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THERMAL CHARACTERIZATION OF STARCH-*g*-ACRYLONITRILE COPOLYMERS

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ABSTRACT

Several graft copolymers of starch with acrylonitrile having different percentage graft-on were prepared by using cerium(IV) initiating system. The percentage graft-on was varied by changing the acrylonitrile concentration in the initial feed. The graft copolymers were characterized by IR spectroscopy and density measurements. The appearance of an absorption band at 2240 cm^{-1} in the graft copolymers was taken as evidence for grafting. The density of starch decreased on graft copolymerization.

Thermal behaviour of graft copolymers was investigated using dynamic thermogravimetry in a nitrogen atmosphere. An improvement in thermal stability of starch was observed on grafting with acrylonitrile. An increase in percentage graft-on resulted in an increase in anaerobic char yield at 550 °C. A graft copolymer sample having 97.7% graft-on had a char yield of 52%, which was higher than polyacrylonitrile.

INTRODUCTION

Thermal degradation of polyacrylonitrile (PAN) and its copolymers has been extensively reported in the literature [1]. The colouration developed in acrylonitrile (AN) homopolymers and copolymers on heating to 150 °C has been attributed to the oligomerization of nitrile group [2–5]. Heating to higher temperatures results in weight loss due to evolution of products (predominantly ammonia and hydrogen cyanide). The residual carbon yield at 1000 °C is influenced by the comonomer used (in copolymers) and is around 28–30% for PAN. Comonomers also influence the cyclization reaction by acting as an initiator or inhibitor or diluents. Effect of comonomers on the thermal degradation of PAN has been systematically investigated by Grassie and McGuchens [6–8].

A literature survey has revealed that thermal degradation of graft-copolymers of acrylonitrile has not been investigated. The present studies which deal with thermal behaviour of starch-*g*-acrylonitrile copolymers were, therefore, undertaken. Several graft copolymers having graft on percentage of AN ranging from 7.7 to 97.7% were prepared using Ce(IV) initiator method.

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Thermal degradation of these graft copolymers in a nitrogen atmosphere was investigated using dynamic thermogravimetry.

EXPERIMENTAL

Starch (IDPL), was used without further purification. Baker analysed reagent grade cerium(IV) ammonium nitrate (CAN) and nitric acid (analytical grade, E. Merck) were also used as obtained. Acrylonitrile (BDH) was purified by washing it with an aq. solution of sodium hydroxide (5%) and distilled water till the washings became neutral. The monomer was dried over anhydrous sodium sulphate for 24 h and distilled before use.

Preparation of graft copolymers

The graft-copolymerization was carried out by taking 15.0 g of starch (i.e. 0.31 mol AGU l^{-1}) in distilled water and stirring at 35 °C for 30 min in order to make a starch slurry. Varying amounts (4.0–40.0 cm^3) of acrylonitrile were added and followed by the addition of CAN (0.005 M) in nitric acid (0.15 N) in three aliquots at 15 min intervals. The reaction was allowed to proceed for another 2 h in an atmosphere of oxygen-free nitrogen. The reaction product was precipitated with methanol and washed several times with water and methanol. The product was then filtered and dried under vacuum at 60 °C to a constant weight.

In order to separate the homopolymer from the graft-copolymers, the product was treated with *N*,*N*-dimethylformamide (DMF) for 100 h at room temperature. The residual product obtained after homopolymer extraction was washed with methanol several times, filtered and dried under vacuum.

The results of nitrogen estimation were used to calculate the value of percentage graft-on by using the following equation:

$$\text{Graft-on}\ (\%) = \frac{\text{Nitrogen}\ (\%) \times 53.06}{14} \tag{1}$$

A Nicolet 5 DX FTIR was used to record IR spectra of graft copolymers in KBr pellets.

For determination of density, polymer disks were prepared by taking 0.25 g of the powdered sample and subjecting it to a load of 5.0 tons for 5 min. The density of the graft-copolymer disks was determined by a density gradient column employing a mixture of carbon tetrachloride and *n*-heptane. The stable position of the specimens in the density gradient column was checked over a period of 50 h.

