

# Characterization and Thermal Stability of Cellulose-graft-Polyacrylonitrile Prepared by Using $\text{KMnO}_4$ /Citric Acid Redox System

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**ABSTRACT:** An effective condition of graft polymerization of acrylonitrile onto cellulose fiber in large volume of  $\text{KMnO}_4$ /citric acid aqueous solution was examined and the produced grafted copolymers were characterized by using SEM, NMR, FTIR, XRD, TGA, and DSC in comparison with component homopolymers. Graft yield, GY, obtained by simple weighting method was close to the value obtained by NMR analysis. Significant change of chemical structure in cellulose fiber, other than graft reaction, was not detected by NMR and FTIR measurements, whereas a decrease in the degree of crystallinity by the reaction was detected by XRD measurement. It was

pointed out that thermograms for grafted samples resembles with that of cellulose at  $T < 370^\circ\text{C}$  and become similar with that for polyacrylonitrile at  $T > 370^\circ\text{C}$  and the mass of residue at  $550^\circ\text{C}$  is proportional to the content of polyacrylonitrile (GY) only. It is concluded that thermal decomposition of both polymers occurs almost independently in grafted polymers and thermal stability of cellulose fiber is not improved. © 2010 Wiley Periodicals, Inc. *J Appl Polym Sci* 116: 1788–1795, 2010

**Key words:** cellulose; graft polymerization; polyacrylonitrile; redox initiation; thermal stability

## INTRODUCTION

Cellulose is one of the most popular natural polymers, which has been widely used in industries and daily lives. To further expand the industrial applications of the cellulose, modification methods of physical and chemical properties of the cellulose have been continuously studied to investigate the required properties.<sup>1–5</sup> Graft copolymerization of vinyl polymers onto cellulose is one of the most extensively studied procedures. Graft copolymerization can be initiated by transition metal ions such as, Ce(IV), Mn(IV), V(V), Cr(III), Cd(II), etc.<sup>6–9</sup> via free radical formation. Among them, Ce(IV) is known as the most efficient one but its higher price and restriction of acid reactant medium limit its wide applications. As another efficient initiating reagent, potassium permanganate ( $\text{KMnO}_4$ ) has been studied<sup>10</sup> for the graft copolymerization of cellulose. Acrylonitrile (AN) is the most frequently tested monomer due to its

highest efficiency<sup>11,12</sup> and further possibility for modification such as alkaline hydrolysis.<sup>11,13</sup>

Graft polymerizations of AN onto cellulose by using  $\text{KMnO}_4$ /thioacetamide<sup>14</sup> and  $\text{KMnO}_4$ /strong acids, e.g., sulphoric acid, hydrochloric acid, perchloric acid, and nitric acid have been reported.<sup>15–17</sup> In these studies, however, no systematic characterization of products was reported. It was reported that thermal resistance of the grafted copolymer was improved.<sup>18–22</sup> In these studies too, characterization of samples are not enough or thermal analysis data are not fully compared with component homopolymers, i.e., cellulose and polyacrylonitrile. Thus the details of change in the thermal properties of grafted copolymers are not well understood. In addition to the aforementioned uncertainty, it is speculated that strong acids may severely damage the cellulose during the reaction so that milder condition would be preferable. However,  $\text{KMnO}_4$ /weak acid systems have not been well studied yet, compared to the aforementioned studies using  $\text{KMnO}_4$ /strong acid systems.

In this work, we report an efficient reaction condition for preparation of cellulose-graft-polyacrylonitrile prepared by using  $\text{KMnO}_4$ /citric acid as initiator, which was efficient for grafting reaction of methyl methacrylate onto cotton fabric.<sup>23</sup> The grafted

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products are examined by scanning electron microscope (SEM) and characterized by using IR spectroscopy, solid-state NMR, and X-ray diffraction (XRD). Thermal resistance of grafted cellulose with different graft yields are analyzed by thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) in comparison with the data for component homopolymers.

## EXPERIMENTAL

### Materials

Bleached Egyptian cotton samples (75 g/m<sup>2</sup>), warp 33 threads/cm, weft 32 threads/cm, supplied by El-Mahalla Company for Spinning and Weaving, Egypt, and was used as received. Acrylonitrile (Aldrich) was purified by distillation, while following reagent grade chemicals are used as received; potassium permanganate and dimethylformamide (DMF) (Kishida Chemical Co., Japan), citric acid and sodium hydroxide (El-Naser Pharmaceutical Chemical Company, Egypt), acetic acid and methanol (Wako Pure Chemical Industries, Japan). Distilled water was used throughout this work.

