

# Synthesis and Characterization of Vegetable Tannin-Vinyl Graft Copolymers Part I. Cutch-Poly(Methyl Acrylate) Graft Copolymers

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## Synopsis

New graft copolymers were synthesized by grafting methyl acrylate onto cutch, a vegetable tanning agent, in acetic acid medium with hydrogen peroxide as the initiator. The graft copolymers were characterized by infrared spectroscopy and thermogravimetric analysis. The dependence of the percentage of grafting, monomer conversion, efficiency of grafting and rate of grafting on the concentrations of initiator, acetic acid, and cutch were investigated. The optimum experimental conditions for grafting were obtained. A probable mechanism of grafting was also proposed.

## INTRODUCTION

In recent years, much attention has been devoted toward the development of newer and modified materials from the naturally occurring macromolecules for improved utilization in current and new applications. Vegetable tanning materials are widely used as tanning agents in manufacture of leather goods and products. It is well known that the working bath of the vegetable tannin extracts contain a large amount of precipitates, which retard the diffusion of tannins into the hides and skins. With a view toward improving some of the properties of the vegetable tanning materials such as homogeneous dispersion in water for obtaining higher filling capacity and to free them from insoluble impurities, investigations are underway to modify these materials by grafting with vinyl monomers. However, very scanty literature is available on the chemical modification of vegetable tanning materials by grafting with vinyl monomers.<sup>1-3</sup> In the present studies, cutch, which is available in abundance in India, was modified by grafting with poly(methyl acrylate) (PMA). The modified products of cutch thus obtained were well characterized and some preliminary experiments were carried out for their utility in the tanning processes.

## EXPERIMENTAL

### Materials

Cutch (commercial sample) was obtained from local tanneries. Methyl acrylate (BDH, AR) was used as received without further purification. All

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other reagents such as hydrogen peroxide, acetic acid, and organic solvents used were of reagent grade.

### Graft Copolymerization Procedure

All grafting reactions were carried out in a thermostatic water bath and in a three-necked, round-bottomed flask fitted with a stirrer, condenser, and a thermometer. A typical experimental procedure was as follows: Cutch was dissolved in acetic acid of known concentrations and collected in a three-necked, round-bottomed flask of one liter capacity. The initiator and monomer were added simultaneously, drop by drop, from dropping funnels for a period of 30 minutes and the reaction was allowed to proceed for four hours at 60–80°C. The reaction mixture was cooled to room temperature and precipitated by adding excess methanol. The crude precipitated product contained the grafted cutch, the unreacted cutch, and the homopolymer. The mixture was left as such for a day with intermittent shaking, thereby allowing the unreacted cutch to be extracted in the methanol. The precipitate was filtered, washed with methanol, and dried at 50°C in a vacuum oven. The residue containing the mixture of homo-PMA and cutch-g-PMA was extracted with toluene for 24 hours by tumbling method to remove homo-PMA. The pure cutch-PMA graft copolymer was then dried and weighed to a constant weight.

### Calculations

The percentage total conversion of monomer, the percentage efficiency of grafting, the percentage of grafting, and the rate of grafting were calculated as follows:

$$\text{Percentage total conversion of monomer} = \frac{\text{Weight of PMA grafted and PMA}}{\text{Weight of methyl acrylate charged}} \times 100 \quad (1)$$

$$\text{Percentage efficiency of grafting} = \frac{\text{Weight of PMA grafted}}{\text{Weight of PMA grafted and PMA}} \times 100 \quad (2)$$

$$\text{Percentage of grafting} = \frac{\text{Weight of PMA grafted}}{\text{Weight of cutch reacted}} \times 100 \quad (3)$$

$R_p$  = rate of polymerization ( $\text{mol L}^{-1} \text{s}^{-1}$ )

$$= \frac{(\text{Weight of total yield}) - (\text{weight of backbone})}{\text{Molecular weight of monomer} \times \text{reaction period (in s)} \times \text{volume of reaction system (in mL)}} \times 1000 \quad (4a)$$

$R_h$  = rate of homopolymerization ( $\text{mol L}^{-1} \text{s}^{-1}$ )

$$= \frac{\text{Weight of homopolymer extracted from the crude graft copolymer}}{\text{Molecular weight of monomer} \times \text{reaction period (in s)} \times \text{volume of reaction system (in mL)}} \times 1000 \quad (4b)$$

$R_g$  = rate of grafting ( $\text{mol L}^{-1} \text{s}^{-1}$ )

$$= R_p - R_h \quad (4c)$$

### Infrared Spectra

Infrared spectra of the polymers were recorded using Perkin-Elmer 983 Infrared spectrophotometer using potassium bromide pellets or films.

