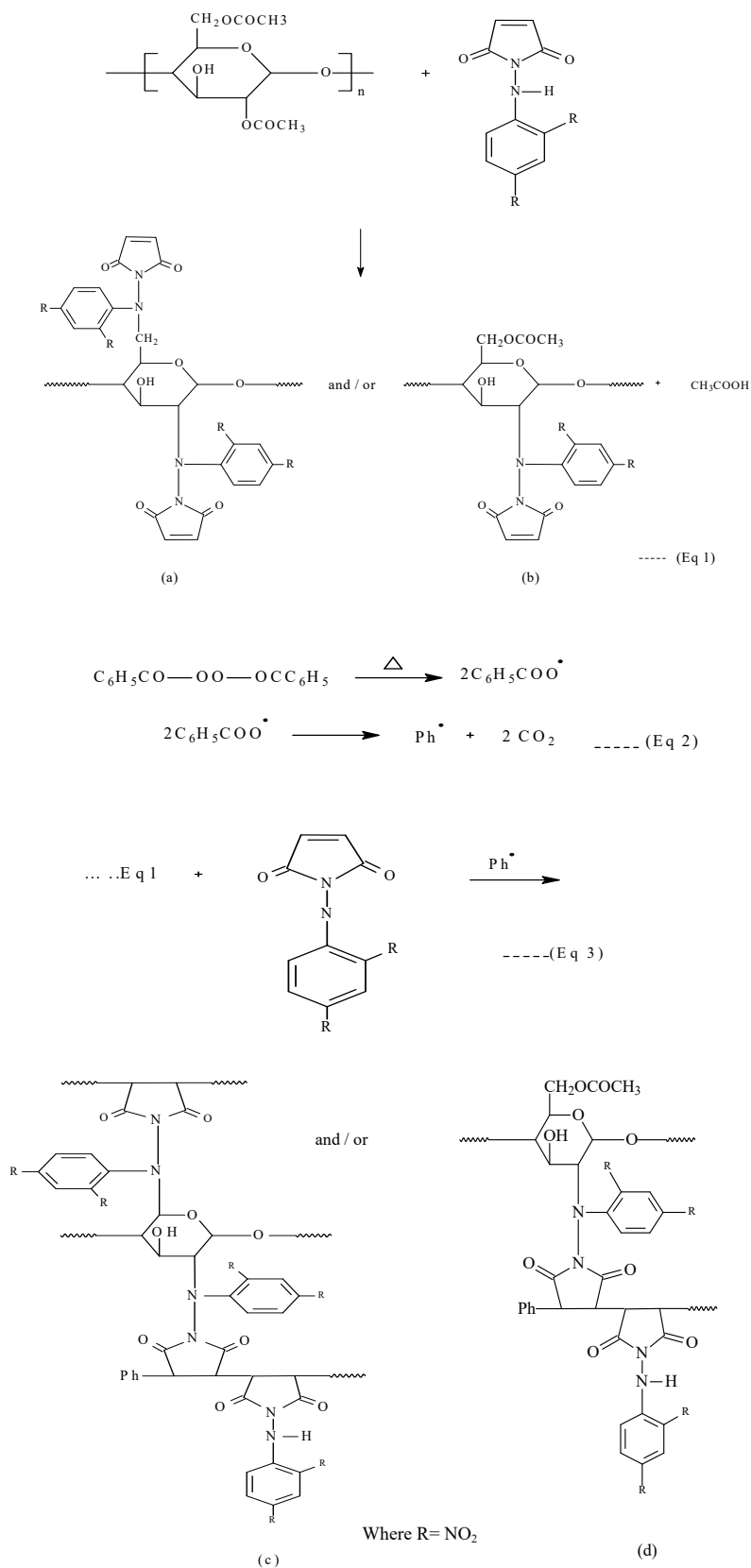


Fig. 3 Suggested reaction mechanism of the grafting process of APhM derivatives onto cellulose acetate