Mercerized cellulose was prepared by the following method. Fabric samples were treated in a tensionless state with 30 wt % NaOH for 15 min at 20°C.<sup>24</sup> Afterwards, the samples were washed with distilled water (70°C) and then acidified with 2% acetic acid and rinsed again with distilled water. Finally, the samples were air dried at room temperature. The same procedure was repeated for three or four times to prepare differently treated mercerized cellulose samples.

### Graft copolymerization

One gram of cotton cellulose was impregnated in KMnO<sub>4</sub> aqueous solution ([KMnO<sub>4</sub>] = 0.05 mol/L). The cellulose material to liquid ratio (*M* : *L*) was kept at 1 : 100 (wt : vol). The treatment was performed at 60°C for 30 min under continuous shaking. Then the sample was washed several times with distilled water.

Graft copolymerization was performed in a reaction flask kept in a thermostatic water bath. By fixing *M* : *L* = 1 : 100 as in the most of other studies, efficiency of graft copolymerization of pretreated cotton cellulose was examined under the following conditions; AN monomer: [AN] = 2–10 vol % (0.3–1.5 mol/L), [KMnO<sub>4</sub>] = 0.005–0.100 mol/L, [citric acid] = 0.01–0.1 mol/L, temperature: *T* = 30–90°C, for different reaction time intervals. After the desired reaction time, the sample was removed from flask and washed with distilled water several times to remove unreacted monomer and dried to constant

weight at 50°C. Polyacrylonitrile homopolymer (h-PAN) was extracted from the product by soaking into water and DMF for about 30 h at 35°C and finally pure cellulose-*graft*-polyacrylonitrile (C-*g*-PAN) was obtained. The extracted h-PAN was precipitated into methanol and dried to constant weight and used to estimate the grafting parameters.

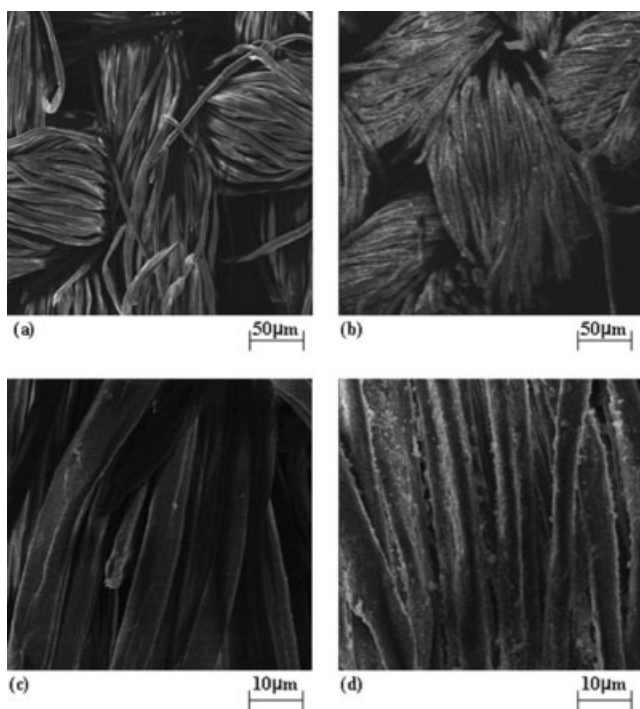
### Measurements

SEM micrographs of the untreated and the grafted cellulose fibers, coated with platinum by means of Hitachi E-1030 ion sputter apparatus, were taken by Hitachi S-4100 scanning electron microscope at an accelerating voltage of 10 kV. IR spectra were recorded with Bio-Rad FTS 6000 spectrometer with 32 scans at the highest resolution of 2 cm<sup>-1</sup>. Approximately 1.0 mg of sample was pressed onto potassium bromide as a thin film (about 10 μm). The XRD measurements were performed with Rigaku RINT2100H/KLC X-ray diffraction instrument with Ni-filtered Cu Kα radiation at room temperature.

