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Polyacrylonitrile Grafted Cassava Starch and its Chemical Modification with Hydroxylamine Hydrochloride

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The graft copolymerization of acrylonitrile (AN) onto cassava starch (CS) with sodium bisulphite and potassium persulphate (KPS) as initiators was prepared. AN was grafted with gelatinized cassava at 70°C via redox method. The monomer ratios and reaction temperature were varied to obtain the maximum grafting efficiency and high grafted yield. The maximum grafting efficiency (91%) and grafted yield (93%) were attained at 50°C with ratio AN:CS 3:1 in 3 h. Poly(AN-grafted (*g*)-CS) was then modified with hydroxylamine hydrochloride ($NH_2OH.HCl$) to convert the nitrile group into absorbing characteristic properties. The poly(AN-g-CS) and amidoxime-modified poly(AN-*g*-CS) were characterized by Fourier transform infrared (FT-IR) spectroscopy, scanning electron microscopy, thermal gravimetric analysis (TGA) and Brauner-Emmet-Teller. The IR spectra proved that the grafting of AN onto CS was successful and the poly(AN-*g*-CS) was successfully modified with $NH_2OH.HCl$. It was shown that the specific surface area, pore volume and average pore diameter of CS were increased from 54.75 $m^2.g^{-1}$, 245.39 $m^2.g^{-1}$,0.336$cm^3.g^{-1}$ to 0.843 $cm^3.g^{-1}$ and 3.95 nm to 13.02 nm, respectively. TGA analysis proved that poly(AN-*g*-CS) and amidoxime-modified poly(AN-*g*-CS) are thermally more stable compared to CS.

Key words: Cassava starch; acrylonitrile; graft copolymerization; chemical modification; hydroxylamine hydrochloride

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Cassava starch is one of the naturally occurring polymers and received great attention for over a decade due to its abundance, easy availability, cheap and a renewable resource [1]. Generally, starch and glycogen are considered as storage polysaccharides whereas cellulose and chitosan serves as the structural materials. They provide mechanical strength to plants [2], which can be applied in fibres [3], films [4], adhesives [5], melt processing plastics [6], hydrogels or drug delivery agents [7]. Polyacrylonitrile (PAN) is a commercially important polymer due to its unique properties which includes hardness and rigidity, chemical resistance, compatibility with certain polar substance and low gas permeability. PAN is easily prepared and consists of reactive groups that can be easily modified by different types of reagents such as hydroxylamine, hydrazine, ethylenediamine through neucleophilic addition and cycloaddition reactions [8]. There are several examples in the literature regarding the graft copolymerization of different vinyl monomers onto cellulose [9,10]. Suspension polymerization of cassava starch with polystyrene was studied by using potassium persulphate as an initiator with water as a medium. The optimum grafting yield was reached with cassava:styrene ratio of 1:3 (by weight) and the reaction temperature and reaction time were 50°C and 2 h, respectively [11]. The copolymerization of cellulose filter paper acrylonitrile by using gamma rays of ^{60}Co with dimethyl formamide as reaction medium was reported before [12]. The cellulose-grafted-acrylonitrile was modified with methacrylate by using ammonium persulphate and azobisisobutyronitrile as initiators in dimethylsulfoxide-paraformaldehyde [13]. Adsorbents containing nitrogen such as hydrazine, amine, thioamideand imidazole functional groups were found to influence the removal of cationic metal ions in water [14]. Modification using hydroxylamine was investigated due to their unique properties towards heavy metal ions [15]. Among the techniques of natural polymer modification, graft copolymerization of vinyl monomers, particularly acrylonitrile (AN) due to its highest grafting efficiency and also subsequent hydrolysis is a unique method and has been a subject of extensive investigation [16].

The research on graft copolymerization of AN with cassava starch (CS) and its chemical modification with hydroxylamine hydrochloride has not been reported in any literature. Due to low utilization and large availability of cassava starch, an attempt was made to incorporate CS with AN and further chemically modified to convert the nitrile groups into amidoxime functional groups as an effective adsorbent for waste water treatment.

EXPERIMENTAL

Materials

Cassava starch was purchased locally in Malaysian market. Acrylonitrile of 99.0% purity was supplied by Merck Inc (United Kingdom). Potassium persulphate (KPS), sodium bisulphide (SBS) and hydroxylamine hydrochloride were supplied by ChemPUR Systerm (Malaysia). Acrylonitrile was purified by passing it through a short column of neutral aluminium oxide. Other chemical reagents; methanol, sodium hydroxide and hydrochloric acid were of analytical grades and were used without further purification.

