

# Studies on the Composites of Cellulose Triacetate (Prepared from Sugar Cane Pulp) and Gelatin

R. RAJINI, U. VENKATESWARLU, C. ROSE, T. P. SASTRY

Bio Products Laboratory, Central Leather Research Institute, Adyar, Chennai 600 020, India

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**ABSTRACT:** Sugarcane waste (bagasse) which is hitherto discarded as a waste at sugarcane parlors and jaggery units was recovered and cellulose triacetate (CTA) was prepared from the same, after isolation of cellulose. Using this CTA, CTA–gelatin composites were prepared. The materials prepared (i.e., sugarcane cellulose, CTA, CTA–gelatin composites) were characterized for their mechanical properties, water absorption capacity, infrared spectroscopy, and scanning electron microscopy. © 2001 John Wiley & Sons, Inc. *J Appl Polym Sci* 82: 847–853, 2001

**Key words:** sugarcane pulp; cellulose triacetate; gelatin; composites; biopolymers

## INTRODUCTION

Cellulose acetate (CA) is commercially used in textile fibers, plastics, and lacquers. Acetate and triacetate fibers of cellulose have lower strength and abrasion resistance than most other man-made fibers and are frequently used with nylon or polyester in combination yarns.<sup>1</sup> CA is ordinarily prepared by a reaction of cellulose with acetic anhydride by using glacial acetic acid as a solvent and perchloric acid or sulfuric acid as a catalyst.<sup>2</sup> In recent years, lots of modifications were made on CA so that it can be used for various end purposes in pharmaceutical, textile, chemical, and leather industries. Jumei and Wenwin<sup>3</sup> have prepared a super hygroscopic capsule membrane by encapsulating an acrylic acid–starch graft copolymer using cellulose acetate. Nagayasu et al.<sup>4</sup> have prepared transparent cellulose triacetate (CTA) films in combination with some plasticizers for its use as photographic film supports and as protecting films on polarizer plates in liquid crys-

tal displays. CTA membranes are used in hemodialysis.<sup>5–7</sup> Chauhan and Mehta<sup>8</sup> have developed a reverse osmosis membrane (ROM) using CTA for desalination of coastal saline water. ROM have also been prepared by using CA by Kim et al.<sup>9</sup> and its physical properties such as solvent evaporation period and shrinkage temperature were studied.

Gelatin is a degraded form of collagen, a connective tissue protein, present in most of the vertebrates.<sup>10</sup> It is well known for its wound-healing properties and several investigating groups have reported on this topic. Sinha and colleagues<sup>11</sup> treated burns with gelatin sheets and opined that this biological dressing prevented secondary infection and fluid loss due to exudation. Yannas and associates<sup>12</sup> mentioned a process for preparing gelatin films from animal products for the purpose of wound healing. Marois and coworkers<sup>13</sup> indicated that carbodimide-crosslinked gelatin could be used as a new coating for porous polyester arterial prostheses. The potentiality of hydrogels composed of gelatin and poly(L-glutamic acid) (PLGA) as a biological glue for soft tissues was studied and compared with a conventional fibrin glue by Otani and coworkers.<sup>14</sup> These

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Correspondence to: T. P. Sastry.

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authors used water-soluble carbodimides to crosslink the aqueous mixture of gelatin and PLGA. The use of gelatin in pectin–gelatin or alginate–gelatin hydrocolloid systems for the preparation of indomethacin-sustained release microparticles have also been studied under controlled pH and temperature conditions.<sup>15</sup>

In the present study, cellulose was prepared from sugarcane pulp and the same was converted into CTA by acetylation reaction. The importance of CTA and gelatin in the field of medicine is known individually, but the combined effect of these two biopolymers in improving the biomaterial itself and the functionality of the same is yet to be understood. With this view, CTA–gelatin composite film was made and its properties as a film/sheet was studied to presume its possible role when applied in an experimental model.

## EXPERIMENTAL

### Materials

Bagasse was collected from local sugarcane juice parlors. Gelatin, pharmaceutical grade, was obtained from MBD Gelatin, Mumbai, India.