Thermogravimetric analysis was carried out on a DuPont 1090 thermal analyser in a nitrogen atmosphere at a heating rate of 10 °C min^{-1} from room temperature to 550 °C. The relative thermal stability of the graft-copolymers was evaluated by determining: (a) initial decomposition temperature (IDT) (obtained by extrapolation), (b) integral procedural decomposition temperature (IPDT) [9], (c) final decomposition temperature (T_f), (d) percentage char yield at 550 °C, (e) temperature of maximum rate of weight loss (T_{max}). A two-step degradation was observed in all s-*g*-AN samples. Therefore, two T_{max} values were obtained from derivative thermogravimetric traces (DTG), and these have been designated as $T_{max\,1}$ and $T_{max\,2}$. The valley point, between two T_{max} in the DTG trace has been taken as T_f. Residual weight at this temperature gave information about the weight loss in first stage.

RESULTS AND DISCUSSION

The graft-copolymerization of acrylonitrile onto starch was studied by varying the amount of acrylonitrile from 0.60 to 6.0×10^{-1} M. The graft-on was found to increase with an increase in the concentration of acrylonitrile. Plot of mol% of AN grafted versus monomer concentration (Fig. 1) shows almost a linear increase in percentage graft-on up to 0.30 M concentration of acrylonitrile. Beyond this, there was a tendency to level off. This is probably due to enhanced homopolymer-forming reactions at higher monomer concentrations. Since all the graft copolymerization reactions were carried for the same duration (i.e. 2 h), therefore, from mol% grafted, the rate of polymerization can be determined.

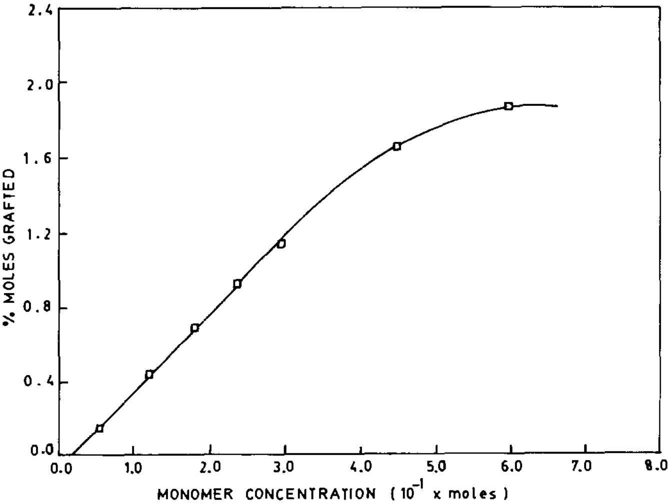

Fig. 1. Effect of monomer concentration on graft-copolymerization of starch with acrylonitrile.

TABLE 1

Graft-copolymerization of AN onto starch

Sample	Monomer concentration ($\times 10^{-1}$ mol)	Nitrogen content (%)	Graft-on (%)	Moles grafted (%)	G.E. (%) [a]
1	0.60	2.03	7.7	0.145	80.2
2	1.20	6.23	23.6	0.445	80.5
3	1.80	9.87	37.4	0.705	78.4
4	2.40	13.06	49.5	0.933	77.1
5	3.00	16.12	61.1	1.152	74.6
6	4.50	23.17	87.8	1.655	67.8
7	6.00	25.78	97.7	1.841	59.4

[a] Grafting efficiency.

The dependence of rate of graft-copolymerization on monomer concentration was evaluated by plotting the log of rate of grafting against log of acrylonitrile concentration. From the slope of this plot (Fig. 2) the order of reaction with respect to monomer concentration was determined and was found to be 1.5 up to an acrylonitrile concentration of 0.3 mol. However, at higher concentrations the order was 1.0.