Synthesis of Poly(AN-*g*-CS)

20 g of dried cassava starch (CS) and 200 ml of deionized water were mixed in a three necked round bottomed flask fitted with a water condenser flask under nitrogen gas and stirred for 1 h to form cassava slurry. The AN monomer was added followed by SBS and KPS. The graft copolymerization was performed at different condition parameters. The CS:AN ratios were varied to 3:1, 2:1, 1:1 and 1:3. (by weight ratio). KPS and SBS concentrations were 0.266 mol.l^{-1} and 0.439 mol.l^{-1}, respectively. The reaction time was 3 h and the reaction temperature were 40, 50 and 60 under nitrogen atmosphere with constant stirring at 250 rpm. The reaction was terminated by pouring the product into 50 ml of methanol and left to precipitate for 1 h. The grafted copolymer was then filtered and washed successfully with 50 ml of methanol and 100 ml of deionized water. The polymer was dried in a vacuum oven at 50 until a constant weight obtained. Homopolymerpolyacrylonitrile (homoPAN) was prepared in the same way.

The removal of the homoPAN from poly(AN-*g*-CS) was accomplished by stirring the poly(AN-*g*-CS) at 200 rpm in dimethyl sulphoxide (DMSO) for 24 h to dissolve the homoPAN. The poly(AN-*g*-CS) was then filtered using an analytical grade membrane and the polymer was washed successfully with 50 ml of methanol and 100 ml of deionized water. The purified poly(AN-*g*-CS) was then dried in a vacuum oven at 50 until a constant weight was obtained. The CS was purified with the same way as above. The grafting efficiency and grafting yield were calculated by using equation 1 and equation 2, respectively [17].

$$\text{Grafting efficiency [\%E]} = \qquad (1)$$

$$\text{Grafting yield [\%Y]} = \qquad (2)$$

Where W1, W2 and W0 are the weight of poly(AN-*g*-CS), weight of AN and weight of CS, respectively.

Modification of poly(AN-g-CS) using hydroxyl amine hydrochloride. 3 g of poly (AN-*g*-CS), 25 ml of methanol and 3 g of hydroxylamine hydrochloride were added into a 250 ml three-necked round bottomed flask fitted with a reflux condenser. The mixture was stirred at room temperature for 2 h. Then, 2 g of NaOH (6 M) was added into the reaction mixture to neutralize the HCl in $NH_2OH.HCl$ and the pH was adjusted to 8 using NaOH (6 M) solution. The reaction was allowed to proceed for 6 h at 70°C under constant stirring. The amidoxime-modified poly(AN-*g*-CS) was then filtered on an analytical grade membrane and washed thoroughly with 50 ml of ethanol and 100 ml of deionized water. The polymer was then allowed to dry in a vacuum oven at 50°C till a constant weight was obtained.

FT-IR analysis. The IR spectra of CS, poly(AN-*g*-CS), amidoxime-modified poly(AN-*g*-CS) and homoPAN were determined using KBr pellets on FT-IR series 100, 1650 Perkin Elmer spectrophotometer (Perkin–Elmer, Los Angeles, United State of America).

Surface area analysis. The surface area of CS, poly(AN-*g*-CS), amidoxime-modified poly(AN-*g*-CS) and homoPAN were carried out using Quantachrome instruments, 1994-2008 version 2.01 (United State of America) by nitrogen adsorption at –196°C.

Scanning electron microscopy (SEM). The micrographs of CS, poly(AN-*g*-CS), amidoxime-modified poly(AN-*g*-CS) and homoPAN samples were acquired using aJSM6400JEOL (Japan) instrument. The sample is mounted on a double-sided tape before coated with gold by ion sputtering method. The images were taken at 5 magnification powers of 450, 900, 1500, 3000 and 5000, respectively, using 15 KV accelerating voltage.

Thermogravimetric analysis (TGA). The degradation behaviour of CS, poly(AN-*g*-CS), amidoxime-modified poly(AN-*g*-CS) and homoPAN were analysed using Mettler Toledo TGA/SDTA851^e (Switzerland), in the temperature range of 35°C–600°C under heating rate of 10°C min^{-1} in nitrogen atmosphere.

RESULTS AND DISCUSSION

Grafting Efficiency and Grafting Yield

As shown in Table 1, poly(AN-*g*-CS) 3:1 obtained the highest grafting efficiencies (85%, 91% and 82%) and grafting yields (89%, 93% and 87%) at 40°C, 50°C and 60°C of reaction temperature, respectively. On the other hand, as the amount of AN in feed reduced to 5 g, the grafting efficiencies decreased to 7%, 23% and 18% at the reaction temperature of 40°C, 50°C and 60°C, respectively. The grafting yields of poly(AN-*g*-CS) 1:3 are the lowest compared to other weight ratios of AN:CS which are at 77%, 81% and 80% at the reaction temperature of 40°C, 50°C and 60°C, respectively. The higher grafting efficiency with the higher amount of AN in feed might be due to the formation of more free radicals, whereby generating more grafting sites and due to availability of extra monomer for grafting. The decrease in grafting efficiency might be due to the decreased of active sites on growing chains [18].

