Preparation and characterization of cellulose triacetate from *Musa paradisiaca* and cellulose triacetate–polyvinyl chloride blends

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Cellulose triacetate (CTA) was prepared from dried banana plant (*Musa paradisiaca)* stem and veins of the leaves, which are hitherto discarded as waste. As the film of CTA showed poor mechanical properties, an attempt to improve its properties was made by preparing a plasticized CTA and polyvinyl chloride (PVC) blend. The films of the blend and their individual partners were made separately and studied for their mechanical properties, chemical modifications and morphological changes. The results of IR, TGA, DMA and SEM of CTA–PVC blends have shown that there was no chemical reaction between CTA and PVC, and at the same time they were compatible with better physico-chemical properties. The important finding from this study is that the average pore size of the CTA–PVA blend is around 1 μm and hence this can be used as filter to remove the bacteria having body diameter greater than 1 μm. These blends can be used in future as ultra filtration membranes with suitable modifications.

Keywords: Blends, cellulose triacetate, filtration membranes, *Musa paradisiaca*, polyvinyl chloride.

CELLULOSE is one of the most important classes of natural polymers. There is considerable industrial and academic interest in cellulose and its derivatives[1–3]. Cellulose esters such as cellulose acetate (CA), cellulose diacetate (CDA), cellulose acetate butyrate (CAB) and cellulose propionate (CP) in combination with other materials are used in textile fibres, plastics, and lacquers and in bio-medical applications[4,5]. CA and cellulose triacetate (CTA) are extensively used for the preparation of haemodialysis and desalination membranes[6]. Since acetate and triacetate fibres of cellulose have lower strength and abrasion resistance than most of the man-made fibres, these are frequently used in combination with synthetic polymers[7–9]. Further, it has been found that among cellulose esters, CTA has the highest thermal stability[10]. The thermal stability of various cellulose derivatives is arranged in the following order and hence CTA has attracted many researchers.

Permselective hollow-fibre membranes using cellulose derivates, e.g. CTA have been manufactured. These membranes are used for various purposes such as haemodialysis, ultra filtration, etc.[6]. The miscibility of CA, CTA, CAB, CP and ethyl cellulose in CO_2 + acetone and CO_2 + ethanol binary fluid mixtures which are considered as alternative solvents for derivatives has been studied[11]. The effects of temperature and pressure on such systems have also been studied. It has been concluded that banana cellulose fibres are suitable for use as raw material for textile and pulp-paper industries, based on the crystallinity, crystallite size and lattice distortion (micro strain) of wild banana (*Musa velutina*) cellulose using X-ray line broadening analysis[12]. Polyvinyl chloride (PVC) is a widely used synthetic polymer known for its toughness and durable nature. A lot of research has been done on improving the properties of PVC for various applications. Recently, new nano-composites that are processed with a plasticized PVC matrix reinforced by cellulose whiskers have been studied for their viscoelastic properties. These cellulose whiskers are obtained from tunicates[13]. The kinetics of thermo-oxidative degradation of PVC/acrylonitrile–butadiene–styrene blends has been reported. A simplified micro-morphological picture of semi-crystalline dioctylphthalate (DOP)–plasticized PVC on the basis of chain statistics was proposed. It was confirmed that the structure of crystallite is composed of only syndiotactic sequences[14]. It was shown that PVC films could be modified chemically without loss of their transparency and surface smoothness, while carrying out the reactions in appropriate mixtures of solvent and non-solvent for the polymers[15]. The importance of CTA and PVC in various industries is well-known. The combined effect of these two polymers in improving the mechanical properties of the blends has not been studied so far.

In the present study cellulose was isolated from stem and veins of the leaves of banana and converted into CTA by acetylation. CTA–PVC blends were made into films and their physico-chemical properties were studied using different analytical techniques.

Dried banana stem and central veins of the leaves (BSV) were used as raw material. PVC (MW-60,000) was supplied by M/s Chemoplast Company.