Solid-state NMR experiments were conducted at two facilities, Tokyo Institute of Technology and Kyushu University with following conditions. The measurements for untreated cellulose and the most efficiently grafted sample are performed by using a Bruker DSX 300 spectrometer (*B*<sub>0</sub> = 7T) with a <sup>13</sup>C resonance frequency of 75.48 MHz at Tokyo Institute of Technology under magic-angle spinning (MAS) condition at ambient temperature. Zirconia rotors (4 mm φ) with Kel-F caps were used to hold the samples. Fifteen kilohertz spinning speed and decoupling with two-pulse phase modulation (TPPM) at  $\gamma B_1/2\pi = 62.5$  kHz were utilized. For cross-polarization (CP/MAS) measurements, a 1H 90° pulse length of 4 μs and a contact time of 0.5 ms were applied, and the pulse sequence for total suppression of spinning side bands was utilized to suppress the side bands caused by MAS when desired.

For other samples and untreated cellulose, the measurements were performed by using Delta2-NMR spectrometer (*B*<sub>0</sub> = 9.4T) with resonance frequency of 100.52 MHz at Kyushu University. Zirconia rotors (6 mm φ) with Aurum tube cape were used to hold samples. Fifteen kilohertz spinning speed and decoupling with TPPM at  $\gamma B_1/2P = 100$  kHz were utilized. For CP/MAS measurements, a 1H 90° pulse length of 5.25 μs and a contact time of 0.5 ms were applied. Note that the consistency of the data at two different instruments/conditions was confirmed by comparing the data of untreated cellulose.

DSC measurements were performed using Seiko DSC-6220 with TAS100 controller in a temperature



**Figure 1** SEM micrographs of untreated cellulose (a,c) and C-g-PAN69 (b,d).

range of 25–450°C. The standard heating rate of 10°C/min was used under dry nitrogen atmosphere for sample mass of about 1.0 mg. TGA was performed by a Seiko TG/DTA6300 in nitrogen atmosphere. The samples (1.1–1.4 mg) were heated from 20 to 600°C at a heating rate of 10°C/min.

## RESULTS AND DISCUSSIONS

### Morphology

SEM micrographs were taken at different magnifications (200×, 1000×) as shown in Figure 1. As the grafted PAN only partially covered the cellulose surface, the morphological characteristics of cellulose are still visible in the grafted samples. It can be seen that the smooth surface of cellulose fibers changed into rough ones with the small clusters of the PAN attached to the surface after graft copolymerization.

### Efficient reaction condition

Efficiency of reaction conditions are examined by weighing methods, which was consistent with NMR analysis shown later. As the total conversion of AN monomer was roughly constant (about 10%) in all the experiments, we compare the efficiency of reaction conditions by two parameters, graft yield (GY) and grafting efficiency (GE), denoting percentage of increased weight of sample after the reaction and percentage of grafted PAN in the total amount of

produced PAN, respectively, calculated by following equations.

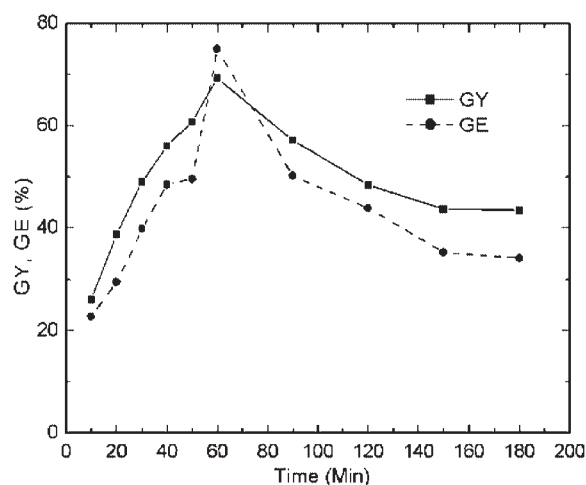
$$\text{GY}(\%) = (W_2 - W_1)/W_1 \times 100$$

$$\text{GE}(\%) = W_4/(W_3 + W_4) \times 100$$

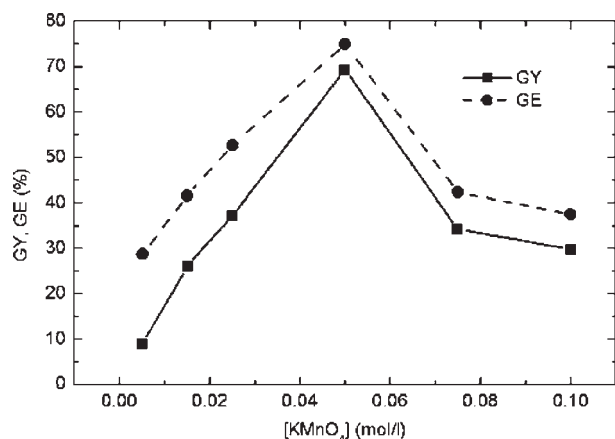
where  $W_1$  is the weight of initial cellulose,  $W_2$  is dry weight of grafted cellulose,  $W_3$  is weight of extracted h-PAN, and  $W_4$  is weight of grafted PAN in the sample.