Table 1. Effect of cassava starch: acrylonitrile (by weight ratio) and reaction temperature on grafting efficiency E (%) and grafting yield Y (%).

Acrylonitrile (g)	Cassava starch (g)	AN:CS (Weight ratio)	Temperature (°C)	Grafting efficiency (%)	Grafting yield (%)
15	5	3:1	40	85	89
15	5	3:1	50	91	93
15	5	3:1	60	82	87
13	7	2:1	40	72	83
13	7	2:1	50	81	88
13	7	2:1	60	57	72
10	10	1:1	40	48	74
10	10	1:1	50	65	83
10	10	1:1	60	55	78
5	15	1:3	40	7	77
5	15	1:3	50	23	81
5	15	1:3	60	18	80

Temperature is another important reaction parameter in determining grafting kinetics (Gurdang and Samad, 2013). As shown in Table 1, both E (%) and Y (%) were increased with reaction temperature from 40 up to 50°C and the E (%) and Y (%) decreased as the reaction temperature reached 60°C. The maximum grafting efficiency was optimum (91%) at 50°C. It was reported that the optimum temperature of initiators for polymerization were 40°C for ammonium persulphate ($(NH_4)_2S_2O_8$:APS), 50°C for potassium persulfate ($K_2S_2O_8$:KPS) and 60°C for bothazobisisobutyronitrile ($C_{14}H_{10}O_4$:BPO) and benzoyl peroxide [19]. Similarly, it was reported that the maximum grafting efficiency in graft copolymerization of starch and poly(methyl methacrylate) (PMMA) with potassium persulphate (KPS) was achieved at 50°C [18].

FT-IR Spectra Analysis

The IR spectra of CS, poly(AN-*g*-CS), amidoxime-modified poly(AN-*g*-CS) and homoPAN are shown in Figures 3(a), 3(b), 3(c) and 3(d), respectively. The IR spectrum of CS [Figure 3(a)] shows characteristic absorptions at 3346, 2983 and 1750–1655 cm^{-1} which correspond to the O-H absorption, C-H stretching and C=O stretching, respectively [17, 12].

PAN [Figure 3(d)] shows characteristic absorption peaks at 2243 cm^{-1} and absorption at the region of 3000 cm^{-1}–2850 cm^{-1} which corresponds to the absorption of nitrile functional group and stretching of C-H group respectively [20,21].

The IR spectra of poly(AN-*g*-CS) [Figure 3(b)] shows the appearance of band at 2243 cm^{-1}