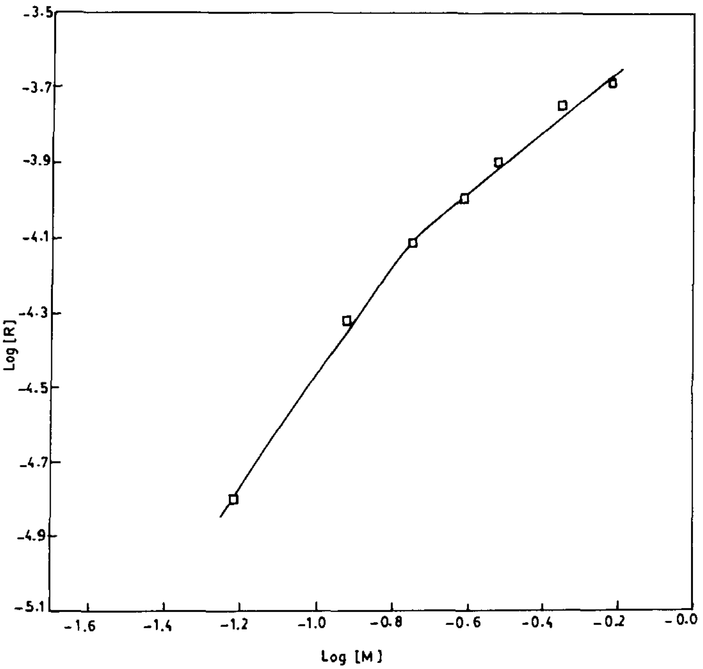

Fig. 2. Plot of log of rate of grafting versus log of acrylonitrile concentration.

The IR spectra of starch, polyacrylonitrile (PAN), and starch-*g*-polyacrylonitrile (s-*g*-PAN) samples in the range 400–4800 cm^{-1} were recorded. In the spectrum of starch, the stretching vibrations of free hydrogen-bonded and polymeric hydroxyl groups appear as broad but strong absorption bands in the 3000–3660 cm^{-1} region. The medium but strong bands observed in 3000–2800 cm^{-1} region are characteristic of ν_{C-H}. A relatively less defined band at 1470 cm^{-1} may be assigned to the internal deformation vibration of CH_2 in CH_2OH groups. A sharp absorption band at 1650 cm^{-1} is observed in starch, and is probably characteristic C–O stretching of the chelated aldehyde group (enolic form). The bands observed in the range 1200–1470 cm^{-1} are characteristic of C–H bending vibrations. Absorptions at 1170, 1080 and 990 cm^{-1} may be assigned to antisymmetric C–O–C stretching, C–O stretching and skeleton vibrations, respectively.

In the IR spectra of s-g-PAN copolymers (Fig. 3) broad and strong absorption bands due to –OH group stretching in the 3100–3660 cm^{-1} region and characteristic absorption bands for starch in the 760–1200 cm^{-1} range were observed. The graft-copolymers were also characterized by the presence of a sharp band at 2240 cm^{-1}, due to nitrile stretching vibrations. This confirms the presence of polyacrylonitrile in the graft-copolymers.

The plot of density of graft-copolymers versus percentage graft-on (Fig. 4) clearly suggests the drastic decrease in the density of starch as a result of

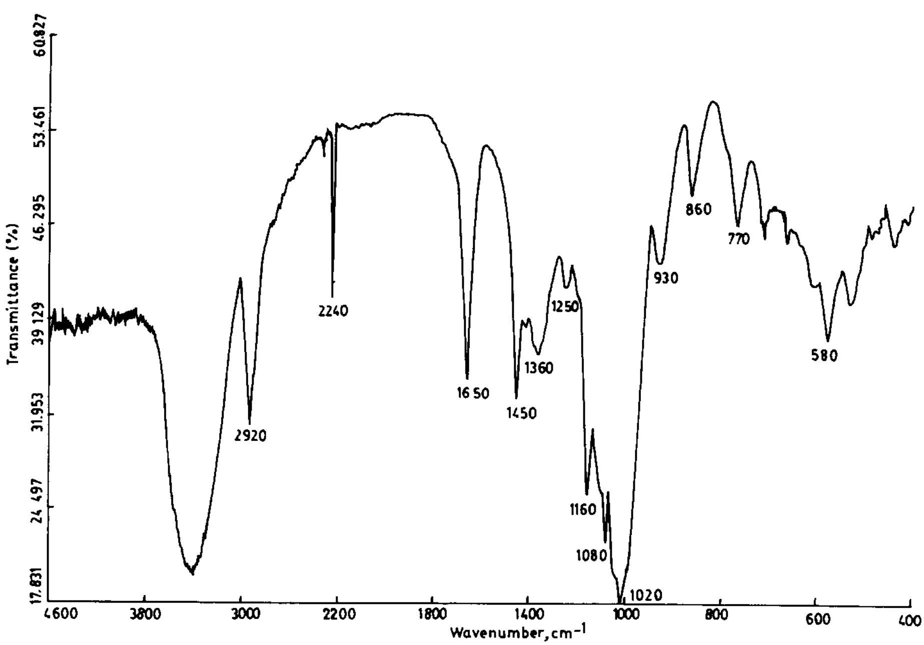

Fig. 3. Typical IR spectrum of starch-*g*-acrylonitrile copolymers (graft-on = 37.5%).

