Grafting, Blending, and Biodegradability of Cellulose Acetate

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ABSTRACT: We performed the graft copolymerization of methyl acrylate and methyl methacrylate on cellulose acetate (CA) by a free-radical method. The grafting was confirmed by gravimetric analysis and IR spectroscopy. Low graft efficiency was observed for the benzoyl peroxide initiator used in the system. Melt blending of CA and nylon 6 was done for CA-rich compositions. The physical and mechanical property measurements showed an improvement over virgin CA properties. The chemical properties, however, did not show any phenomenal advancement. A CA/starch (90/10) blend was prepared and studied for biodegradation during soil burial. The gravimetric and mechanical property results indicated possible degradation. © 2003 Wiley Periodicals, Inc. J Appl Polym Sci 91: 1716–1723, 2004

Key words: graft copolymers; blending; biodegradable; mechanical properties

INTRODUCTION

Cellulose plastics have played a vital role in the development and perfection of many fabrication methods. However, with the invention of more and more synthetic polymers, their prominence has declined. Cellulose plastics have their source in naturally occurring material. Hence, the scientific community has started to concentrate on ways to improve the properties of cellulose plastics by means of grafting and blending.

In the case of synthetic polymers, the desired properties can be achieved by a change in the composition of the monomers added during their manufacture. Cellulose plastics have their composition already fixed by nature. Thus, chemical modification provides a way to achieve desired properties in the polymer. Grafting provides a method for the preparation of new polymeric materials with improved and desirable properties.[1] The grafting of synthetic polymers onto cellulose and cellulose derivatives is a useful way to improve the qualities of both materials and to expand the range of their applications. Cellulose acetate (CA) grafting is a process aimed at the introduction of some branches of synthetic polymers into the main polysaccharide chain to confer specific additional properties to the substrate itself without destroying its intrinsic characteristics.[2]

Graft copolymerization can be initiated by free-radical, ionic processes or by γ-irradiation. Grafting by free-radical polymerization is the most widely used technique.[3] Initiation of graft copolymerization by a free-radical mechanism can occur by a redox process on the substrate or by a chain-transfer process to the substrate.

Lee et al.[4] studied the grafting of ethylene-*co*-maleic anhydride and styrene-*co*-maleic anhydride copolymers onto CA and methyl cellulose and reported graft yields of 79–90%. Basu et al.[5] studied the grafting of *N*-vinyl carbazole on CA films with a simultaneous Co/60-γ irradiation grafting technique. Nie et al.[6] studied the upper limit of grafting conversion and phase homogeneity in a CA/poly(styrene-*co*-maleic anhydride) grafting reaction system. They also studied the dimensional stability and mechanical properties and found improvement in grafts when compared to CA. Razik[7] studied the grafting of dichlorodimethylsilane onto CA in a homogeneous medium. The photoinitiated copolymerization of furfuryl methacrylate on the CA matrix with γ irradiation[8] has also been reported.

The grafting reaction between CA and acrylic monomers adds new traits to CA. The incorporation of hydrophobic methyl acrylate (MA) and methyl methacrylate (MMA) can help improve the dimensional stability of CA. However, the volume of improvement is dependent on the efficiency of grafting, and its determination is of prime importance.

The utilization of polymer blends is an increasingly important segment of the plastics industry. Hence, polymer blends have been widely investigated, which

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has also been done because of their simplicity and efficiency for the development of new high-performance materials.[9] In our previous article,[10] we reported the miscibility of CA and nylon 6 (N6) for CA-rich compositions. This work prompted us to melt blend the two polymers and study the properties.

Public awareness has increasingly demanded biodegradable and environmentally friendly materials. The effects of the degree of substitution (DS) in each anhydro glucose unit of cellulosics on microbial attack were studied by Siu.[11] CA films have been shown to be biodegradable in various environments.[12] Buchanan et al.[13] showed that CA films with DS values of 1.7 and 2.5 were partially degraded, resulting in weight loss and decrease in thickness and tensile strength. They further suggested that the synergistic action of the enzymes esterase and cellulase produced by microorganisms was responsible for the microbial attack on CA. Mayer et al.[14] reported that blends of CA (DS = 2.5) and starch had acceptable properties for injection-molded applications and were biodegradable and nontoxic.