First, the influence of the temperature was examined at  $T = 30\text{--}90^\circ\text{C}$  and found that both GY and GE have maximum at around  $70^\circ\text{C}$ , irrespective of other conditions. The effect of [AN] was examined at  $70^\circ\text{C}$  and found that both GY and GE increased up to 8% (1.2 mol/L) then become almost constant at higher concentrations. Thus, other conditions were examined at  $70^\circ\text{C}$  and [AN] = 10 vol %. Figure 2 presents reaction time dependencies of GY and GE. It is evident that GY and GE have maximum at 60 min. The effect of the  $[\text{KMnO}_4]$  on GY and GE is shown in Figure 3. Both GY and GE showed a maximum at around 0.05 mol/L. Also, [citric acid] showed a maximum at 0.02 mol/L. We speculate that at highly activated conditions, that is, higher  $T$  and higher  $[\text{KMnO}_4]$  and [citric acid], side reactions such as homopolymerization and chain-transfer reactions are more activated than graft copolymerization, resulting in respective peak condition.

From aforementioned results, the most efficient condition of graft copolymerization at fixed  $M : L = 1 : 100$  was determined as  $[\text{KMnO}_4] = 0.05$  mol/L, [citric acid] = 0.02 mol/L, [AN] = 10 vol % (1.5 mol/L),  $T = 70^\circ\text{C}$ , and time = 60 min. A sample with  $\text{GY} = 69.3\%$  was obtained at the



**Figure 2** Effect of time on the grafting parameters obtained at a condition  $[\text{KMnO}_4] = 0.05$  mol/L,  $M : L$  ratio = 1 : 100, temperature =  $70^\circ\text{C}$ , monomer [AN] = 1.5 mol/L, and [citric acid] = 0.02 mol/L.



**Figure 3** Effect of  $\text{KMnO}_4$  concentration on the grafting parameters tested at reaction time of 60 min. other conditions are the same of Figure 2.

mentioned condition. Samples with lower GY are prepared at lower [AN]. Grafted copolymers from mercerized cellulose (Mer-C-*g*-PAN) are also prepared by the mentioned condition. GY and GE values of all the samples are tabulated in Table I. Hereafter; samples are distinguished by using GY values (eg. C-*g*-PAN69 for sample with GY = 69.3 %).

### Characterizations of grafted cellulose

To obtain GY (%) more precisely,  $^{13}\text{C}$  CP MAS NMR spectra are analyzed following the literatures.<sup>25–30</sup> In Figure 4, the  $^{13}\text{C}$  CP MAS NMR spectra of grafted cellulose samples are shown with the fully assigned spectrum of untreated cellulose (Un-C).<sup>30</sup> The relative ratio of the peaks at ~ 89 for crystalline (4c) and 84 ppm for amorphous (4a) indicates that pure cotton cellulose is mostly crystalline, though it is difficult to obtain the degree of crystallinity from these spectra. In the spectra for C-*g*-PAN, additional signals, that is, an intense and clear distinguishable

**TABLE I**  
Grafting Parameters of the C-*g*-PANs and Mer-C-*g*-PAN

Substrate	Concentration of monomer (%)	GE (%)	GY (%) <sup>a</sup>	GY (%) <sup>b</sup>
C- <i>g</i> -PAN28	2.00	37.2	27.7	25.0
C- <i>g</i> -PAN49	6.00	40.4	49.1	55.3
C- <i>g</i> -PAN68	8.00	50.6	68.4	—
C- <i>g</i> -PAN69	10.0	74.9	69.3	70.2
Mer-C1- <i>g</i> -PAN84 <sup>c</sup>	10.0	76.8	84.0	76.8
Mer-C2- <i>g</i> -PAN84.5 <sup>d</sup>	10.0	77.3	84.5	—

<sup>a</sup> Weighting method.