### Preparation of CTA

CTA was prepared by modifying the method described in the earlier studies.<sup>2</sup>

Bagasse was cut into 1 × 1 in. length pieces and boiled with 1*N* sodium hydroxide for 2 h to remove noncellulosic materials. Later bagasse was washed thoroughly with water to attain pH 7.0 and sun dried to get a moisture content of about 12%. This material was ground to 75- to 750- $\mu$ m-size powder in a wiley mill and termed as sugarcane cellulose (SCC).

Acetic acid (75 mL, AcOH) was added to 10 g of SCC and the mixture was stirred for 1 h. Later,

AcOH was squeezed out and 70 mL of acetic anhydride was added to AcOH-treated SCC along with 0.5 mL perchloric acid and shaken for 30 min to facilitate the acetylation of cellulose. The mixture was then diluted by using 200 mL of water and dialyzed against water until the CTA suspension formed attains pH 7.0. This suspension was found to contain 5.2% of solids and denoted as CTA. This CTA suspension is used for further experiments to prepare composites with gelatin. The degree of substitution of CTA was estimated as described earlier<sup>2</sup> and found out to be 2.82.

### Preparation of Gelatin Solution

Gelatin (10 g) was dissolved in 100 mL of water at 55°C in a water bath and dried in a polythene tray at 60°C to obtain a film, denoted as G.

### Preparation of CTA–G Composites

Different proportions (Table I) of CTA and G solutions were mixed, crosslinked with 1% of glutaraldehyde solution (25%), and plasticized by using 1% ethylene glycol. The pH was maintained at 7.0. The preparations were dried separately in polythene trays at 60°C to obtain films and stored in polythene covers.

### Characterization

The analyses of the products prepared (i.e., SCC, CTA, G, CTA–G) were carried out to study water absorption capacity, tensile strength, infrared spectra, and scanning electron microscopy.

### Water Absorption Capacity

The water absorption capacities of different compositions of CTA and G were determined according to the method followed by Rao et al.<sup>16</sup> A small piece of each sample of known weight, dried to a

**Table I** Water Absorption Capacity of CTA–G Composites

Sample No.	CTA (mL)	G (mL)	Percentage Swelling Time			
			1 h	2 h	3 h	24 h
1	37.5	12.5	—	—	—	—
2	25.0	25.0	105	114	121	134
3	12.5	37.5	180	205	220	222
4	05.0	45.0	215	271	275	280
5	00.0	50.0	268	311	320	347

**Table II Mechanical Properties of CTA-G Composites**

Sample No.	CTA	G	Elongation at Break (%)	Tensile Strength (N/mm <sup>2</sup> )
1	37.5	12.5	3.3	1.902
2	25.0	25.0	5.3	7.203
3	12.5	37.5	80.3	7.512
4	5.0	45.0	292.6	8.031
5	0.0	50.0	386.4	8.857

constant weight at 100°C, was allowed to swell in distilled water at room temperature (22°C). The swollen weight of the samples were determined by first blotting the samples with filter paper and then accurately weighing the sample. The weight of the swollen pieces were recorded by every 1, 2, 3, and 24 h. Percentage of swelling of the samples at a given time was calculated from the formula:

$$E_s = \frac{W_s - W_0}{W_0} \times 100$$

where  $W_s$  is the weight of the sample (moist) at a given time,  $W_0$  is the initial weight of the sample, and  $E_s$  is the percentage of swelling at a given time.

### Tensile Strength

Two dumbbell-shaped specimen, 4 mm wide and 10 mm long, were punched out of the prepared