In this article, we report the results of (1) the graft copolymerization of CA and acrylic monomers, (2) the melt-blending of CA and N6 in their miscibility range, and finally, (3) the biodegradation and loss in mechanical properties of blends of CA and starch.

EXPERIMENTAL

Graft copolymerization

The graft copolymerization of MA and MMA monomers (synthesis grade, E. Merck, India) onto CA (Mysore Acetates and Chemicals Co., Mandya, India; acetyl value as combined acetic acid = 53.5–55.5% w/w; efflux time = 263.4 s at 30°C for a 0.1 g/dL solution) was carried with a benzoyl-peroxide (BPO) free-radical initiator obtained from Loba Chemicals (India). About 10 g of CA powder was weighed into a 500-mL reaction vessel. Acetone (100 mL) was poured into this, and CA was completely dissolved with a magnetic stirrer. Then, it was treated with 0.5 g of BPO initiator, and the stirring was continued. The initiator was allowed to form free radicals and interact with the substrate for 10 min at 60°C. This treatment was followed by the addition of about 5 g of monomer. The graft polymerization was allowed to proceed for 6 h at 60°C under an inert atmosphere (nitrogen). At the end of 6 h, the reaction mass was taken into a separating funnel. The unreacted monomer and homopolymer were removed with benzene through repeated extraction (three times). Finally, the resultant graft was washed with methanol and dried at 60°C for 3 h in a vacuum oven.

Blending

The melt-blending of predried cellulose acetate molding granules (CAMG)/N6 (CAMG: Mysore Acetates

and Chemicals Co., specific gravity = 1.28–1.32; N6: viscosity-average molecular weight = 20,700 g/mol, SRF, India) was carried out in a Haake twin-screw extruder (Germany) (CTW100; maximum torque = 200 Nm). The melt-blending was done for CAMG compositions of 90, 85, and 80 wt % in the blends. The temperatures of the different zones of the extruder were maintained at 145, 170, 195, and 215°C, respectively. The test specimens were prepared by the injection-molding of the blend pellets with a Klockner Windsor screw-type injection-molding machine (India) (maximum injection pressure = 1700 kg/cm²) by setting the temperature profile of the process at 150°C, 180°C and 215°C.

Biodegradation

The melt-blending of CA and starch was carried out with the Haake twin-screw extruder with a temperature profile of 145, 160, 170, and 215°C. The mixture of CAMG and starch powder (a 90/10 composition predried at 70°C for 2 h) was melt-blended and palletized in a similar way as discussed earlier. The test specimens were prepared by the injection-molding of the blends (predried at 70°C for 2 h) with the Klockner Windsor screw-type injection-molding machine with a temperature profile at 150, 180, and 215°C.

Characterization of graft copolymers

The graft copolymers were characterized by physical and instrumental methods. The calculation of graft parameters such as percentage weight conversion (WC%), percentage graft yield (GY%), and percentage graft efficiency (GE%) was done with the following relations:[15]

$$WC\% = \frac{W_2}{W_1} \times 100 \qquad (1)$$

$$GY\% = \frac{W_2 - W_1}{W_1} \times 100 \qquad (2)$$

$$GE\% = \frac{W_2 - W_1}{W_3} \times 100 \qquad (3)$$

where W_1 is the weight of original CA taken, W_2 is the weight of grafted CA after extraction and drying, and W_3 is the weight of monomer added.

Specific gravity

A precision analytical balance equipped with a stationary support for an immersion vessel above the balance pan was used. A corrosion-resistant wire for suspending the specimen was also used. A glass bea-
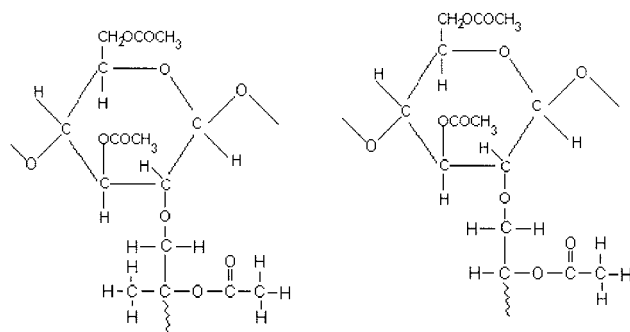
Figure 1 Structures of CA-*g*-PMMA and CA-*g*-PMMA.