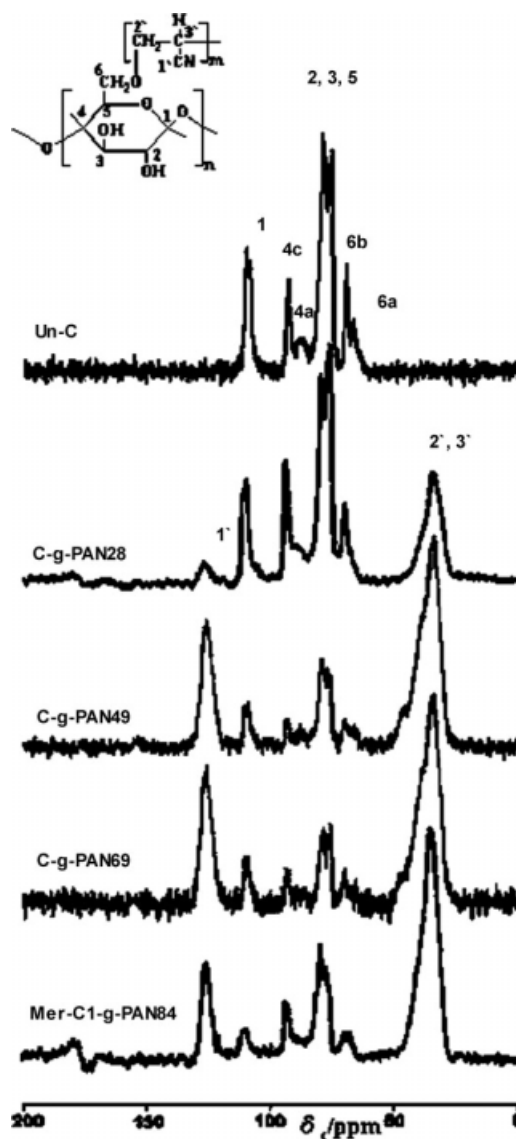
<sup>b</sup> By NMR method.

<sup>c</sup> Mer-C1, 3 times.

<sup>d</sup> Mer-C2, 4 times.

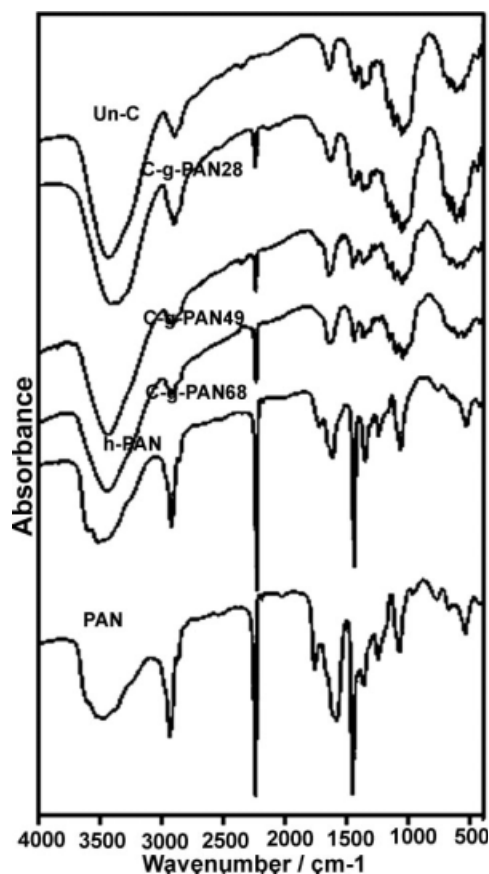
peak at 125 ppm due to the nitrile carbons and the broad resonance centered around 40 ppm due to the carbon resonance of the PAN backbone are observed. No substantial modifications of cellulose resonances in the 60–110 ppm region can be observed for grafted cellulose samples, indicating that the grafting process does not remarkably change the chemical structure of the cellulose matrix, in agreement with a previous work.<sup>31</sup>

The GY values are evaluated as the ratio between the area of the nitrile carbon resonance (peak 1') and the sum of areas of peak 1' and anomeric carbon resonance (peak 1). The results are also reported in Table I to compare with the GY obtained by weighting methods. Both data are in good agreement with



**Figure 4**  $^{13}\text{C}$  CP MAS NMR spectra of untreated cellulose (Un-C), cellulose-*graft*-PAN samples (Un-*g*-PANs), and mercerized cellulose-*graft*-PAN, mercerized three times (Mer-C1-*g*-PAN).