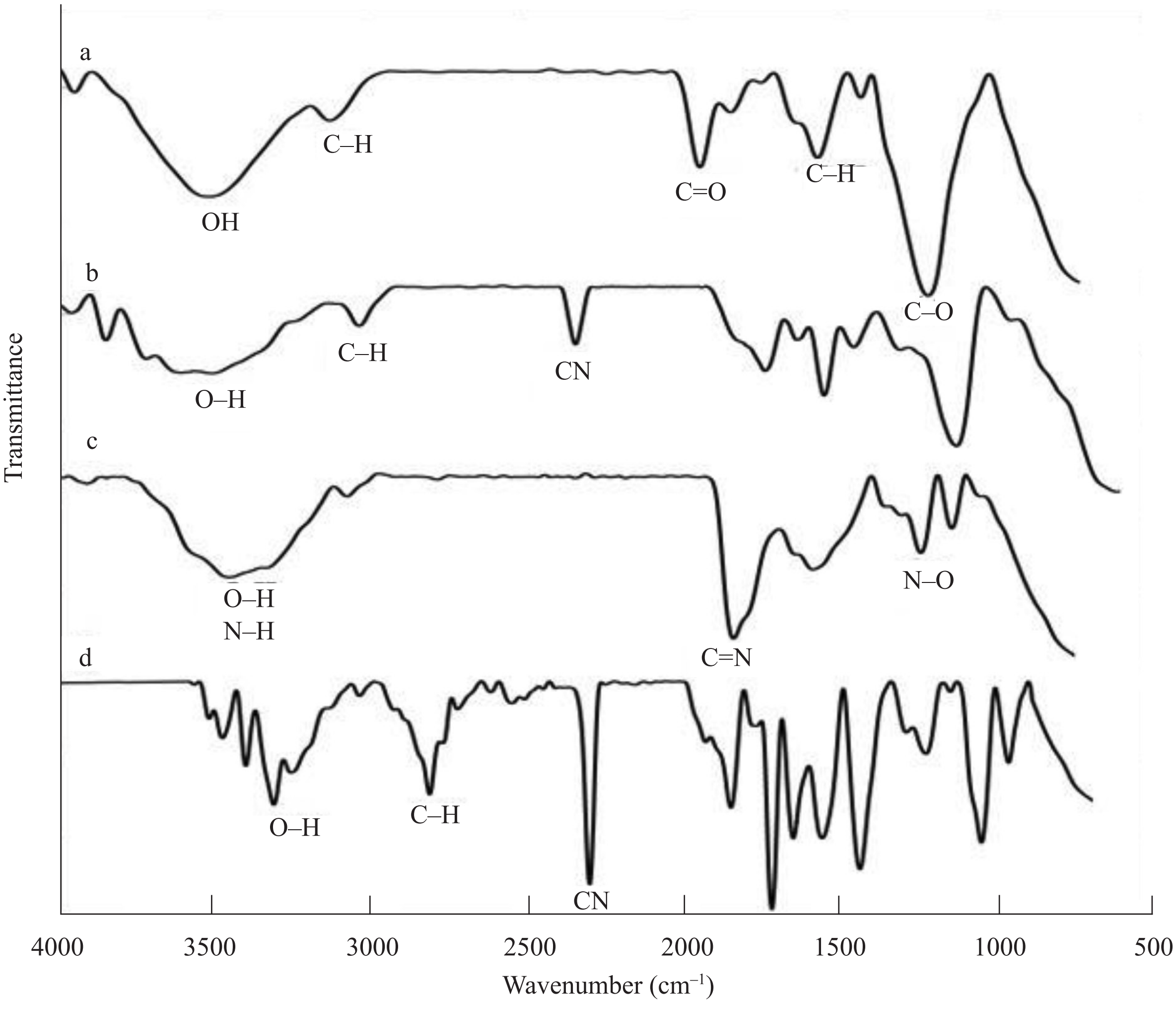


Figure 1. IR spectra of (a) CS (b) poly(AN-g-CS) (c) amidoxime-modified poly(AN-g-CS) and (d) homoPAN.

that was assigned to the CN functional group and a broad band at the region of 3600 cm^{-1}–3300 cm^{-1} that corresponded to the O-H functional group contributed by the CS unit in poly(AN-*g*-CS). These observations confirmed the graft copolymerization of CS with AN.

In the case of amidoxime-modified poly(AN-*g*-CS) [Figure 3(c)], the band at 2243 cm^{-1} that corresponded to the C≡N absorption completely disappeared and new bands emerged at 1655 cm^{-1} and 968 cm^{-1} which corresponds to the vibrational stretching of C=N and N-OH bands respectively [22]. The characteristic peak of the amine group (NH_2) at 3400 cm^{-1}–3300 cm^{-1} is overlapped with OH stretching vibrations (3600 cm^{-1}–3300 cm^{-1}). The band observed at 980 cm^{-1} was assigned to the stretching vibration of the N-O bond from the oxime group [20]. The IR spectrum of modified poly(AN-*g*-CS) confirmed the successful chemical modification of poly(AN-*g*-CS) with hydroxylamine hydrochloride.

SEM Analysis

The surface morphology of CS, poly(AN-*g*-CS), amidoxime-modified poly(AN-*g*-CS) and homoPAN are shown in Figures 2 (a), (b), (c) and (d), respectively. The micrograph [Figure 2(a)] shows that the particle shape of CS was greatly interfered due to grafting with AN and modification with hydroxylamine hydrochloride. As shown in Figure 2(a), CS had irregular, oval shape with a fine granular surface, whereas the surface of poly(AN-*g*-CS) [Figure 2(b)] had rough surface with small and irregular distribution of pores. Meanwhile, the amidoxime-modified poly(AN-*g*-CS) [Figure 2(c)] appeared as soft, sticky surface with a wider pores of irregular distribution. The micrograph of homoPAN [Figure 2(d)] has micro-size particles and this micro-sized beads are expected to have a significant improvement on the surface areas of poly(AN-*g*-CS) and amidoxime-modified poly(AN-*g*-CS) when incorporated with homoPAN and therefore are expected to improve the adsorption of heavy metal ions [20].