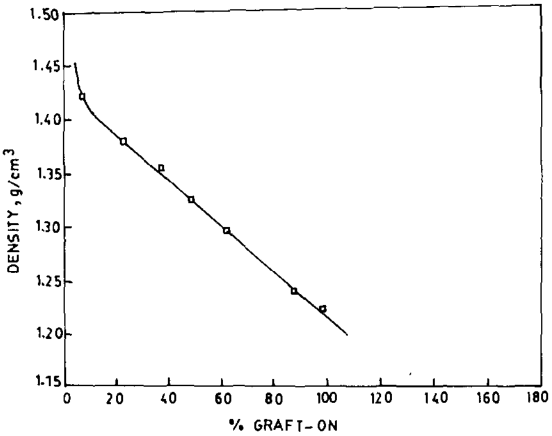

Fig. 4. Plot of density of graft copolymers versus percentage graft-on.

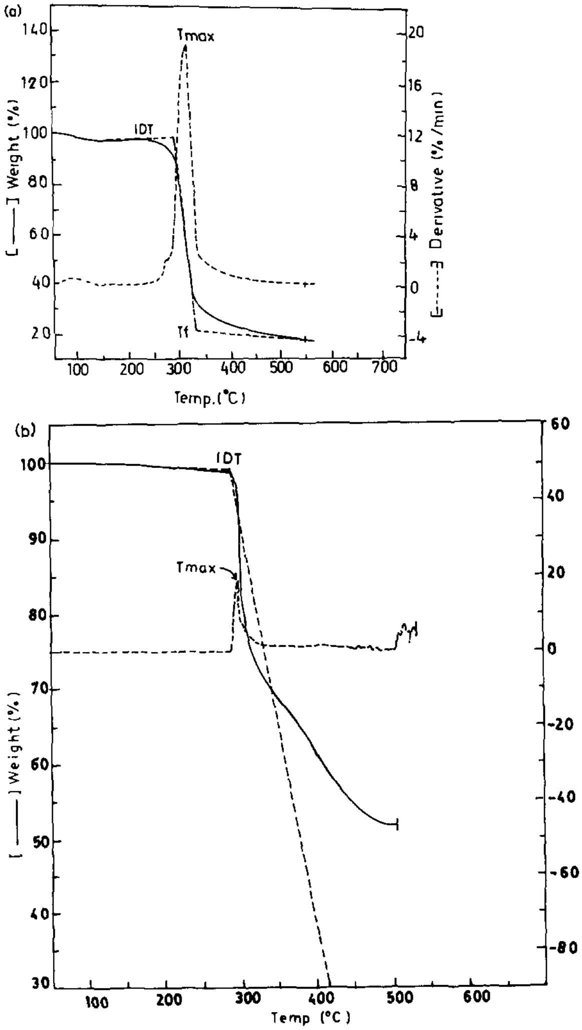

Fig. 5. Thermogravimetric traces of (a) starch and (b) PAN.