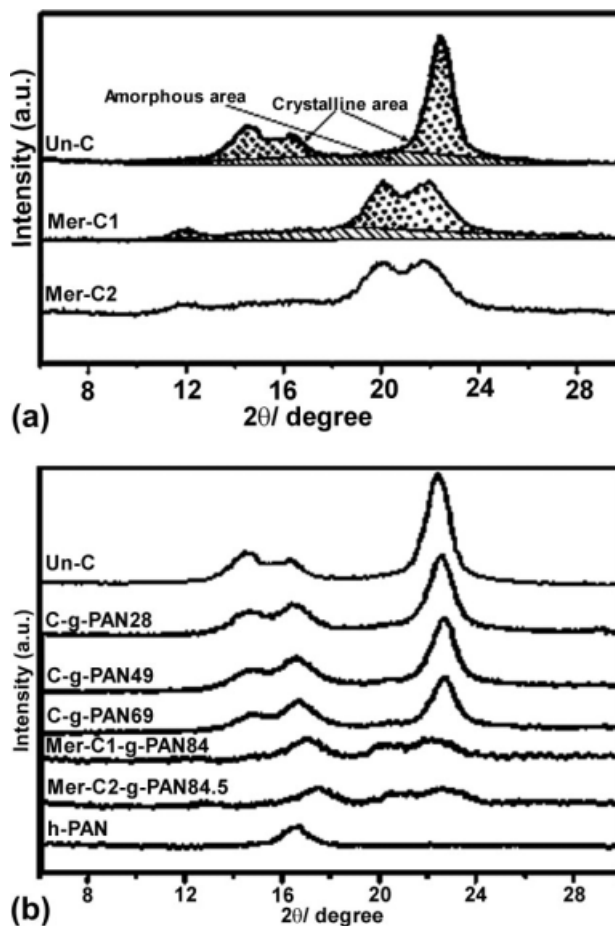
**Figure 5** FTIR Spectra of Un-C, C-g-PAN samples, extracted h-PAN, and pure PAN sample.

each other supporting the reliability of weighting methods.

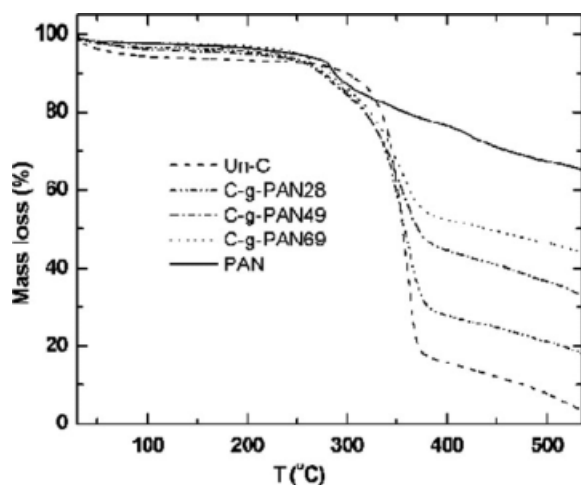
Figure 5 presents the IR-spectra of Un-C, C-g-PAN, and extracted h-PAN together with a spectrum for pure PAN. The IR spectra of extracted h-PAN and pure PAN are almost the same, denoting that extracted byproduct is almost pure PAN. On the basis of general assignment of absorption bands of cellulose,<sup>32</sup> the wide band observed at  $3424\text{ cm}^{-1}$  can be assigned to the  $-\text{OH}$  stretching of the cellulose and its width was ascribed to the formation of inter and intramolecular hydrogen bonds. The band at  $2907\text{ cm}^{-1}$  was assigned to the asymmetric stretching of C–H, whereas the band at  $1632\text{ cm}^{-1}$  was ascribed to adsorbed water and the bands at  $1428$  and  $1369\text{ cm}^{-1}$  to the angular deformation of C–H. The C–O ether bond shows stretching at  $1162\text{ cm}^{-1}$  whereas the C–O alcohol bond shows stretching at  $1058\text{ cm}^{-1}$ . A sharp peak at  $2243\text{ cm}^{-1}$ , the most apparently observed for h-PAN, is the stretching vibration mode of the nitrile groups. Also absorption bands at  $839\text{ cm}^{-1}$  and  $751\text{ cm}^{-1}$  are observed due to the rocking absorption of methylene groups in PAN. All of these bands are absent in the IR spectrum of pure cellulose. Most of the other peaks are related to the carbohydrate backbone. The

stretching peak intensity of the hydroxyl group at  $3424\text{ cm}^{-1}$  decreased whereas the stretching peak of the nitrile group at  $2243\text{ cm}^{-1}$  increased with increase of GY. These results also assure the grafting reaction without remarkable change of chemical structure of the cellulose matrix, consistent with NMR spectra.