### Thermogravimetric Analysis

The thermogravimetric analysis (TGA) of the polymers was carried out with a 990 Du Pont-Thermal Analyser in nitrogen atmosphere at a heating rate of  $20^\circ\text{C}/\text{min}$ .

## RESULTS AND DISCUSSION

### Structure of Cutch

Cutch, which is botanically known as *Acacia catechu*, is a polyphenol and is made of a mixture of products of varying degrees of polymerization containing several molecules of catechin and/or catechin-like substances.<sup>4</sup> The ingredients generally present in cutch are catechin, galocatechin, dicatechin, and catechin tetramer.<sup>5</sup> The structures of some of these compounds and polyphenolic groups which can be utilized for further modification are as shown in Figure 1.

Oxidative polymerization of phenols in aqueous systems through the liberation of free radicals on the phenolic hydroxyls and the rearrangement mechanisms were given by Allan et al.<sup>6</sup> for the phenolic pollutants from water by oxidative coupling to lignocellulosic substrates.

Trakhtenberg and Savchuk<sup>1</sup> have also proposed that oxidants (initiators, for example, hydrogen peroxide) can create free radicals on the phenolic hydroxyls of polyphenolic vegetable tanning agents such as oak, spruce, and willow extracts.

We suggest below a similar possible mechanism for the graft copolymerization of methyl acrylate onto cutch using hydrogen peroxide as an initiator.

### Mechanism of Graft Copolymerization

Hydrogen peroxide is dissociated into radicals which interact with the phenolic OH groups of the vegetable tanning materials forming phenoxy

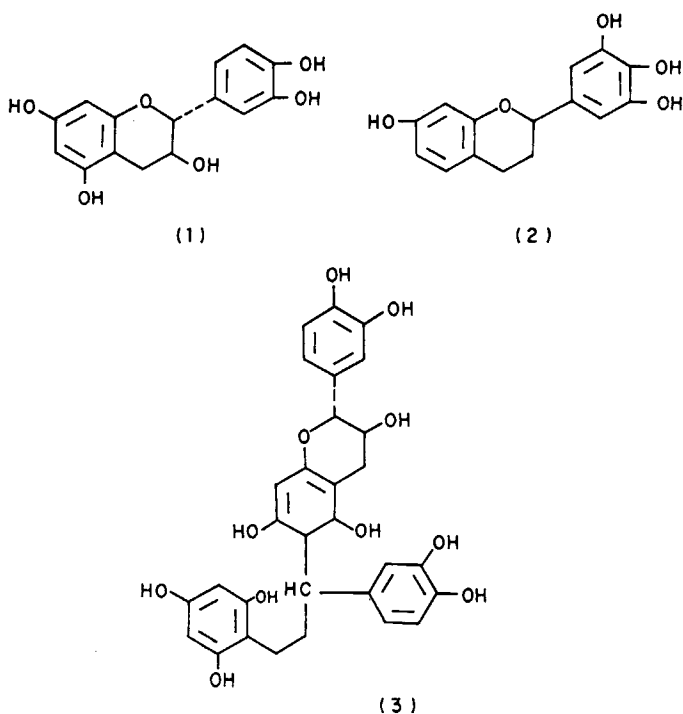
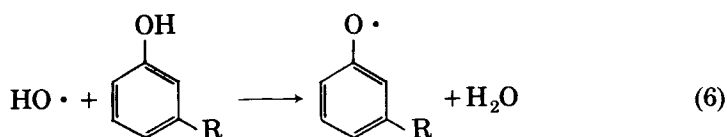
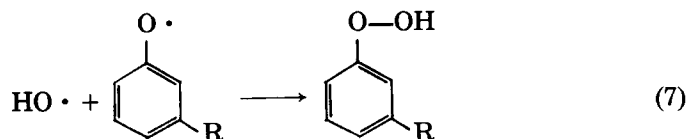


Fig. 1. Schematic structures of ingredients of cutch: (1) catechin; (2) gallocatechin; (3) dicatechin.