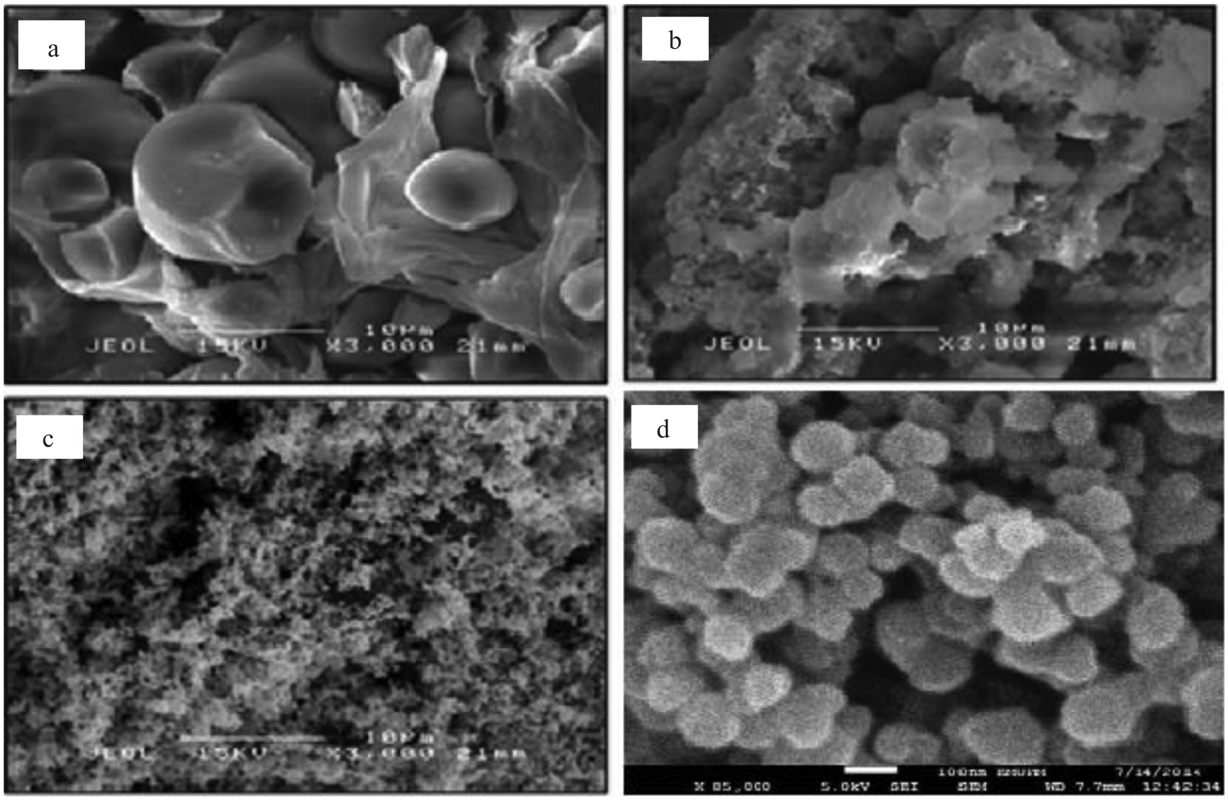


Figure 2. The SEM images of (a) CS (b) poly(AN-*g*-CS) (c) amidoxime-modified poly(AN-*g*-CS) and (d) homoPAN.

Thermogravimetric Analysis

Thermograms of CS, poly(AN-*g*-CS), amidoxime-modified poly(AN-*g*-CS) and homoPAN are shown in Figures 3(a), (b), (c) and (d), respectively. The TG curve of CS [Figure 3(a)] had two stages of weight loss, which corresponded to two different types of degradation. The weight loss in the first stage (30°C–100°C) was due to vaporization of moisture. The second stage (300°C–500°C) showed a sharp DTA peak which revealed that the weight loss was fast with the maximum weight loss (70%). In the case of poly(AN-*g*-CS), four stages of degradation steps were observed [Figure 3(b)]. The TG curve of poly(AN-*g*-CS) showed a small weight loss of ~2% at the initial stage (30°C–100°C), which was due to the evaporation of water. The second stage obtained ~1% weight loss at temperature range between 250°C–280°C. The third stage (298°C–334°C) shows a sharp DTA curve revealed that the weight loss was fast with maximum weight loss of ~25% which was due to the degradation of poly(AN-*g*-CS). The sharp and intense DTA curve at the third stage indicated that all type of reactions during the treatment of poly(AN-*g*-CS) are taking place concurrently and the molecular fragmentation was generally favoured leading to the weight loss of poly(AN-*g*-CS) [23]. The char yield of poly(AN-*g*-CS) was 14% at 600°C. In the case of amidoxime-modified poly(AN-*g*-CS), the thermogram had three stages of decomposition pattern [Figure 3(c)]. The first stage (50°C–100°C) was due to vaporization of water with ~7% of weight loss. The second stage of degradation was a sharp DTA curve that was associated with maximum weight loss of ~34%. The third stage produced a char yield of 18% at temperature between 380°C–420°C. Similar observation was found by Athawale and Lele [24], as cassava starch obtained two-step of characteristics thermogram, where the major weight loss (75%) took place at the second step within the temperature range of 233°C–368°C. The TG curve of homoPAN had three stages of decomposition pattern [Figure 3(d)]. The first stage (50–150) was due to the vaporization of water with 3% weight loss. The second stage degradation (250–380) showed a sharp DTG curve which indicated that the weight loss was rapid with a maximum weight loss of 22%. The sharp and intense DTG curve at the second stage also indicated that all types of reaction during the heat treatment of homoPAN was taking place concurrently and the molecular fragmentation is mostly favoured leading to weight loss of homePAN [25]. The third stage showed ~17% of weight loss at region 380°C–450°C due to the decomposition of CO_2 and H_2O. The final stage showed a steady and slow weight loss up to 600 with a char yield of 58%.