The XRD spectra for Un-C and mercerized cellulose (Mer-C) are shown in Figure 6(a). It is obvious that the spectrum of Un-C shows the diffraction peaks at  $2\theta$  values of  $14.5$ ,  $16.3$ , and  $22.5$ , characteristics of the (101), (10 $\bar{1}$ ) and (002) reflections of cellulose I, respectively. On the other hand, the spectra of Mer-Cs have three new peaks located at  $2\theta$  angles of  $12.1$ ,  $20$ , and  $21.7$ , which are characteristics of the (101), (10 $\bar{1}$ ) and (002) diffraction planes of cellulose II, respectively.<sup>33</sup> Very gradual tails of these peaks reflect amorphous part of cellulose so that the degree of crystallinity, Cr (%), of cellulose fibers are calculated from the areas of crystalline and amorphous areas as shown by dots and hatches in the figure.<sup>34,35</sup> The Cr of Un-C is 78.6% whereas that of Mer-C treated three times (Mer-C1) and four times



**Figure 6** (a) X-ray diffraction of untreated cellulose and mercerized cellulose samples. (b) X-ray diffraction of untreated cellulose, grafted samples, and h-PAN.



**Figure 7** TG curves of untreated cellulose, C-g-PAN with different percentage of the graft yield and pure PAN.

(Mer-C2) are 61.5 and 50.0%, respectively. These lower Cr may be the reason for higher GY values obtained for Mer-Cs shown in Table I.

Figure 6(b) shows the X-ray diffraction spectra of Un-C, grafted samples (C-g-PAN), and extracted h-PAN. The spectrum of h-PAN shows diffraction peak at  $2\theta$  values of 16.7, which is characteristic of (100) plane of a hexagonal structure.<sup>36</sup> This diffraction peak has the same  $2\theta$  value of the (10 $\bar{1}$ ) plane of cellulose. From Figure 6(b), it can be seen that the position of the peaks is invariable, but the Cr decreases with the grafting. The Cr values of C-g-PAN28, C-g-PAN49, C-g-PAN69, Mer-C1-g-PAN48, and Mer-C2-g-PAN48.5 are 53.2, 50.0, 46.2, 43.3, and 42.1, respectively. These results clearly show a remarkable decrease in the degree of crystallinity after graft copolymerization, though the values only slightly decrease with the increase of GY. The change in the morphology from smooth surface of fibers to rough ones (Fig. 1) may be a consequence of grafting which may also influence on the degree of crystallinity.

### Thermal analysis

Figures 7 and 8 represent results for TGA and DSC for PAN, Un-C, and grafted samples. At a first sight, it is clear in Figure 7 that cellulose almost fully decomposed, while PAN has a large amount of residue at the end of measurement. The grafted samples show intermediate behaviors. With further inspections, we can point out the following characteristic behaviors.

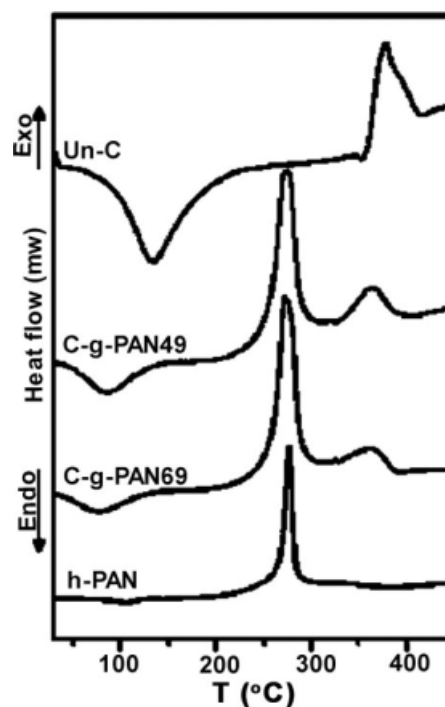
At low temperature region in Figure 7, rt - 250°C, the mass loss was 6% for cellulose, while it was lower than 5% for other samples. Endothermic peaks are observed for cellulose and grafted samples at around 100°C, which became smaller with the

increase of GY and not observed for C-g-PAN. Thus, the aforementioned mass losses at this stage can be attributed to desorption of water. The difference between cellulose and the grafted cellulose can be attributed to the presence of hydrophobic PAN chains.