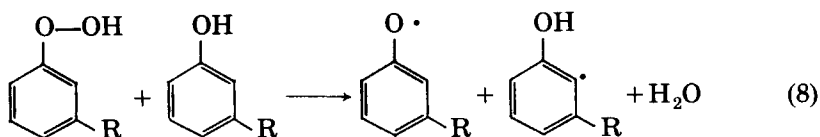
radical



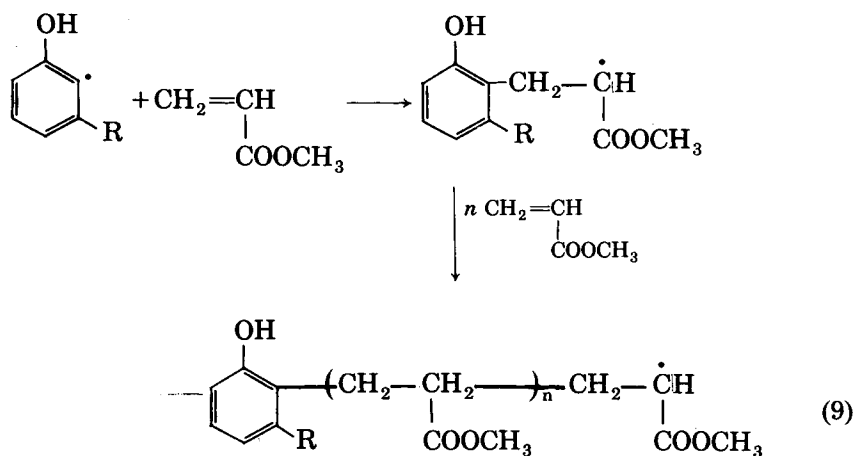
Due to delocalization of unpaired electrons, this radical possesses low reactivity and cannot initiate graft copolymerization. However, it is capable of interacting with more reactive radicals.



The obtained hydroperoxide forms an oxidation-reduction system with vegetable tanning agents and this results in the following reaction



Due to the formation of a stable phenoxy radical, this reaction is energy-wise more profitable than the thermal decomposition of hydrogen peroxide (nearly 13 kcal/mol is only required for conducting this reaction, whereas nearly 40 kcal/mol is required for thermal decomposition of hydrogen peroxide). The phenoxy radical reacts with OH as in (7) while the radical with active center in *ortho* position to OH group initiates graft copolymerization.



#### Various Experimental Factors Influencing the Grafting Reaction Effect of Initiator Concentration

Hydrogen peroxide was chosen as an initiator for grafting PMA onto cutch since our preliminary experiments and also the literature indicated that  $Ce^{4+}$  and other redox initiators are not very effective in these grafting reactions. The effect of concentration of hydrogen peroxide on the grafting of MA onto cutch is shown in Table I. It can be seen from Table I that maximum amount of grafting was achieved (283%) with MA when hydrogen peroxide concentration was 0.1324 mol/L. At a higher concentration, 0.1765 mol/L, the degree of grafting was almost nil. It was also found that the grafting efficiency was maximum at 0.1324 mol/L initiator concentration and the increase was

TABLE I  
Effect of Concentration of Initiator on the Grafting of Methyl Acrylate onto Cutch<sup>a</sup>

Sample no.	Concentration of hydrogen peroxide (mol/L)	Total conversion of monomer (%)	Grafting efficiency (%)	Percentage of grafting	$\frac{R_g^b}{R_h}$
CI <sub>1</sub>	0.0441	57.5	7.0	14.5	0.0752
CI <sub>2</sub>	0.0882	55.0	45.5	142.8	0.8330
CI <sub>3</sub>	0.1324	85.0	76.5	282.9	3.1670
CI <sub>4</sub>	0.1765	37.5	Nil	Nil	Nil

<sup>a</sup> Reaction conditions: [acetic acid] = 1.75 mol/L; [methyl acrylate] = 2.22 mol/L; weight of cutch = 10 g/100 mL reaction mixture; temperature = 60–80°C; time = 4 h.

<sup>b</sup>  $R_g$  = rate of grafting;  $R_h$  = rate of homopolymerization.

TABLE II  
Effect of Concentration of Acetic Acid on the Grafting  
of Methyl Acrylate onto Cutch<sup>a</sup>

Sample no.	Concentration of Acetic Acid (mol/L)	Total conversion of monomer (%)	Grafting efficiency (%)	Percentage of grafting	$\frac{R_g}{R_h}$ <sup>b</sup>
CI <sub>3</sub>	1.750	85.0	76.5	282.9	3.167
CA <sub>1</sub>	2.625	79.0	15.0	59.0	0.176
CA <sub>2</sub>	3.500	39.0	Nil	Nil	Nil

<sup>a</sup>Reaction conditions: [hydrogen peroxide] = 0.1324 mol/L; [methyl acrylate] = 2.22 mol/L; weight of cutch = 10 g/100 mL reaction mixture; temperature = 60–80°C; time = 4 h.