CTA was prepared by modifying the method described in earlier studies[16]. The raw material was cut into 1 × 1 inches pieces and boiled in 1 N sodium hydroxide solution for 2 h to remove non-cellulosic materials. It was then washed with water to attain pH 7.0 and sun-dried to get moisture content of about 11–12%. The material thus obtained was ground to 100–700 μm size powder in a Willy mill to obtain banana cellulose (BC).

α-Cellulose was estimated according to a procedure described earlier[17].

For the acetylation of cellulose, to 10 g of BC, 50 ml acetic acid, 100 ml toluene and 0.5 ml perchloric acid (72%) were added and stirred vigorously. After 1 min, 50 ml of acetic anhydride was added and stirred for 15 min. Then an equal volume of water was added to the reaction mixture to precipitate CTA. The degree of acetylation of cellulose was determined by the method described by Tanghe *et al.*[16] and found out to be 2.7.

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Table 1. Effect of DOP concentration on CTA + PVC blends

	PVC: 10% (w/v) solution		CTA: 3.3% (w/v) solution		
Specimen no.	Concentration of CTA solution (ml)	Concentration of PVC solution (ml)	Concentration of DOP (ml)	Tensile strength (N/mm^2)	Extension at break (%)
1	15	1	0.1	6.37 ± 0.32	3.41 ± 0.17
2	15	1	0.2	8.07 ± 0.41	4.33 ± 0.22
3	15	1	0.3	7.73 ± 0.39	5.24 ± 0.26
4	15	1	0.4	5.59 ± 0.28	5.07 ± 0.25
5	15	1	0.5	4.31 ± 0.22	6.49 ± 0.32

Mean and standard deviation were calculated from five different samples.

Table 2. Mechanical properties of CTA + PVC blends

	PVC: 10% (w/v) solution		CTA: 3.3% (w/v) solution		
Specimen no.	Concentration of CTA solution (ml)	Concentration of PVC solution (ml)	Concentration of DOP (ml)	Tensile strength (N/mm^2)	Extension at break (%)
1	15	0	0	2.19 ± 0.11	0.53 ± 0.03
2	15	0	0.2	4.13 ± 0.21	1.24 ± 0.06
3	0	3	0.2	0.54 ± 0.03	67.33 ± 3.34
4	15	3	0.2	12.93 ± 0.64	0.74 ± 0.03
5	15	2.5	0.2	14.23 ± 0.71	2.41 ± 0.12
6	15	2	0.2	11.10 ± 0.56	2.00 ± 0.10
7	15	1.5	0.2	9.90 ± 0.51	3.15 ± 0.15
8	15	1	0.2	8.07 ± 0.40	1.91 ± 0.09

Mean and standard deviation were calculated from five different samples.

CTA solution (3.3% w/v) was prepared by dissolving CTA in chloroform. PVC solution (10% w/v) was prepared by dissolving PVC in tetrahydrofuran (THF). The two solutions were mixed in different compositions for the preparation of CTA–PVC blends (Tables 1 and 2), using DOP solution as a plasticizer. To a known quantity of CTA solution, DOP was added followed by an aliquot of PVC solution. The mixture was stirred continuously for half an hour and poured into a glass plate measuring 12 × 10 × 0.3 cm and dried at room temperature (30°C). The experiments were done in triplicate.

Analyses of the products prepared, viz. cellulose, CTA, PVC, CTA–PVC blends were carried out to study their physico-chemical, mechanical and morphological properties and IR spectroscopy.

Two dumb-bell-shaped specimens of 4 mm wide and 10 mm long were punched out of the prepared film. Mechanical properties such as tensile strength and percentage strain at break were measured using an Instron 4501 tensile testing system at an extension rate of 100 mm/min, fixing the sample in the holders.

To provide proof of conversion of cellulose into CTA and the chemical nature of the individual constituents in the blend, infrared (IR) spectra of samples prepared were taken at a wavelength of 4000–400 cm^{-1} with Nicolet Impact 400 Fourier Transform infrared spectrophotometer using KBr pellet containing 2–6 mg of the sample.