ker was used as the immersion vessel. A test specimen of the graft copolymer of about 1 g was cut and weighed in air. Then, the specimen was suspended from the wire attached to the balance and immersed completely in distilled water. The weight of the specimen in water was determined. The specific gravity of the specimen was calculated with the following relation:

$$\text{Specific gravity} = \frac{a}{(a+w) - b} \quad (4)$$

where a is the weight of the specimen in air, b is the weight of the specimen and wire in water, and w is the weight of the partially immersed wire.

Spectroscopic characterization

For IR studies, samples were run as thin films on NaCl discs. Dilute solutions (2%) of CA graft samples in an acetone solvent were placed on a clean, polished NaCl disc, and the solvent was slowly evaporated. A transmission spectrum of the sample was then obtained in a PerkinElmer IR2000 Fourier transform infrared spectrometer (USA).

Characterization of CAMG/N6 blends

Density was measured as per ASTM D 792 with a Mettler Toledo AG 204 density tester (Switzerland). The melt flow index (MFI) of the blends was determined as per ASTM D 1238. Tensile properties were measured according to ASTM D 638 and flexural properties according to ASTM D 790 with a universal testing machine H50KM (UK), with a 50-kN load cell. A shore D durometer (Hiroshima, Japan, with a 100 scale) was used to measure hardness in accordance with ASTM D 2240. The chemical properties were determined as per ASTM D 543 specifications.

TABLE I
Graft Parameters

Graft copolymer	WC%	GY%	GE%
CA-*g*-PMA	101.11	1.11	2.22
CA-*g*-PMMA	101.73	1.73	3.46

Characterization of CAMG/starch blends

Soil burial test

We prepared a soil bed by mixing soil and manure in a ratio of approximately 1:1 in a pot. We controlled the moisture content in the pot in the approximate range 20–30% by adding distilled water as needed.[16] The blend specimens were buried in the soil bed. The control specimens of CA of a similar type were also placed within the soil. The arrangement was maintained at room temperature.

The mechanical properties were measured as discussed earlier for CAMG/N6 blends.

RESULTS AND DISCUSSION

Graft copolymers

Both the graft copolymer samples were whitish and brittle in nature. The free-radical polymerization mechanism to result the graft copolymer could be represented as follows:
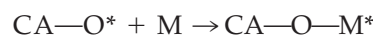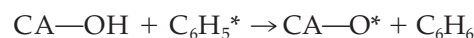
$$C_6H_5OCO{-}OCOC_6H_5 \xrightarrow{\Delta} 2C_6H_5OCO^*$$

$$2C_6H_5OCO^* \rightarrow 2C_6H_5{^*} + 2CO_2 \uparrow$$

$$CA{-}OH + C_6H_5{^*} \rightarrow CA{-}O^* + C_6H_6$$
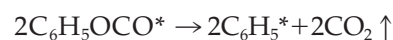
$$CA{-}O^* + M \rightarrow CA{-}O{-}M^*$$