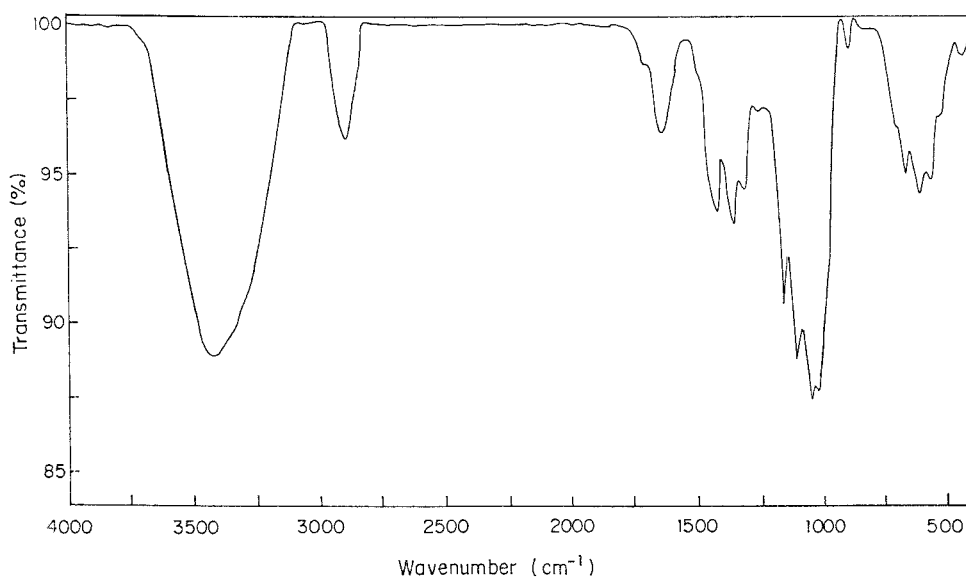
films. Mechanical properties such as tensile strength and percentage strain at break were measured by using an Instron 4501 tensile testing system at an extension rate of 100 mm/min, after fixing the samples in the holders.

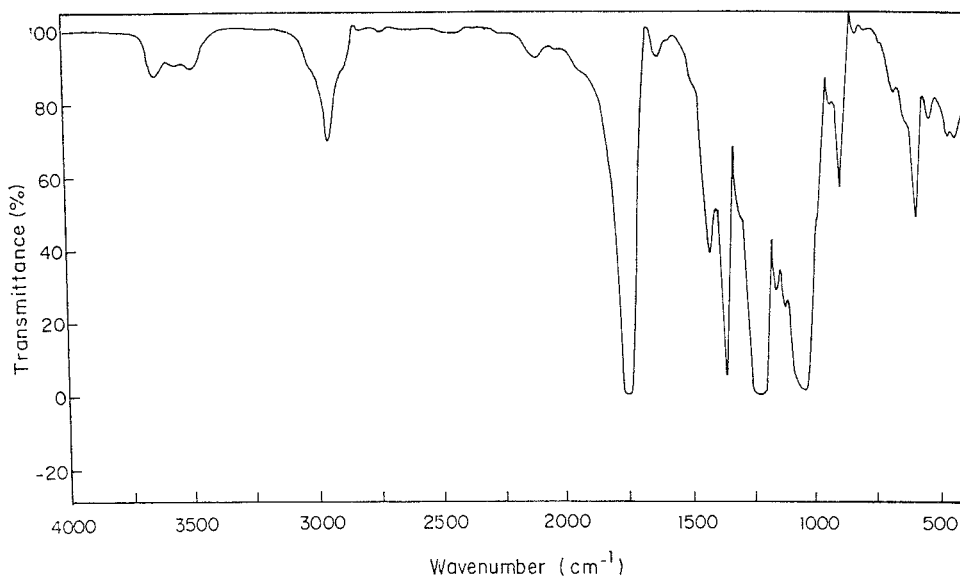
### Infrared Spectroscopy

To provide proof of conversion of cellulose into CTA and the chemical nature of the CTA-G composite, IR spectra were taken for SCC, CTA, G, and CTA-G by using Nicolet impact 400 Fourier transform infrared spectrophotometer, using a 500-mg KBr pellet containing 2–6 mg of the sample.

### Scanning Electron Microscopy (SEM)

To study the surface morphology of the samples, SEM pictures were taken by using a JSM 5300 scanning electron microscope.