The surface morphology of all the experimental samples was studied using JSM 5300 scanning electron microscope.

Thermo gravimetric analysis (TGA) of the samples was carried out using a Seiko SSC 5200 H in nitrogen atmosphere (80 ml/min) at a heating rate of 10°C/min. Primary weight loss of these materials as a function of temperature was recorded using this study.

Dynamic mechanical analysis was carried out using strips of films (20 × 10 × 0.2 mm^3) using a DMA 2980 dynamic mechanical analyser (TA Instruments) at a frequency of 1 Hz and strain amplitude of 20 m in the temperature range –100°C to +100°C at the rate of 5°C/min.

Polymer blends are popular because they are cost-effective and have the potential for design of materials with properties tailored to a specific use[18]. However, the biodegradability of a product is of utmost importance nowadays. Therefore, an attempt has been made in this study to prepare a degradable material CTA from *Musa paradisiaca* plant waste and its properties have been improved by blending it with a synthetic polymer (PVC) and a plasticizer (DOP). Cellulose content in the waste was found to be 80% on solid weight basis. CTA is soluble in chloroform and PVC is soluble in THF. As both chloroform and THF are miscible and form a homogenous solution, the films formed are homogenous blends.

The CTA film exhibited poor mechanical properties with tensile strength of 2.1951 N/mm^2 and elongation at break of 0.5326%. This may be mainly due to the crystalline nature of the polymer backbone, which is made up of 1 → 4-glycoside linkage. There are many chemical as well as physical methods by which one can improve the mechanical properties of a polymer. Here we have

attempted the blending method in which suitable additives were physically mixed with the polymer. First, a suitable plasticizer like DOP was added to the polymer and its mechanical properties were studied. The CTA–DOP film exhibited only a marginal improvement in the mechanical properties (Table 1). So a synthetic polymer suitable for this system with appreciable mechanical property was selected. As PVC along with a plasticizer exhibits good mechanical properties, it was selected as a suitable partner for CTA. First, the amount of DOP for which the film showed better mechanical properties was optimized. This was done by keeping the ratio of CTA and PVC as constant in the blend and altering the amount of DOP. Films thus prepared were analysed for their mechanical properties. The data obtained showed (Table 1) that the film containing 0.2 ml DOP exhibited better tensile strength. This may be due to optimal volume for a particular composition of PVC and CTA that occupies intermolecular spaces or gaps and gives better tensile properties. After optimizing the quantity of DOP, the ratio of CTA and PVC was optimized. For this, the amount of DOP and CTA was fixed and the amount of PVC was varied (Table 2). The data obtained indicated that when the amount of PVC was increased, the tensile strength of the films initially increased and then decreased. The blend with CTA : PVC : DOP ratio as 15 ml : 2.5 ml : 0.2 ml showed maximum tensile strength of 14.23 N/mm^2 and elongation at break of 2.41%. This may be due optimal concentration of CTA that forms an interstitial matrix with the PVC that gives better tensile strength. This particular blend was used for IR, TGA, DMA and SEM studies.

The IR spectrum of CTA–PVC–DOP (Figure 1) blend shows the characteristic peaks of all the three components, i.e. CTA, PVC and DOP[19–22] (e.g. for CTA, ester carbonyl group (C=O) stretching vibration band at 1740–1750 cm^{-1}; CH_2 stretching vibration bands for PVC at 2965 and 2910 cm^{-1}; a characteristic phthalate band from 1350 to 1250 cm^{-1} with a peak at 1285 cm^{-1} for DOP). As there are no shifts of the peaks of any group in the CTA–PVC–DOP spectrum, it was confirmed that it is a physical blend and no chemical reaction has taken place between them.