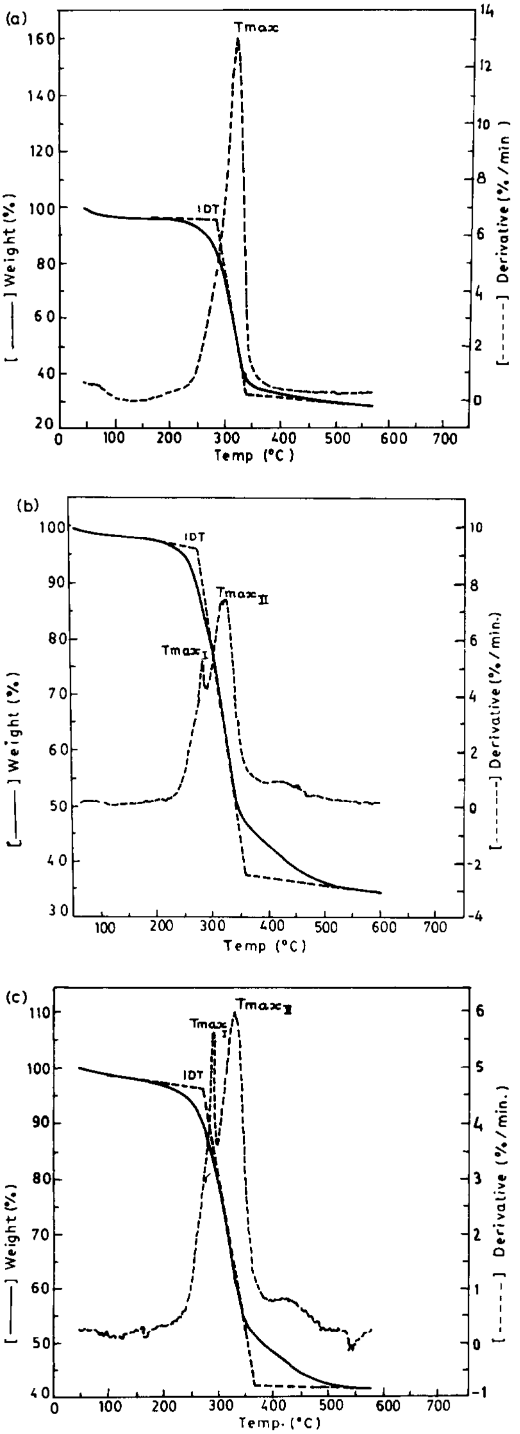

Fig. 6. Thermogravimetric traces of starch-*g*-PAN samples having (a) 7.7, (b) 37.6 and (c) 49.5% graft-on.

grafting of PAN. An increase in percentage graft-on results in a decrease in density. The polyacrylonitrile in s-g-PAN modifies symmetry and packing of the starch granules, thereby causing a drastic decrease in density.

Thermal degradation of starch, PAN and s-g-PAN copolymers in an inert atmosphere of nitrogen was examined using their thermogravimetric (TG) and derivative thermogravimetric (DTG) curves (Figs. 5–7), and the results are reported in Tables 2 and 3.

The main decomposition of all the samples starts above 275 ° C. However, early weight loss in some samples may be attributed to the desorption of water. In the case of starch (Fig. 5a), decomposition starts ≈ 280 ° C, and, in the case of graft-copolymers (Figs. 6–7) it starts at a slightly lower temperature. Initial decomposition temperature (IDT) values for the graft-copo-

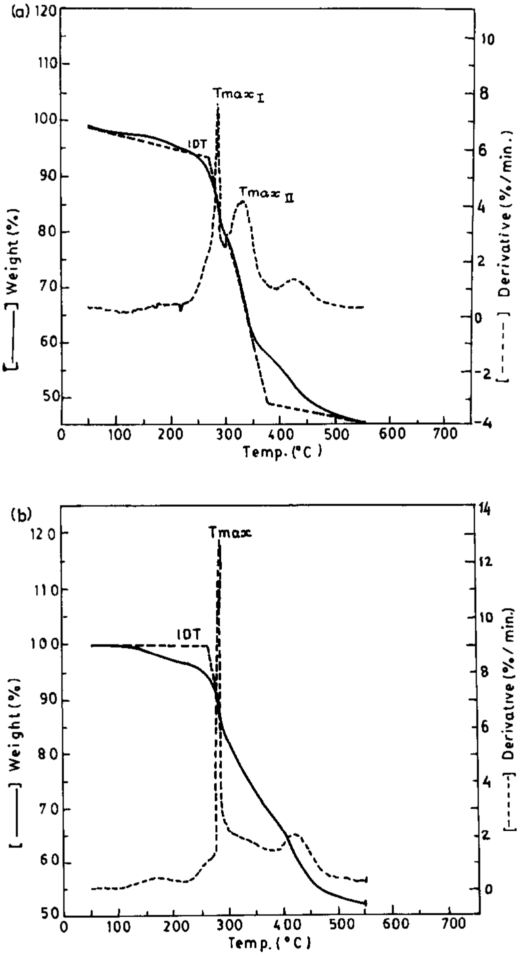

Fig. 7. Thermogravimetric traces of starch-*g*-PAN samples having (a) 61.1 and (b) 97.7% graft-on.