TABLE II
Specific Gravity and Melt Temperature Values of the Graft Copolymers

Material	Specific gravity	Melt temperature (°C)
CAMG	1.33–1.36	200–230
CA-*g*-PMA	1.32	210–215
CA-*g*-PMMA	1.30	210–220
PMA	1.22	—
PMMA	1.17–1.20	—
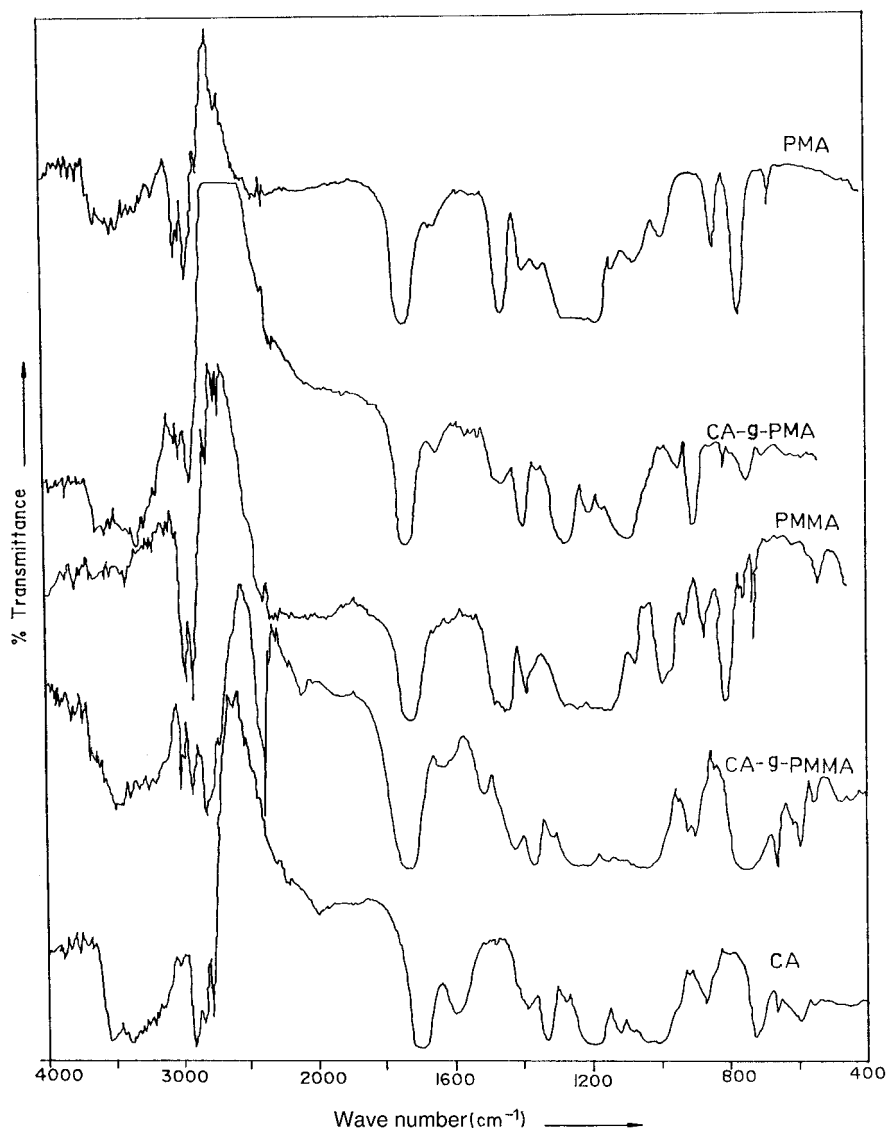
Figure 2 IR spectra of the prepared graft copolymers.

$$CA—O—M^* + nM \rightarrow CA—O—M^*_{(n+1)}$$

$$CA—O—M^*_{(n+1)} + CA—O—M^*_{(m+1)} \rightarrow$$

Graft copolymer

where CA—OH is cellulose acetate, CA—O* is the cellulose acetate radical, CA—OM* is the graft copolymer radical, and M is MA (CH$_2$=CH—COOCH$_3$) or MMA (CH$_2$=CCH$_3$—COOCH$_3$).

The structure of graft copolymers prepared in this study is shown in Figure 1. When BPO molecules are subjected to thermal energy, they decompose to yield phenyl radicals (C$_6$H$_5$*). The percentage acetyl groups present in the CA are not altered by the grafting of vinyl monomers.[17] This confirms that OH groups of CA are the probable sites for grafting, in agreement with Lee and Biermann and Nie and Narayan.[18,19] Thus, C$_6$H$_5$* radicals interact with the hydroxyl groups present in the CA backbone, producing CA macroradicals, which initiate grafting.