The SEM images of CTA (Figure 2 *a*) and PVC (Figure 2 *b*) show surface morphologies with the pores uniformly distributed throughout the film. The pores of CTA are not spherical in shape and their diameter falls in the range

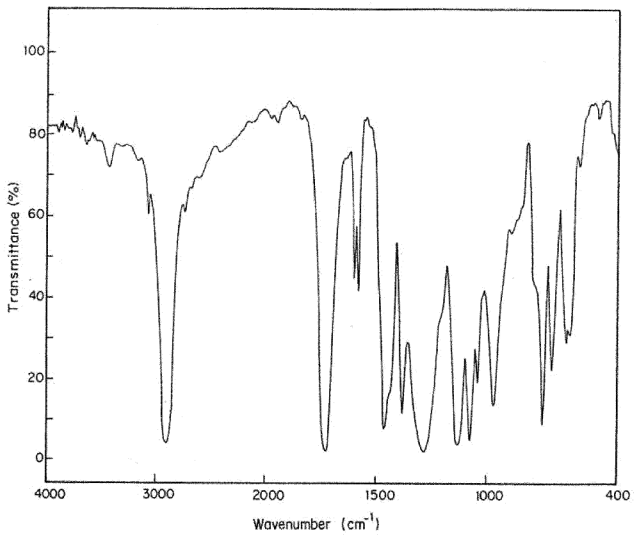

Figure 1. FTIR spectrum of PVC–CTA–DOP blend.

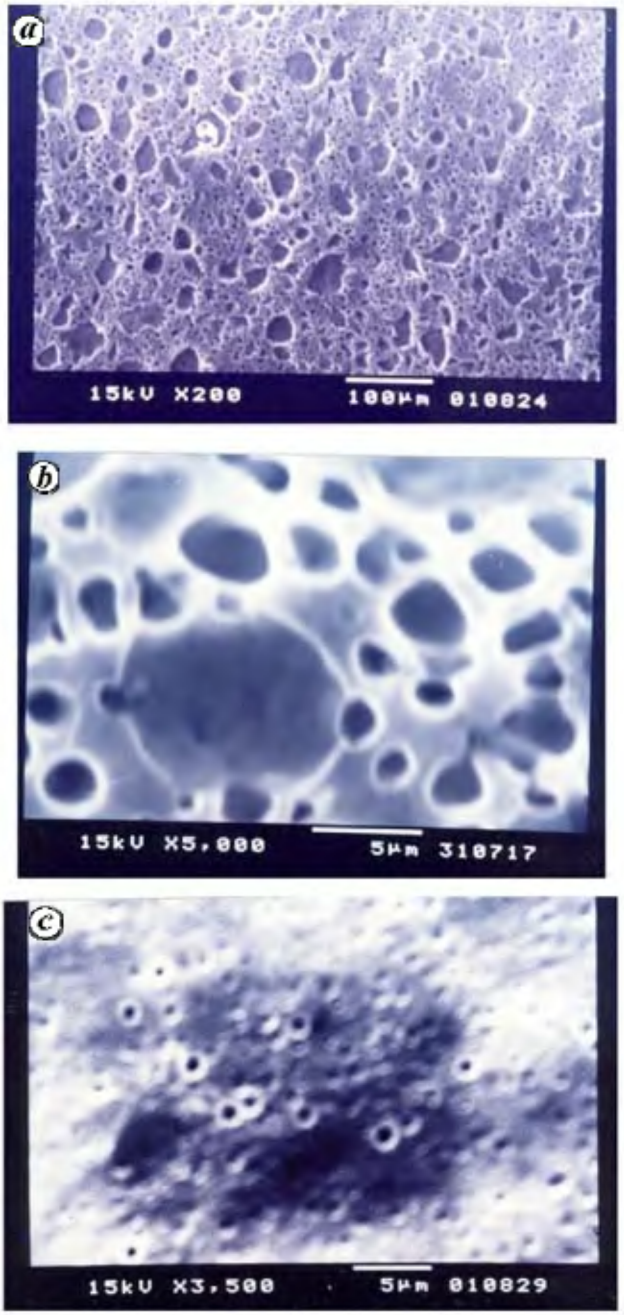

Figure 2. Scanning electron micrographs of CTA (***a***), PVC (***b***) and CTA–PVC blend (***c***).