TABLE 2

Results of thermogravimetric analysis of starch, PAN and S-*g*-PAN samples in a nitrogen atmosphere

Sample	Graft-on (%)	IDT (°C)	Temperature of various percentage decompositions			IPDT [a] (°C)
			T_{20} (°C)	T_{40} (°C)	T_{50} (°C)	
Starch	0	292.0	302.0	315.0	320.0	342.3
PAN	0	288.0	306.0	412.0	450.0	382.4
s-*g*-PAN	7.7	285.0	292.0	315.0	323.0	349.0
s-*g*-PAN	37.5	278.0	298.0	328.0	346.0	357.8
s-*g*-PAN	49.5	271.0	296.0	329.0	380.0	366.9
s-*g*-PAN	61.1	266.0	299.0	360.0	445.0	378.1
s-*g*-PAN	97.7	262.0	312.0	428.0	–	385.9

[a] IPDT values calculated in the 50–500 °C range.

lymers are also lower than that of starch and PAN homopolymer, and an increase in percentage graft-on further reduces IDT (Table 2).

The decomposition of starch takes place mainly in a one-step reaction (Fig. 5a), and about 80.0% of starch is degraded from 280 to 340 °C. The decomposition of PAN also takes place mainly in one step with a loss of 52.5%. In the case of graft-copolymers (Figs. 6–7 and Table 3), the low grafted samples degrade predominantly in a one-step reaction, whereas highly grafted samples (i.e. 61.1 and 97.7%) degrade in two or three distinct

TABLE 3

Results of derivative thermogravimetric (DTG) analysis of starch, PAN and s-*g*-PAN samples in nitrogen

Sample	Graft-on (%)	$T_{\max 1}$ ($T_{\max 2}$) [$T_{\max 3}$] (°C)	T_{f1} (T_{f2}) [T_{f3}] (°C)	Weight loss Step 1 (Step 2) [Step 3] (%)	Char yield at 550 °C (%)
Starch	0.0	322.0	355.1	79.3	19.5
PAN	0.0	300.0	430.0	52.5	47.0
		(410.0)			
s-*g*-PAN	7.7	319.0	337.2	68.6	25.6
s-*g*-PAN	37.6	285.0	295.0	29.0	34.5
		(322.3)	(380.0)	(26.0)	
s-*g*-PAN	49.5	275.0	290.0	13.0	41.5
		(325.2)	(377.0)	(37.0)	
		[425.0]	[500.0]	[7.5]	
s-*g*-PAN	61.1	284.0	301.0	20.0	45.0
		(329.6)	(385.0)	(22.5)	
		[425.0]	[480.0]	[10.0]	
s-*g*-PAN	97.7	284.0	341.0	25.3	52.0
		(419.1)	(500.0)	(22.7)	

steps. The percentage weight loss during first step degradation is decreased as the percentage graft-on increases.

Temperatures of various percentage weight losses (i.e. 20, 40 and 50%) were also recorded from thermogravimetric traces, and are given in Table 2. Temperature of 20% weight loss of starch and PAN was higher than most of the graft copolymers, except the sample having 97.7% graft-on. However, the temperature of 40 and 60% weight-loss graft-copolymer samples was higher than that of starch.

The integral procedural decomposition temperature which sums up the overall shape of thermogravimetric trace was calculated in the temperature range 50–500 ° C for all the samples (Table 2). IPDT for starch and PAN is 341 and 382° C, respectively, and for graft-copolymers it was also between these values, except for the graft-copolymer having 97.7% graft-on. IPDT values of s-g-PAN copolymers also increased from 349.0 to 385.9 ° C as the percentage graft-on increases. This observation thus confirms the higher thermal stability of graft-copolymers of starch.

Temperatures of maximum rate of weight loss were obtained from differential thermogravimetric traces (Table 3). In starch only one T_{max} at 322° C was observed. Major weight loss in PAN ($\approx$ 40%) also occurred in a single step with a T_{max} at 300 ° C. Between 400–500 ° C about 8% weight loss was observed with T_{max} at 410 ° C. In copolymer samples one, two or three T_{max} values were obtained, depending on the percentage graft-on. For example, in a sample having 7.7% graft-on, T_{max} corresponding to starch degradation was observed at 319° C. In samples having 37.6% graft-on T_{max} values corresponding to major weight loss of PAN (285 ° C) and starch (322° C) were observed. In samples having 49.5 and 61.1% graft-on, three T_{max} corresponding to starch and PAN degradation were obvious. The sample having 97.7% graft-on did not exhibit the T_{max} corresponding to starch degradation at 322° C. The char yield at 550 ° C is also affected by the percentage graft-on. Higher char yield than PAN was obtained in a copolymer having 97.7% graft-on (Table 3).

These results thus indicate that thermal behaviour of starch, as well as PAN, is modified on graft copolymerization.

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