The graft copolymers obtained after repeated extraction with benzene were subjected to drying at 70°C in a vacuum oven for 6 h. After they were cooled to room temperature in a desiccator, the weights of the copolymers were noted with a precision analytical balance. An increase in weight was observed in both copolymers compared to the weight of CA taken originally for the graft copolymerization. The increase in weight of the copolymers to the weight of cellulose taken indicated pos-

TABLE III
Characteristic IR Absorption of CA, PMMA, and PMA

CA		PMMA and PMA	
Group	Wave number (cm^{-1})	Group	Wave number (cm^{-1})
OH stretching	3400–3200	Asymmetric and symmetric CH_2 stretching vibrations	2800–2975
C=O stretching	1700–1780	Ester methyl stretching vibrations	2900–3025
CH_3 asymmetric deformation	1430–1470	Carbonyl vibrations	1700–1780
CH_3 symmetric deformation	1365–1385	—	—
Acetate C—C—O stretching	1210–1250	—	—
C—O stretching	~ 1050	—	—

sible grafting.[15] The different graft parameters calculated are given in Table I.

The amount of grafting of the monomers on CA was below 2% for both of the copolymers, which is expressed as GY%. The overall efficiency of the graft copolymerization reaction was expressed by graft efficiency. The graft efficiency was higher for CA-*g*-poly (methyl methacrylate) (PMMA) (3.46%) over that for CA-*g*-poly (methylacrylate) (PMA; (2.22%). This showed that with the use of a BPO initiator, MMA could be grafted on to CA more efficiently than MA on to CA. This could be attributed to the higher reactivity of MMA to CA than that of MA.[20]

The specific gravities of both copolymers and ungrafted polymers are given in Table II. The values were between those for the pure components and much closer to that of CA, following the rule of mixtures. This was expected because of the lesser graft efficiency. The free-radical initiator is believed to effect grafting by a chain-transfer mechanism.[21] GE% obtained with BPO was rather low. This could be attributed to the nature of the BPO initiator. During grafting, homopolymerization is in competition with the grafting process because of the nature of BPO, which is highly reactive,[22] favoring homopolymerization. The increase in graft efficiency depends on the supply of amount of monomers to the substrate. The large amount of homopolymer deposits blocked the way of monomer molecules to the CA macroradicals, resulting in a decrease in graft yield.

The melt temperature of the graft copolymers and ungrafted CA determined in this investigation are also

given in Table II. Because, CA degrades before attaining melting temperature, normally CA is compounded with stabilizers such as dimethyl phthalate or diethyl phthalate. For the sake of comparison, the melt temperature of CAMG was also considered. The grafting of MMA and MA vinyl monomers onto CA reduced the melt temperatures of the respective graft copolymers. This was attributed to following: (1) the strong hydrogen bond present in the CA homopolymer was reduced because of grafting and (2) the close packing of molecules was decreased due to the development of microvoids on grafting.[23]

The IR spectra of pure CA, pure PMMA, pure PMA, and their grafts (dissolved in acetone) are shown in Figure 2. The characteristic peaks of CA, PMMA, and PMA are shown in Table III. All of the prominent peaks pertaining to CA, namely, C—O (1050 cm^{-1}), C—C—O (1235 cm^{-1}), CH_3 asymmetric deformation (1370 cm^{-1}), CH_3 symmetric deformation (1432 cm^{-1}), C=O (1750 cm^{-1}), and OH (3400 cm^{-1}), were clearly observed in the CA spectrum. In addition to these peaks, the characteristic peaks of PMMA/PMA were also observed in the respective graft systems. Clear peaks were observed at 3000, 2926, and 2823 cm^{-1} in the spectrum of the CA-*g*-PMMA system. These peaks corresponded to the CH_3 stretching in the ester methyl group of PMMA, the CH_2 asymmetric and symmetric stretching of PMMA, respectively. Similarly, peaks were observed at 3025 and 2075 cm^{-1} in the spectrum of CA-*g*-PMA due to CH_3 stretching in the ester methyl group and CH_2 asymmetric stretching. In ad-

TABLE IV
Density and MFI Values of CA/N6 Blends

Blend composition (CA/N6)	Density (g/cc)	MFI (g/10 min)
100/00	1.277	2.52
90/10	1.261	2.56
85/15	1.254	2.62
80/20	1.242	2.72
0/100	1.112	17.31