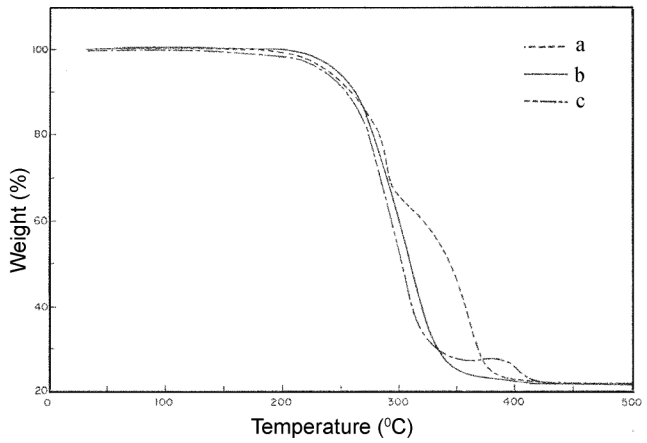

Figure 3. Thermograms of CTA (a), PVC (b) and CTA–PVC blend (c).

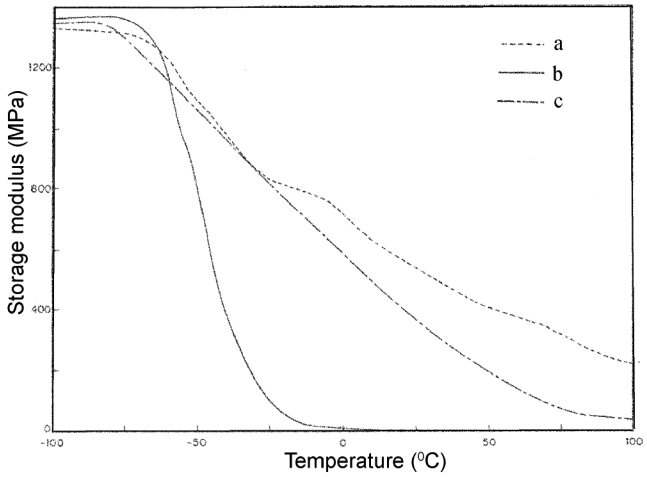

Figure 4. Dynamic mechanical curves of CTA (a), PVC (b) and CTA–PVC blend (c).

10–50 μm, whereas in the case of PVC the pores are more or less spherical in shape and their diameter falls in the range 1.5–10 μm. The SEM image of CTA–PVC blend (Figure 2 *c*) provides an interesting information. The surface morphology is smooth and the pores are uniformly distributed on the entire surface of the region. The pores are almost spherical in shape and the average diameter is around 1 μm. Reduction in the pore size can be observed in the CTA–PVC film when compared with those of PVC or CTA. This may be due to matrix formation of the two materials. The average pore size of the blend is around 1 μm, which is comparable to that in bacteria, which falls in the range 0.2–0.5 μm. Hence bacteria with a body diameter greater than 1 μm can be filtered using this blend. Its efficacy as a filtering membrane will be examined in future studies.

Figure 3 shows the TGA curves for PVC, CTA and CTA–PVC blend. CTA recorded a two-step weight loss (a, Figure 3); the first weight loss (37.96%) observed between 251 and 292°C is due to the decomposition of CTA and the second weight loss (51.46%) is attributed to the char oxidation. The decomposition of PVC begins at 260°C and proceeds up to 331°C, with a total weight loss of 77.4% (b, Figure 3). Whereas CTA–PVC blend (c, Figure 3) shows a two-step weight loss, with maximum weight loss at 310°C and 462°C. The increase in the thermal decomposition of the CTA–PVC blend may be explained due to the fact that the molten PVC wicks into the CTA fibre, resulting in a scaffolding effect. This also shows that PVC content in the blend is the controlling factor, which affects the thermal decomposition pattern of CTA.