Surface Area Analysis

Table 1 shows the parameters of porous structure of CS, poly(AN-*g*-CS), amidoxime-modified poly(AN-*g*-CS) and homoPAN. The specific surface area, pore volume and average pore diameter of CS are 55 $m^2.g^{-1}$ 0.336 $cm^3.g^{-1}$ and 3.95 nm, respectively. As the AN was grafted onto the CS, the specific surface area, pore volume and average pore diameter were increased to 103 $m^2.g^{-1}$, 0.421 $cm^3.g^{-1}$ and 7.41 nm, respectively. However, as the poly(AN-*g*-CS) was chemically modified with hydroxylamine hydrochloride, the specific surface, pore volume and average pore diameter further were increased to 245 $m^2.g^{-1}$, 0.843 $cm^3.g^{-1}$ and 13.02 nm, respectively. That seemed to confirm the view that mesopores vastly contributed to overall porosity of poly(AN-*g*-CS) and amidoxime-modified poly(AN-*g*-CS). In addition, as for a comparison, the specific surface

Table 2. Morphology of the CS, poly(AN-*g*-CS), amidoxime-modified poly(AN-*g*-CS) and homoPAN.

Polymer	BET specific surface area ($m^2.g^{-1}$)	Specific pore volume ($cm^3.g^{-1}$)	Average pore diameter (nm)
Cassava starch (CS)	55	0.336	3.95
Poly(AN-*g*-CS)	103	0.421	7.41
Amidoxime-modified poly(AN-*g*-CS)	245	0.843	13.02
HomoPAN	6	0.225	0.77