Fig. 4 Suggested reaction mechanism of the grafting process of 2,4-di (NO<sub>2</sub>)PhAM onto cellulose acetate

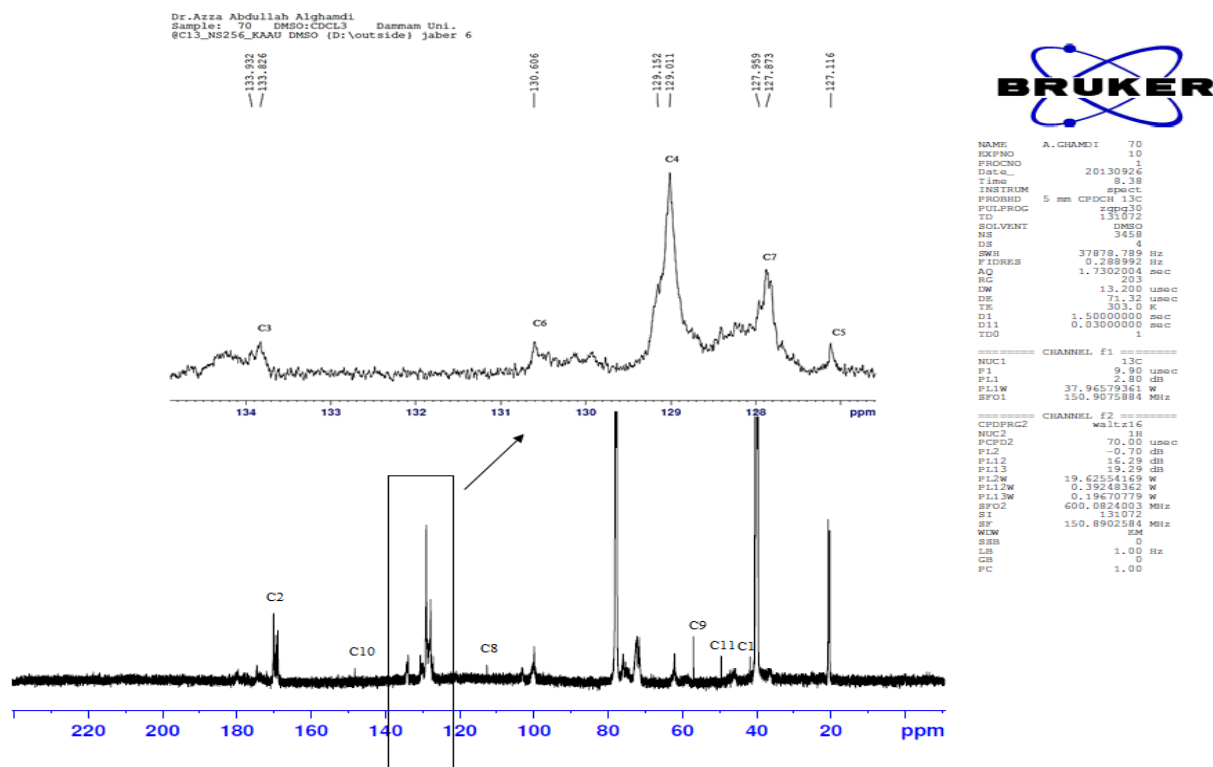
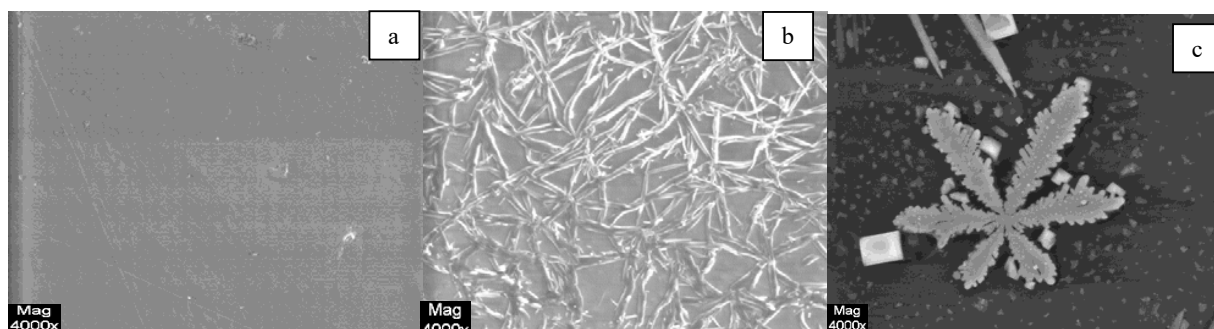
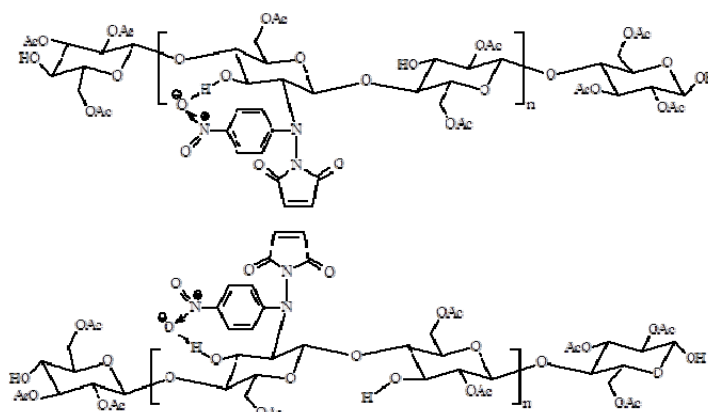
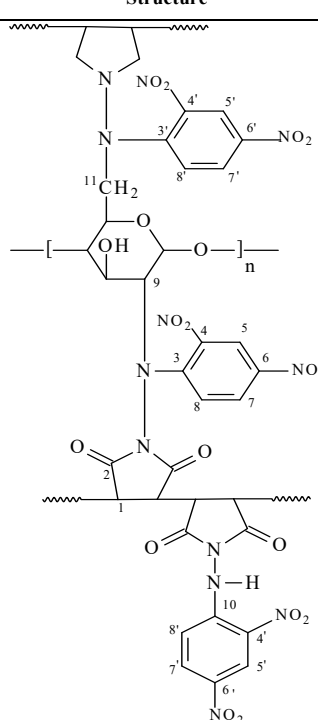
Fig. 5 <sup>13</sup>C-NMR spectrum of CA-g-2,4-di(NO<sub>2</sub>)APhMFig. 6 ESEM morphology of polymeric film (a) CA and (b) CA modified by 4-(NO<sub>2</sub>) APhM [7] (c) CA grafted by 2,4-di (NO<sub>2</sub>)APhM