<sup>b</sup> $R_g$  = rate of grafting;  $R_h$  = rate of homopolymerization.

gradual with increase in the initiator concentration. The amount of homopolymer produced was found to be very high at 0.441 mol/L initiator concentration (see Table IV). The same trend was also found in the grafting efficiency values. Initially, the free radicals liberated by decomposition of hydrogen peroxide were mainly utilized for the homopolymer formation; as the concentration of hydrogen peroxide was further increased, hydrogen peroxide may react with cutch, thereby liberating phenoxy free radicals on the backbone leading to the grafting reaction. However, at 0.1765 mol/L it appears that the free radicals are mainly involved in the termination reactions and the mutual annihilation of the liberated free radicals. This may be the reason why there was no grafting at 0.1765 mol/L initiator concentration.

#### Effect of Acetic Acid Concentration

Acetic acid has been used to solubilize cutch since it is not completely soluble in water. The acetic acid medium was selected to perform the grafting reactions since it makes possible graft copolymerization in a homogeneous medium as well as to obtain the end product having a pH range suitable for tanning purposes.

The effect of acetic acid in the media on the grafting of MA onto cutch was evaluated by varying the concentration of acetic acid from 1.75 to 3.5 mol/L. It is found from Table II that the grafting efficiency, percent grafting, and the ratio of  $R_g/R_h$  decreased with the increase in the concentration of acetic acid.

#### Effect of Concentration of the Backbone

It can be seen from Table III that the grafting efficiency increased with the increase in the quantity of cutch used for the grafting reaction. The efficiency increased from 50.5% at 5 g of cutch/100 mL reaction mixture to 98% at 20 g of cutch/100 mL reaction mixture. The amount of cutch utilized for grafting was very low at lower contents of cutch (5 g/100 mL reaction mixture). This may be the reason for the very high percent grafting shown in Table III for 5 g of cutch/100 mL reaction mixture.  $R_g/R_h$  values followed the same trend as that of grafting efficiency data by showing higher value at higher concentrations of cutch.

TABLE III  
Effect of Concentration of Backbone (Cutch) on the Grafting  
of Methyl Acrylate onto Cutch<sup>a</sup>

Sample no.	Weight of cutch for 100 ml of total reaction mixture (g)	Total conversion of monomer (%)	Grafting efficiency (%)	Percentage of grafting	$\frac{R_g}{R_h}$ <sup>b</sup>
C <sub>1</sub>	5	87.0	50.5	1082.0	1.024
CI <sub>3</sub>	10	85.0	76.5	282.9	3.167
C <sub>2</sub>	15	80.0	80.0	115.9	3.930
C <sub>3</sub>	20	85.5	98.0	132.3	39.680

<sup>a</sup>Reaction conditions: [acetic acid] = 1.75 mol/L; [methyl acrylate] = 2.22 mol/L; [hydrogen peroxide] = 0.1324 mol/L; temperature = 60–80°C; time: 4 h.

<sup>b</sup> $R_g$  = rate of grafting;  $R_h$  = rate of homopolymerization.

TABLE IV  
Analysis of Crude Cutch-PMA Graft Copolymers<sup>a</sup>

Sample no.	Composition of crude graft copolymers (%)				Total yield (g)
	Cutch		PMA		
	Reacted	Unreacted	Grafted	Homopolymer	
CI <sub>1</sub>	25.58	20.93	3.72	49.77	21.50
CI <sub>2</sub>	16.67	30.95	23.81	28.57	21.00
CI <sub>3</sub>	17.04	19.53	48.21	15.22	27.34
CI <sub>4</sub>	34.29	22.86	0	42.86	17.50
CA <sub>1</sub>	15.50	23.26	9.147	52.09	25.80
CA <sub>2</sub>	38.13	18.95	0	44.75	17.52
C <sub>1</sub>	3.62	18.71	39.17	38.50	22.39
C <sub>2</sub>	35.40	13.10	41.04	10.46	31.07
C <sub>3</sub>	34.02	19.85	45.00	1.13	37.13

<sup>a</sup>Reaction conditions are as given in Tables I, II, and III.