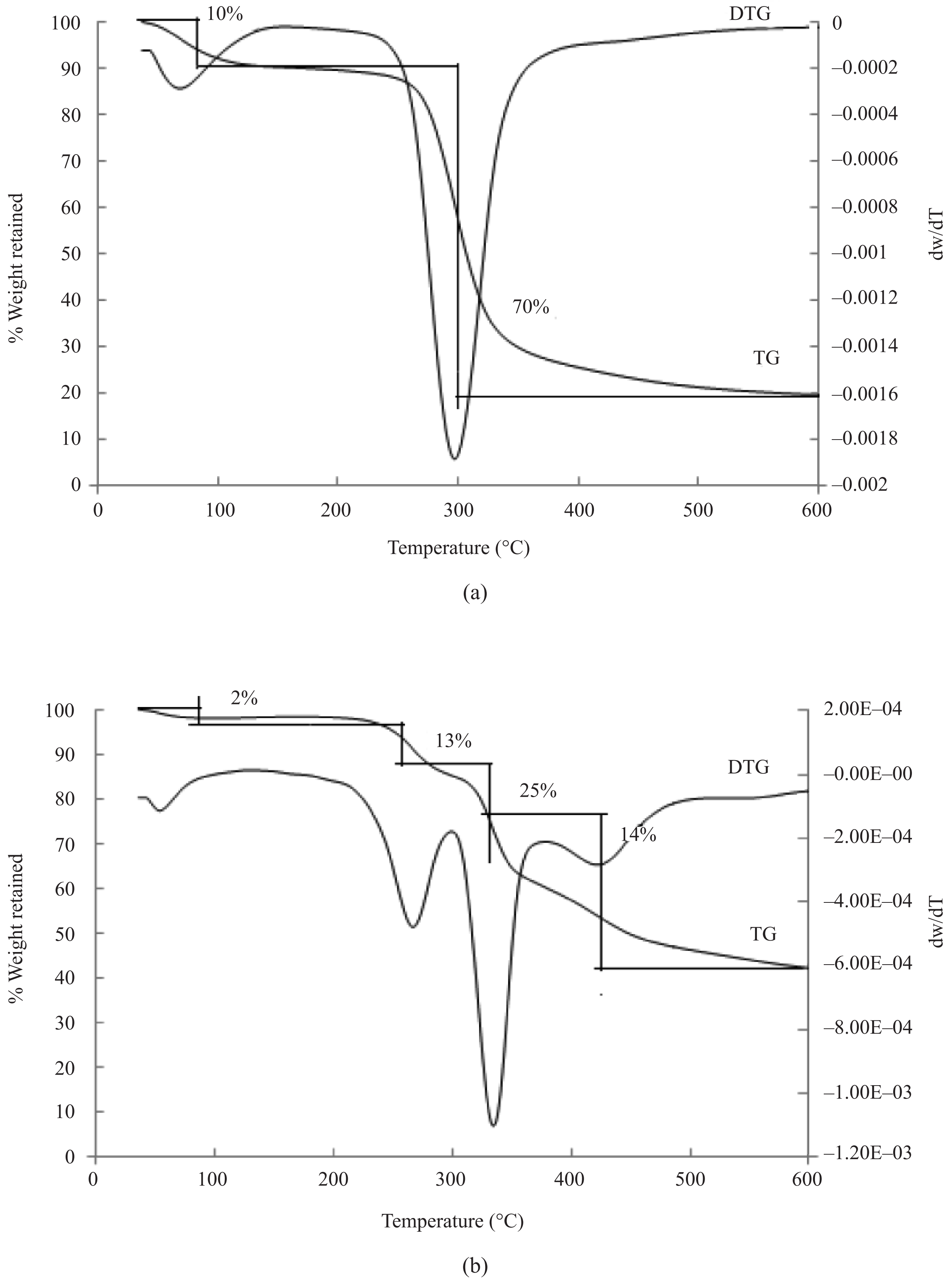
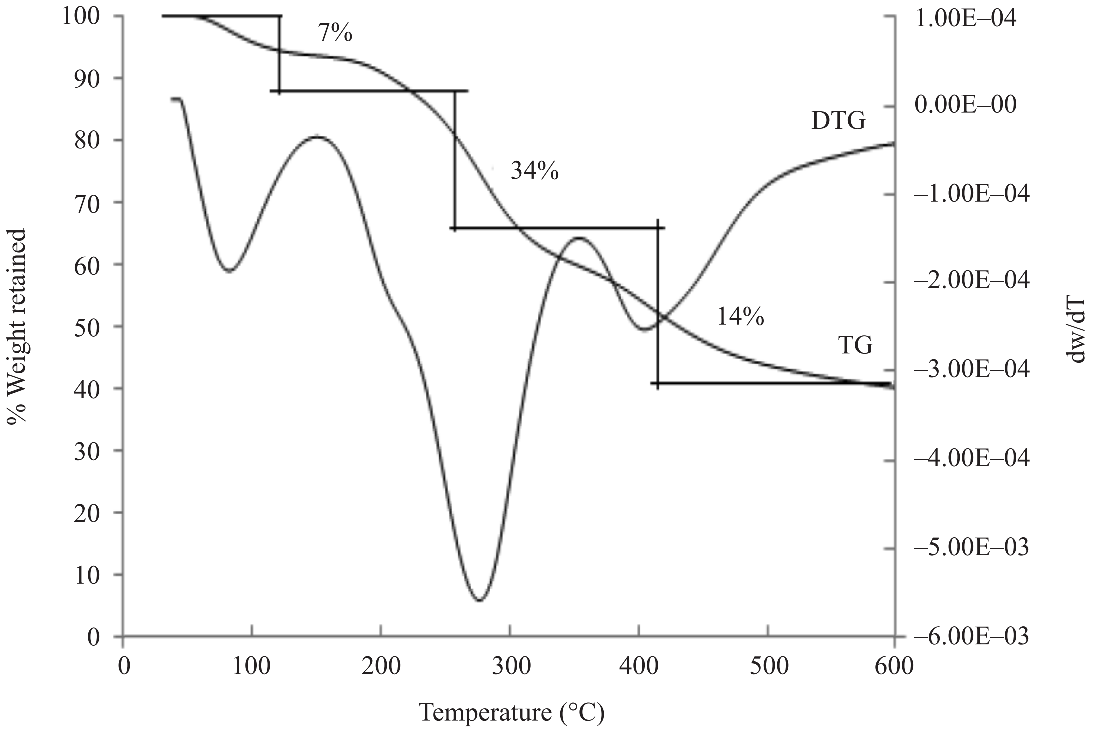
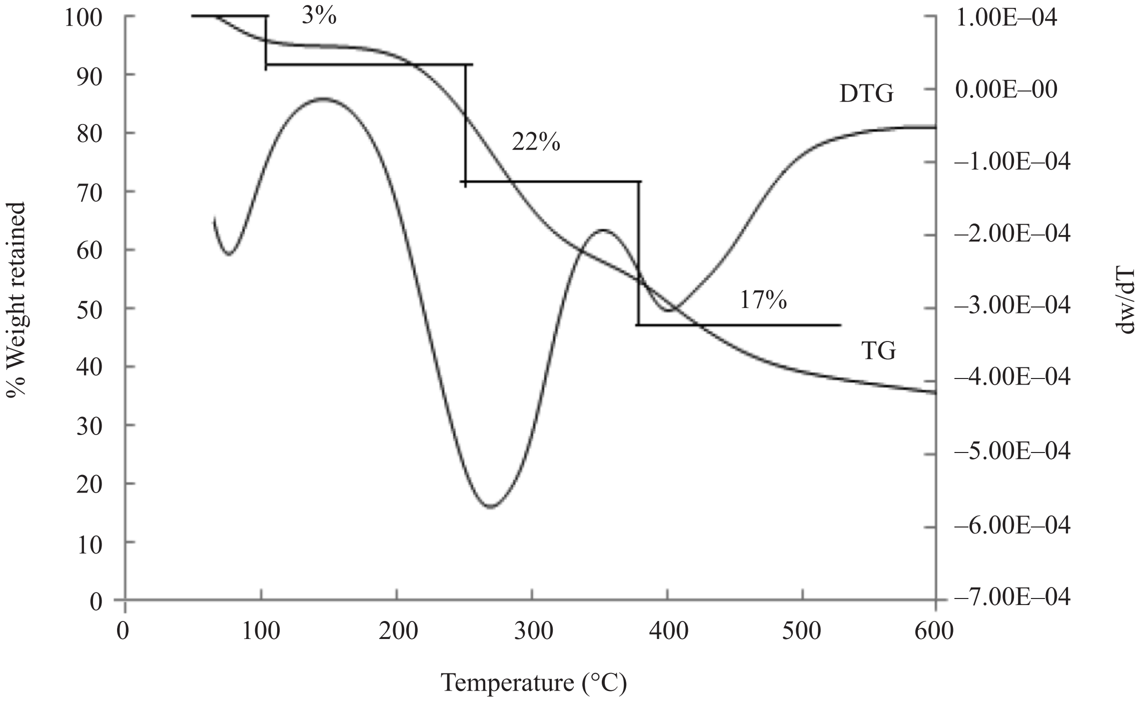