**Figure 1** FTIR spectrum of SCC.

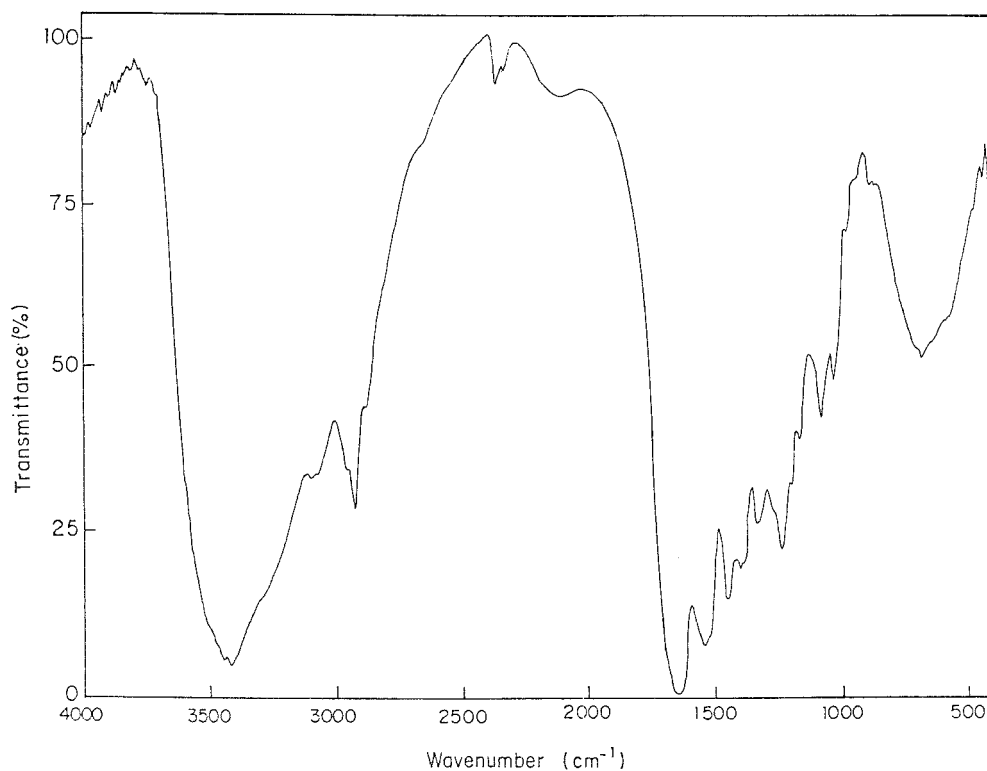


**Figure 2** FTIR spectrum of CTA.

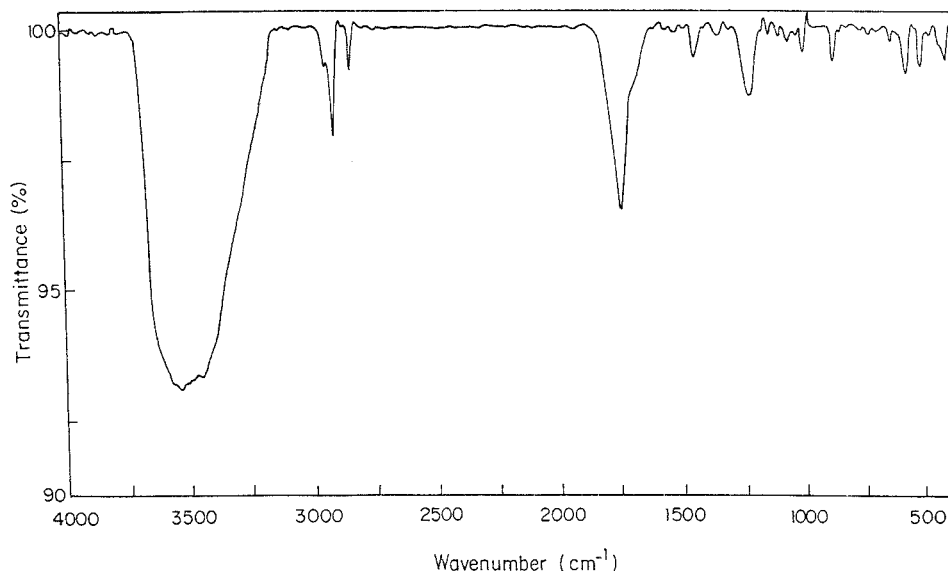
## RESULTS AND DISCUSSION

Presently, a combination of synthetic and natural polymers are finding increased applications in various industries such as textile, pharmaceuti-

cal, and leather. However, the biodegradability of the product is of utmost importance in the present day world to reduce the environmental pollution. Therefore, an attempt was made in this study to combine the two biodegradable compounds, CTA



**Figure 3** FTIR spectrum of G.



**Figure 4** FTIR spectrum of CTA-G.

and gelatin. Glutaraldehyde was used as a crosslinker in the study to impart stability to the biological materials upon storage.