TABLE V
Tensile Property Values of CA/N6 Blends

Blend composition (CA/N6)	Tensile strength (MPa)	Tensile modulus (MPa)	Elongation at break (%)
100/00	31.99	827	23.21
90/10	42.79	898	19.29
85/15	43.30	1014	17.14
80/20	44.88	1053	17.14
0/100	60.36	2264	15.23

TABLE VI
Flexural Strength and Hardness Values of CA/N6 Blends

Blend composition (CA/N6)	Flexural strength (MPa)	Hardness value (shore D)
100/00	42.78	83
90/10	51.68	83
85/15	54.92	84
80/20	55.72	84
0/100	64.12	85

dition to these, the spectra of both of the grafts had a broad peak at 720 cm^{-1} due to methylene rocking vibrations, which invariably always appear in compounds with at least four contiguous CH_2 groups.[24] These results confirmed the grafting.

CAMG/N6 blends

The density values of the blends at 28°C are shown in Table IV. The density values of pure CAMG and N6 are also shown for comparison. With the incorporation of N6 into CAMG, a steady decrease in density was observed. MFI measurements were made at 230°C with a load of 2.16 kg to study the effect of the presence of N6 on the flow properties of CAMG, and the results are shown in Table IV. A steady increase in MFI from CAMG to the blended composition was found. MFI values increased with the addition of N6 because of the higher MFI values of N6.

The tensile properties of pure and blend samples were measured at a grip separation speed of 60 mm/min with a gauge length of 70 mm and are presented in Table V. The increase in tensile strength of 90/10 CA/N6 was considerable (34%) compared to that of pure CAMG. A further increase in the N6 level increased tensile strength but to a small extent. A steady increase in the tensile modulus was observed for all three blends studied. The percentage elongation decreased for the blends. This reduction increased with greater amounts of N6 in the blends.

Flexural strength was measured at a strain rate of 5.4 mm/min, and the values are given in Table VI.

With just 10% N6 in the blend, flexural strength increased by about 21% compared to pure CAMG. Because CAMG and N6 had almost the same level of hardness, the resulting blends also had the same hardness, as shown in Table VI.

CA blends were exposed to different chemical reagents/solvents to investigate the effect of chemical environments on the blends. Chemical reagents were selected in such a way that a range of chemical environments, such as acid, base, oxidizing agent, reducing agent, organic solvent, and salt solution, were covered. The change in weight and color of the blends was recorded after the sample was exposed for 7 days at room temperature, and the results are presented in Table VII. No color change was observed, but there was a change in weight. From the results, one can see that the blends surprisingly showed less resistance to a weak acid (acetic acid). The blends showed sensitivity toward a strong base (sodium hydroxide). They were resistive to salt solution, toluene, methanol, and ammonium hydroxide. The percentage absorptions of water, hydrogen peroxide, and methanol were between those of corresponding homopolymers. The percentage water absorption increased with increasing N6 content in the blend. The blends and the homopolymers degraded in 5% potassium permanganate solution. This indicated a possible chemical degradation and, hence, showed that the blends were sensitive to an oxidizing agent.

CAMG/starch blends

The starch-filled CA blend with the ratio 90/10 wt % (CA/Starch) was obtained by melt blending. Blends with starch contents of 20 and 30% were also tried, but at these compositions, starch was thermally degraded. Hence, studies were restricted only to a 90/10 CA/starch blend.

The density of the blend measured at 28°C was 1.285 g/cc. This was higher than the density of CAMG, as expected (density of starch 1.48–1.53 g/cc).

The specimens buried in the soil were taken out in three batches, after intervals of 1, 2, and 3 months.

TABLE VII
Chemical Resistivity Values of CA/N6 Blends

Blend composition (CA/N6)	Change in weight after treatment for 7 days at room temperature (%)								
	10% HCl	10% acetic acid	20% toluene	25% methanol	25% NaCl	10% H_2O_2	10% NaOH	10% NH_4OH	Water
100/00	5.8	6.1	4.5	4.4	0.7	2.2	45.4	3.3	2.2
90/10	9.1	11.6	5.8	5.3	1.4	3.5	54.4	6.0	3.3
85/15	9.4	14.1	5.6	5.5	1.1	3.5	64.1	8.2	3.3
80/20	11.2	12.9	4.3	4.4	1.4	4.5	37.6	9.1	3.3
0/100	8.8	11.5	5.3	9.7	1.3	5.4	5.5	8.4	5.4

When exposed to 5% $KMnO_4$ solution, the specimens were chemically degraded.