Figure 3. TG and DTA curves for (a) CS (b) poly(AN-*g*-CS).



(c)



(d)

Figure 3 (Cont.). TG and DTA curves for (c) amidoxime-modified poly(AN-*g*-CS) and (d) homoPAN.

Table 3. Specific surface area of modified starch [26].

Source of starch		Specific surface area, $m^2.g^{-1}$
Potato	Unmodified	0.24
	Modified with amylase	0.40
Wheat	Unmodified	0.53
	Modified with amylase	0.70
Maize	Unmodified	0.69
	Modified with amylase	0.65
Oat	Unmodified	1.22
	Modified with amylase	1.26

area of poly(AN-*g*-CS) and amidoxime-modified poly(AN-*g*-CS) (Table 2) was higher compared to the porosity of chemically modified potato, wheat, maize and oat, respectively (Table 3) [26].

CONCLUSION

It has been demonstrated that the synthesis of poly(AN-*g*-CS) via redox method and its chemical modification with hydroxylamine to form amidoxime-modified poly(AN-*g*-CS) were successful. The optimum redox polymerization condition were 3 h of reaction time at 50°C with 0.266 $mol.l^{-1}$ of KPS and 0.439 $mol.l^{-1}$ of SBS. The formation of the poly(AN-*g*-CS) and amidoxime-modified poly(AN-*g*-CS) were confirmed by FTIR analysis. The specific surface area of CS was increased after grafting with AN and further increased after chemical modification with hydroxylamine hydrochloride ($NH_2OH.HCl$). The morphology of CS was greatly affected due to grafting and chemical modification as determined by the SEM. The TG analysis showed that poly(AN-*g*-CS) and amidoxime-modified PAN-*g*-CS were thermally more stable compared to the CS.

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