#### Water Absorption Capacity

The CTA-G film made by using 3 parts 5% (w/v) CTA suspension and 1 part 10% (w/v) gelatin solution was not stable when placed in the water and resulted in disintegration. Stepwise substitution of CTA using gelatin in the subsequent experiment (Table I), however, improved the stability of the film in the water. The water absorption also increased with respect to an increase in gelatin content. Therefore, it is clear from these observations that the stability and water absorption properties are imparted only because of the presence of crosslinked gelatin. Since gelatin is a very good film former with wide applications, as mentioned in the earlier part of this article, it can hold another versatile substance CTA for effective application in its combined form.

#### Tensile Strength

The mechanical properties of various combinations of CTA and gelatin are presented in Table II. Films of gelatin and CTA were made separately as controls. Of these, gelatin film showed a high value of tensile strength (8.587N/mm<sup>2</sup>) and elongation at break (386.4%) because of its flexible random coil peptides and presence of various

interacting groups. On the contrary, the CTA is a substituted linear polysaccharide chain containing 1 → 4 glycoside linkages. Additionally, interaction of these molecules because of chemical forces from among the polysaccharides cannot be expected because there are no reactive groups (free —OH) present in the side chain. Moreover, the acetylated cellulose does not form a solution, as the gelatin does, but only a suspension. Therefore, the CA could not form a continuous film. As could be seen from Table II, the gradual incorporation of substituted cellulose in the gelatin decreased the mechanical properties of the film made out of composite. The introduction of CTA particles in the gelatin might have affected the continuity of the film and thereby resulted in an early break (elongation at break) in the samples containing higher amounts of CTA. Similarly, gradual reduction in the tensile-strength value was also observed with the increase of CTA level in the composite.

#### Infrared Spectroscopy (IR)

IR spectra of SCC, CTA, G, and CTA-G are shown in Figures 1 to 4. The IR spectrum of SCC is similar to those reported earlier for cellulose.<sup>17</sup> It is observed that the —OH stretching vibration with strong intensity broadbands around (3700–3200 cm<sup>-1</sup>), showing a peak at 3420 cm<sup>-1</sup>. —OH inplane deformation vibration can be seen from 1457 to 1324 cm<sup>-1</sup> (medium intensity) and C—O



(a)



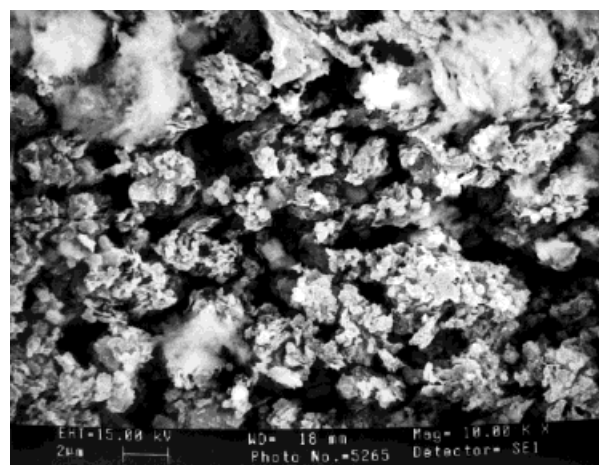
(b)

**Figure 5** (A) Scanning electron micrograph of SCC ( $\times 1000$ ). (B) Scanning electron micrograph of SCC ( $\times 10,000$ ).

stretching vibration bands from 1165 to 1025  $\text{cm}^{-1}$  (four intense bands). The pattern of bands below 1250  $\text{cm}^{-1}$  serve as a key to the identification of cellulose (carbohydrate).