Table IV shows the data of the analysis of crude cutch-PMA graft copolymers. Based on the grafting efficiency (Table III) and the analysis of crude cutch-PMA graft copolymers, Sample C<sub>3</sub> appears to be the best one. The analysis of this sample is given below:

Total yield	37.13 g
Efficiency of grafting	98%
Percent grafting	132.3
$R_g/R_h$	39.68

#### Characterization of Cutch-Vinyl Graft Copolymers Infrared Spectra

Proof of grafting has been provided by infrared spectra of representative samples of graft copolymers. In Figure 2, the infrared spectra of untreated

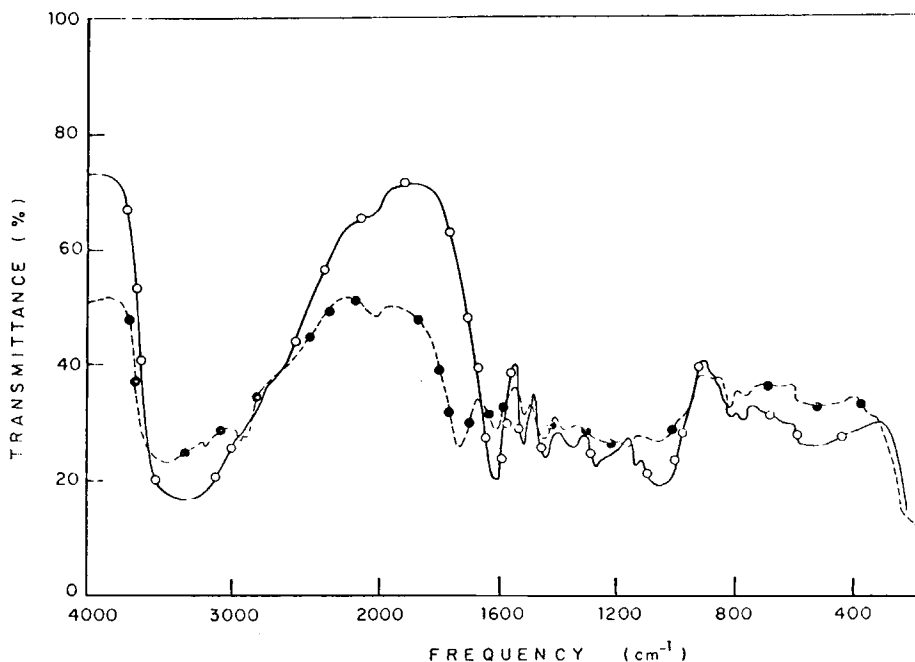


Fig. 2. Infrared spectra of: untreated cutch (○); cutch grafted with PMA (●).

cutch and PMA-grafted cutch are given. The infrared spectrum of pure cutch showed the presence of phenolic hydroxyl groups at  $3400\text{ cm}^{-1}$  and a peak at  $1610\text{ cm}^{-1}$  which is due to the aromatic ring C—C stretching. The infrared spectrum of cutch-g-PMA showed characteristic absorption bands of PMA at  $1730\text{ cm}^{-1}$  (carbonyl of ester group) in addition to the phenolic hydroxyl and the aromatic ring C—C stretching peaks at  $3400\text{ cm}^{-1}$  and  $1610\text{ cm}^{-1}$ , respectively. Thus the infrared spectrum of the pure graft copolymer after the removal of both homopolymer and unreacted cutch clearly indicated the evidence for grafting of PMA onto cutch.

### Thermogravimetric Analysis

The thermogravimetric (TG) and differential thermogravimetric (DTG) curves of the various polymers studied are shown in Figure 3. As can be seen in the figure, the ungrafted cutch and PMA gave TG curves characterized by one onset, whereas the TG curves of the grafted cutch and the physical mixture of cutch and PMA exhibited plateaus initiated at temperatures around  $360^{\circ}\text{C}$  and  $325^{\circ}\text{C}$  (Table V), respectively, and two onsets associated with the two-stage decomposition process. It was reflected on the shape of the DTG curves which were bimodal for the grafted cutch and the physical mixture of cutch and PMA.