Visual observations of all of the specimens were made. The development of white spots on the surface of all of the specimens was observed. The number of such spots increased with increasing burial time.

All of the samples buried were analyzed gravimetrically. The samples were dried at 70°C for 2 h after they were taken from the soil. Then, they were conditioned at room temperature for 24 h before their weights were determined. The blended and control specimens exposed for 3 months showed a distortion in their dimensions after drying. A reduction in weight was noted for all of the specimens. The percentage loss in weight of the specimens buried for different time intervals is listed in Table VIII. The reduction in the weight of the control samples may have been due to the diffusion of plasticizers.[25]

The control samples showed reductions in weight by 4.29, 5.56, and 6.44% for 1, 2, and 3 months, respectively. The reductions in weight for the blended samples were 4.36, 7.39, and 8.91% for the same respective periods. Thus, increases in weight loss for starch-blended specimens by 1.63, 32.91, and 38.35% for the three respective periods were observed. This indicated that the starch-incorporated blend underwent biodegradation during soil burial.

Most of the studies[11–14] on the biodegradability of CA have been based on the weight loss of the CA specimens. However, some studies based on strength loss have also been made.[25,26] In this investigation, the tensile and flexural specimens of blended and control specimens were tested for loss in respective strengths after burial for different time intervals. The specimens buried for 3 months were distorted in their shape, because of which the measurement of their dimensions was not possible. The tensile strength and flexural strength values of CAMG and the CAMG/starch blends after soil burial for different periods are given in Table IX. Losses in properties were observed for all of the buried samples. The loss was higher for the CAMG/starch blend, and the loss in strength increased with increasing burial time. This evidence confirmed that the presence of starch in the blend caused biodegradation.

TABLE VIII
Weight Loss in Pure CA and the CA/Starch Blend for Different Burial Periods

Period of soil burial (month)	Pure CA (% weight loss)	CA/starch (% weight loss)	Increase in weight loss in the blend (%)
1	4.29	4.36	1.63
2	5.56	7.39	32.91
3	6.44	8.91	38.35

TABLE IX
Mechanical Properties of Pure CA and the CA/Starch Blend Before and After Soil Burial

Period of soil burial (month)	Tensile strength (MPa)		Flexural strength (MPa)	
	Pure CA	CA/starch blend	Pure CA	CA/starch blend
0	31.99	31.17	42.78	32.76
1	31.15	30.64	42.44	26.60
2	30.35	29.55	42.05	23.72

CONCLUSIONS

The graft copolymerization of the vinyl monomers MMA and MA onto CA with BPO initiator was carried out. The process yielded low graft efficiency in both of the copolymers. The formation of graft copolymers was confirmed by physical methods such as specific gravity and melt temperature measurements. This was further confirmed by IR spectroscopic analysis.

Melt blends of CA and N6 were studied for CA-rich compositions. The flowability of CA/N6 remained almost similar to that of CA, as indicated by only a marginal increase in MFI. However, the tensile strength and flexural strength increased by 34 and 21%, respectively with just 10% of N6 in the blend. A further increase in N6 resulted in only a small increase in these properties. Hardness remained almost the same as that of the constituent polymer, irrespective of their composition. The chemical-resistance studies of CA/N6 blends showed sensitivity toward acetic acid and sodium hydroxide. Exposure of these to 5% $KMnO_4$ showed chemical degradation, indicating their excessive sensitivity to oxidizing agents.

The blends of CA/starch and their biodegradability were also examined in this study. A CA/starch blend in the ratio 90/10 wt % was melt-blended with a twin-screw extruder. Blending with a higher amount of starch was not possible, as starch was thermally degraded. Soil burial up to 3 months resulted in a weight loss of the blend, indicating possible biodegradation. Mechanical properties, such as tensile and flexural strength, also decreased after soil burial. Thus, the biodegradability of the CAMG (DS-53.5–55.5)/starch blend was confirmed.

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