However, in the IR spectrum of CTA, a bond with very strong intensity is seen at around 1740–1750  $\text{cm}^{-1}$ , which represents the ester carbonyl bond (C=O) stretching vibration. Obviously, the absence of OH stretching-vibration bands, which are observed in the IR spectrum of cellulose (3700–3200  $\text{cm}^{-1}$ ), confirms the total conversion of hydroxyl groups into ester groups in the process of acetylation.

Further evidence by the presence of C—O—C stretching vibration bands can also be seen at 1215  $\text{cm}^{-1}$ , accompanied by weaker bands in the

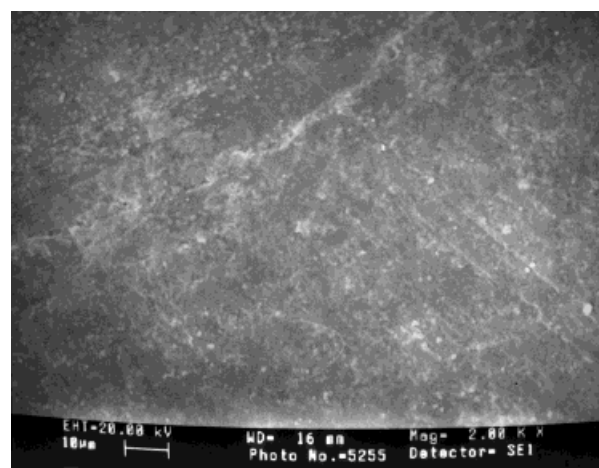


**Figure 6** Scanning electron micrograph of CTA ( $\times 10,000$ ).

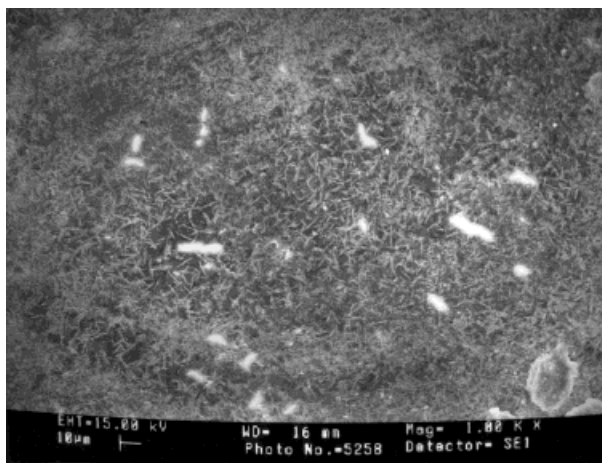
region 1164–1124  $\text{cm}^{-1}$ , and the overtone of C=O stretching vibration (a weak band near 3488  $\text{cm}^{-1}$ ).

The IR spectrum of gelatin (Fig. 3) shows the characteristic amide absorption bands at 1660, 1550, and 1245  $\text{cm}^{-1}$ . The OH groups of the amino acids in gelatin represent a broadband from 3700 to 3200  $\text{cm}^{-1}$  with a peak at 3400  $\text{cm}^{-1}$ .

The IR spectrum of CTA-G (Fig. 4) shows the peaks of —OH groups of gelatin and ester carbonyl peak of CTA. The amide peaks of gelatin are suppressed because of the reaction of the glutaraldehyde with the amide groups of gelatin. As there are no shifts of the peaks of any group in CTA-G spectrum, it is confirmed that CTA-G is only a composite and no chemical reaction occurred between the two compounds.



**Figure 7** Scanning electron micrograph of G ( $\times 2000$ ).



**Figure 8** Scanning electron micrograph of CTA-G ( $\times 1000$ ).

### Scanning Electron Microscopy

The beautiful fibrous morphological structure SCC is seen in Figure 5(A) and (B). Figure 6 shows the SEM picture of CTA, which clearly indicates its nonfibrous nature. Figure 7 shows a dense outer surface of gelatin film. Figure 8 shows the SEM picture of CTA-G, in which it is clearly seen that there is not much difference or change in the CTA-G when compared to the morphological structures of CTA and G separately. The SEM pictures clearly indicate that the CTA-G is only a physical composite and there is no chemical reaction or bonding taking place between the two compounds.

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