In Table V, various characteristic thermal decomposition temperatures for cutch, cutch-g-PMA, PMA, and the physical mixture of cutch and PMA studied are summarized. It can be seen that the cutch-g-PMA began to decompose at higher temperatures compared to the pure cutch, whereas the physical mixture started decomposing at the same temperature as that of



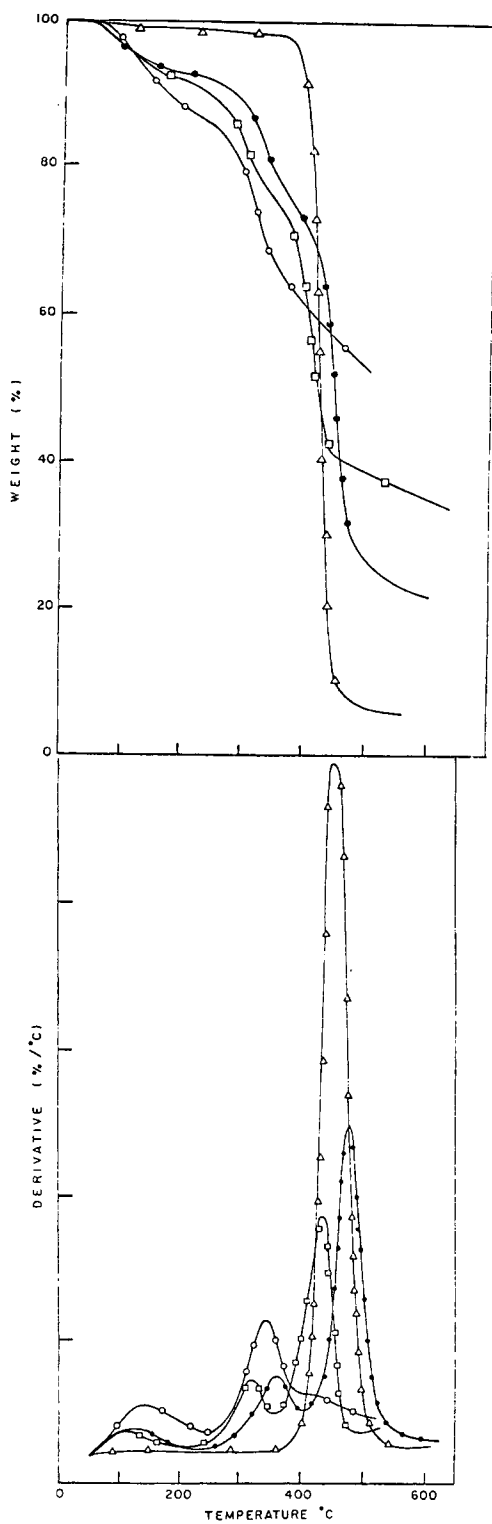


Fig. 3. Thermogravimetric (TG) and differential thermogravimetric (DTG) curves of: cutch (○); cutch grafted with PMA (●); PMA (Δ); Physical mixture of cutch and PMA (□).

TABLE V  
Effect of Grafting of PMA on the Thermal Behavior of Cutch

Name of the polymer	IDT <sup>a</sup>	$T_{\max}^b$		$T_p^c$
		$T_{\max} I$	$T_{\max} II$	
Cutch	260	340	—	—
Cutch-g-PMA	280	365	480	360
PMA	375	450	—	—
Physical mixture of PMA and cutch	260	325	440	325

<sup>a</sup>Initial decomposition temperature.

<sup>b</sup>Temperature of maximum rate of weight loss ( $T_{\max} I$ , first maximum;  $T_{\max} II$  second maximum).

<sup>c</sup>Initial plateau temperature.

cutch (260°C). The grafted cutch gave two temperatures of maximum rate of weight loss ( $T_{\max}$ ). The first  $T_{\max}$  ( $T_{\max} I$ ) of grafted cutch corresponds to the  $T_{\max}$  of pure cutch. An increase of 25°C in the grafted cutch was observed for the value of  $T_{\max} I$ .  $T_{\max} II$  of cutch-g-PMA (480°C) corresponds to the  $T_{\max}$  of homo-PMA ( $T_{\max} I$ , PMA 450°C) which showed an increase of 30°C. However, in the case of the physical mixture, the  $T_{\max} I$  at 325°C and  $T_{\max} II$  at 440°C correspond to  $T_{\max} I$  at 365°C and  $T_{\max} II$  at 480°C of the cutch-g-PMA, respectively. These data indicated that the cutch-g-PMA showed higher thermal stability by 40–45°C as compared to the physical mixture of cutch and PMA. These results gave a clear indication that cutch has been really grafted by PMA rather than giving a physical mixture.

Some experiments are being carried out to evaluate the use of the cutch-g-PMA copolymer product for tanning hides and skins as compared to the unmodified cutch. The results will be published elsewhere.

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