In the temperature range 250–370°C, there also exists certain difference between thermograms (TG) and DSC data for cellulose and grafted cellulose. About 10% mass loss at 250–300°C in TG and an exothermic DSC peak at around 270°C are observed for the grafted polymers, which are similar to the data of PAN. In the same stage, mass loss of cellulose was more gradual. In the temperature range 300–370°C, large mass losses are observed. The mass of cellulose steeply decreased with temperature while that of PAN decreased gradually and this trend continued to the final temperature, where the mass loss was 77% for cellulose and in the range of 55–30% for the grafted samples.

Table II gives the results of the total mass loss in the range of 100–380°C for cellulose and the grafted samples. The measured mass loss obtained from the TG analysis was compared with the calculated mass loss. Both masses loss are nearly similar to each other, indicating that the most degradation of cellulose content in the samples has been occurred until 370–380°C in comparison to the pure cellulose as clear from the TG curves and the data in Table II.

The characteristics of TG for grafted samples resembles with that of cellulose at  $T < 270^\circ\text{C}$  and



**Figure 8** DSC thermograms of untreated cellulose, C-g-PAN, and pure PAN.

**TABLE II**  
**Characteristics of the Thermal Degradation of Cellulose, Cellulose-g-PAN, and PAN Polymer at Heating Rate 10°C/min**

Sample	Mass loss (100–380°C) (%)				Residue Rs (%) <sup>a</sup>	PAN	
	Measured	Calculated		Total		Measured <sup>b</sup>	Calculated <sup>c</sup>
		Cellulose	PAN				
Un-C	77.7	77.7	—	77.7	2.00	—	—
PAN	20.4	—	20.4	20.4	66.0	1.0	1.00
C-g-PAN28	67.4	56.2	5.7	61.9	18.8	0.277	0.287
C-g-PAN49	50.2	39.6	10.0	49.6	33.0	0.491	0.502
C-g-PAN69	43.2	23.9	14.2	38.1	43.9	0.693	0.673

<sup>a</sup> From TG at 550°C.

<sup>b</sup> Weighting method.

<sup>c</sup> From TG analysis.

become similar with that for PAN at  $T > 270^\circ\text{C}$  and have intermediate values of homopolymer. At around  $370^\circ\text{C}$ , a large and broad peak is observed in DSC data for cellulose. Also smaller ones are observed for the grafted samples, indicating that these peaks correspond to the decomposition of cellulose. From these results, we specify that the mass loss from  $300^\circ\text{C}$  up to  $370^\circ\text{C}$  is mainly due to the degradation of cellulose content in the samples while that at higher temperature is mostly due to PAN residue. Note that small amount of residue (char) of cellulose at around  $370^\circ\text{C}$  almost completely disappear at  $550^\circ\text{C}$ .

For quantitative analysis, the mass of residue at  $550^\circ\text{C}$  and its percentage to the original sample mass (Rs %) is tabulated in Table II. Further, the ratios between residues (Rs of graft samples: Rs of PAN) are also tabulated and compared with the ratio obtained from weighting methods (Table I). The corresponding data are similar to each other, implying that the residual amount at  $550^\circ\text{C}$  from the TG is from the PAN and is not related to the cellulose. From these results, we conclude that thermal stability of cellulose is not improved by grafting PAN. Thermal decomposition of both polymers occurs almost independently in grafted polymers, which is a natural consequence since PAN only partially covers the surface of cellulose fiber. We also propose that TGA can be used as a simple and fast method to obtain the grafting yield in cellulose-graft-PAN.

## CONCLUSIONS

Graft polymerization of AN onto cellulose fiber initiated by  $\text{KMnO}_4$ /citric acid in aqueous solution was examined and the grafted copolymers were characterized by using NMR, FT-IR, XRD, TG, and DSC. Graft yield, GY, obtained by simple weighting method was close to the value obtained by NMR analysis. The most efficient condition of graft copolymerization was  $[\text{KMnO}_4] = 0.05 \text{ mol/L}$ , [citric

acid] =  $0.02 \text{ mol/L}$ , [AN] = 10 vol % ( $1.5 \text{ mol/L}$ ),  $T = 70^\circ\text{C}$ , and time = 60 min; sample with GY = 69.3% was obtained. It was observed by SEM that PAN only partially covers the surface of cellulose fiber. Significant change of chemical structure in cellulose fiber, other than graft reaction was not detected by NMR and FT-IR measurements, but decreases in the degree of crystallinity by the reaction was detected by XRD measurement. By comparing TGA and DSC data for grafted samples with those of component homopolymers, it is concluded that thermal decomposition of both polymers occurs almost independently in grafted polymers. Grafted PAN does not improve the thermal stability of cellulose fiber.

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