Fig. 7 Schematic representation showing the formation of hydrogen bonding between the nitro groups of monomer moieties and cellulose acetate [7]

TABLE III  
<sup>13</sup>C-NMR CHEMICAL SHIFTS (δ PPM) CHARACTERISTICS OF [CA-g-2,4-di(NO<sub>2</sub>)APhM] SAMPLE

Structure	Carbon atom	<sup>13</sup> C-NMR (δ ppm)
	1	41.7
	2	169.4
	3	132.5
	4	129.1
	5	127.1
	6	130.6
	7	127.8
	8	112.6
	9	57.0
	10	148.2
	11	49.5

### C. Thermal Properties

The thermal properties of the CA-g-4-(NO<sub>2</sub>)APhM and CA-g-2,4-(di-NO<sub>2</sub>)APhM copolymers were investigated using Thermogravimetry. The results are illustrated in Fig. 8 and Table IV.

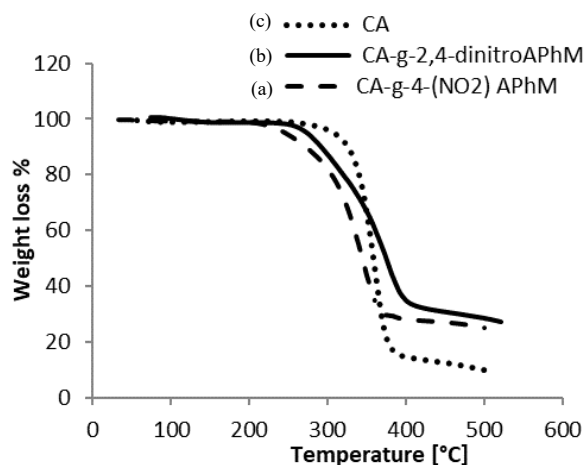


Fig. 8 Thermogravimetry (TG) of CA grafted with (a) 4-(NO<sub>2</sub>)APhM 6.66 % and (b) 2,4-di (NO<sub>2</sub>) APhM 20 % as compared that of CA (c)

The results of thermogravimetry of CA-g-4-(NO<sub>2</sub>)APhM revealed that the increase in percentage of graft led to slight decrease in an initial decomposition temperature (T<sub>0</sub>), this

might be attributed to the decrease in crystallinity of the polymeric matrix due to the increase in the number and length of the branches built by the graft process. However, the increase in percentage of graft led to decrease in weight loss percentage at high temperature. This might be the probability of the long branches to wrap around the CA backbone protecting it from degradation at high temperatures.

The results revealed that CA-g-2,4-di(NO<sub>2</sub>)APhM exhibited high thermal stability than CA-g-4-(NO<sub>2</sub>)APhM as shown from its higher (T<sub>0</sub>) value and lower weight loss percentage. The reasonable explanation of the higher thermal stability of CA-g-2,4-di(NO<sub>2</sub>)APhM is the presence of two nitro groups in each repeating unit, rather than one only for CA-g-4-(NO<sub>2</sub>)APhM, capable to undergo hydrogen bonding which hydroxyl groups of glucopyranose ring as shown in (Fig. 7) which increase the ordering of the polymeric matrix. This explanation agrees with the appearance of well distinguish crystals in ESEM (Fig. 6).

TABLE IV  
 THERMAL ANALYSIS OF CA SAMPLES GRAFTED BY N-(PHENYL AMINO) MALEIMIDE DERIVATIVES [MONOMER CONCENTRATION 0.06MOL/L, INITIATOR CONCENTRATION 0.02 MOL/L AT 70 °C FOR 20 H]

Graft copolymers	Degree of graft	T <sub>0</sub>	Wt loss (%) at 500°C
CA	250		89.3
CA-g-4(NO <sub>2</sub> )APhM	6.66 %	220	75.3
CA-g-2,4-di(NO <sub>2</sub> )APhM	20 %	235	71.7

### IV. CONCLUSION

The graft copolymerization of cellulose acetate with 4-nitro amino phenyl maleimide and 2,4-dinitro amino phenyl maleimide led to decrease the percentage of total weight loss at (500 °C). The CA-g-2,4-di(NO<sub>2</sub>)APhM copolymer exhibited higher thermal stability than the CA-g-4-(NO<sub>2</sub>)APhM as shown from their initial decomposition temperature (T<sub>0</sub>) and weight loss percentage at high temperatures. The extra thermal stability of CA grafted by dinitro derivative was attributed to the replacement of the acetate groups at two positions (C2 and C6) per unit. The copolymerization with 4-(NO<sub>2</sub>)APhM was occurred only for the acetate group at position 2.

The nitro groups possess the ability to perform hydrogen bonds with hydroxyl groups of glucopyranose ring. These hydrogen bonds enhanced the order of the polymeric matrix, thus offering more crystalline parts as shown in the ESEM morphology. Thus the ordering of the polymeric matrix is considered as the main reason for the highest thermal stability of CA-g-2,4-di(NO<sub>2</sub>)APhM as compared to that the CA-g-4-(NO<sub>2</sub>)APhM.

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