The storage modulus vs temperature plots of plasticized CTA, plasticized PVC and the CTA–PVC blend is shown in Figure 4. A sudden drop in storage modulus with temperature corresponds to a transition taking place in the polymer side groups or the backbone. CTA exhibits a two-step transition (a, Figure 4), the first step corresponding to the side-group movement (acetyl groups) and the second one corresponding to the T_g of the plasticized CTA. PVC shows a single-step transition corresponding to the glass transition temperature (b, Figure 4). On the other hand, the CTA–PVC blend exhibits a T_g intermediate to that of plasticized PVC and CTA (c, Figure 4) showing that it is a highly compatible system. In other words, there is complete phase mixing.

The results of IR, TGA, DMA and SEM of CTA–PVC blends have shown that there was no chemical reaction between CTA and PVC, and at the same time they were compatible with improved physico-chemical properties. As these blends are porous, they can be used in future as ultra filtration and dialysis membranes with suitable modification.

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Zaherite – the key mineral in Alleppey mudbank formation and on the possibility of creating mudbanks artificially

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X-ray diffraction and chemical analysis of Alleppey mudbank sediments have shown the presence of zaherite ($Al_{12}(SO_4)_5(OH)_{26}\cdot 20H_2O$), which has not been reported from this area so far. Mudbank sediments are characterized by abnormally high water content. Clay particles are randomly oriented due to the presence of zaherite, making them extremely porous. The porous mud at the top and consolidated mud at the bottom with transitional boundary in between is collectively called as 'dispersed mud', which is responsible for wave damping and mudbank formation. If zaherite or similar type of mineral can be introduced in the required proportion into the clay, it may be possible to create mudbanks artificially.

Keywords: Damping, dispersed mud, mudbanks, zaherite.

MUDBANKS are calm patches of water within an agitated sea, formed due to wave damping, and appear close to the shoreline of Kerala during the southwest monsoon. They are known fishing grounds and help in protecting the coast from erosion. Contrary to earlier views that mudbanks appear during the southwest monsoon and disappear during the northeast monsoon[1,2], recent studies[3] have proposed the persistent nature of Alleppey mudbanks. Detailed physical, chemical and oceanographic studies have been carried out in Alleppey mudbanks[1–15], which has brought out most of their characteristics. However, explanations for the possible mode of formation are not free from ambiguity.

A review on the formation of mudbanks by earlier workers is summarized here. Converging littoral currents and associated offshore flow are responsible for the formation of large quantity of suspended sediments, resulting in the formation of a mudbank[2]. Due to some natural forces the mud accumulated at water depths greater than 20 m moves to near-shore areas where other forces combine to stir the mud up and develop a suitable periphery around the suspended mud; thus a mudbank would come into existence[4]. Transportation of mud from offshore towards the mudbank areas is another cause for mudbank formation[10]. The fall in salinity during the southwest monsoon was also suggested as another reason for inducing the mud in suspension, which in turn results in the formation of mudbanks[2,13]. Sub-terraneous injection or seepage of water/loose mud from lagoons due to differential hydrostatic pressure could also be the cause for mudbank formation[1,14,15]. The monsoonal seabed displays greatly reduced bulk density which could be due to the presence of methane gas which is forced into the surficial sediments either by wave pumping or by seaward flowing sub-bottom freshwater[5]. The infra-gravity waves and far infra-gravity waves coupled with strong shoreline reflections and undertow play an important role in the dynamics associated with the mudbanks off Kerala during the monsoon season[6]. Differences in stress rate of strain relationships exist between the semi-consolidated bottom mud and dense suspensions generated from the natural bottom[7]. Due to the convergence of wave energy, fluid mud is deposited at specific near-shore sites resulting in the occurrence of localized mudbanks[8].

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