

Preparation and characterization of starch /cellulose composite

Sherif Mohamed Abdel Salam Keshk^{1,2,a}, Elsayed Yousef³ & Ahemd Omran¹

¹Chemistry Department, Faculty of Science, King Khalid University, Abha 61413, Saudi Arabia

²Basic Science Departement, Institute of Environmental Studies and Research, Ain-Shams University, Caico, Egypt

³Physics Department, Faculty of Science, King Khalid University, Abha 614 13, Saudi Arabia

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Novel preparative method for starch/cellulose composite in different ratios has been reported. The composite is obtained by mixing cellulose extracted from paper garbage and corn starch in PEG/NaOH solution. Starch/cellulose composite is characterized by different techniques, namely XRD, TGA and optical absorption measurements. From XRD data, it is observed that cellulose would lead to expand the d-spacing of (1 $\bar{1}0$ plane and decrease the d-spacing of (110) plane of starch. The UV absorption peaks are shifted towards the longest wavelengths in the visible region for starch/cellulose composite. However, the refractive index value decreases from 1.44 to 1.08 and consequently the dielectric constant value decreases from 2.07 to 1.16 with increasing the starch ratio. Furthermore, the glass transition temperature increases from 107 °C for starch to 115 °C for starch/cellulose composite. However, the excess in starch ratio leads to increase in local crosslink density in the composite network.

Keywords: Cellulose, Differential scanning calorimetric, Starch, Thermal properties, X-ray diffraction

1 Introduction

Starch is a macromolecule made up of α -D-glucose units that is available in two forms. One is amylose molecule that is linear and the other one is amylopectin with highly branched structure¹. Unfortunately, Starch has several unfavorable properties, such as (i) its high viscosity that makes cumbersome its processing compared to conventional polymers, (ii) its tendency to attain high moisture uptake and high shrinkage in the mold, and (iii) its relatively weak mechanical properties¹⁻³. Starch properties can be improved by blending with synthetic and natural polymer⁴⁻⁷. Starch can be chemically blended with hydrophilic polymers via substitution followed by copolymerization, oxidation and hydrolysis⁷⁻¹⁰. The low cost of starch makes it especially attractive to use in the blended forms with synthetic polymers¹⁰. Most of the blended starch structures are completely amorphous and totally degradable material. Poly lactic acid (PLA) is a common organic acid polymer and it is similar to polyethylene and polypropylene in behavior. PLA is used mainly as packaging material for meat, fruit, vegetable, and yogurt. However, starch/poly lactic acid blend had higher crystallinity and tensile strength with lower water absorption values than those of starch¹¹⁻¹⁴. The use of natural fibers as reinforcing composite

materials had important advantages, when compared with their synthetic or inorganic counterparts, owing to biodegradability, high availability, low cost, low energy consumption, low density, high specific strength, high sound attenuation and comparatively easy processing ability¹⁵. Several studies have been published dealing with the preparation and characterization of starch blended with different cellulose substrates, namely commercial regenerated cellulose fibers, vegetable fibers, microcrystalline cellulose, micro fibrillated cellulose and cellulose nano-crystallites¹⁶⁻²⁰. In general, these studies depend on other additives with starch rather than starch itself. Furthermore, a convenient preparation of starch/mercerized cellulose in sodium hydroxide solution was reported. X-ray results confirmed the interaction between both mercerized cellulose and starch itself due to a possible enhancement in the close packing of the starch²¹. The present study describes the preparation of starch/cellulose composite in PEG/NaOH solution. The characterization of composite with different ratios has been evaluated using X-ray diffractometric, UV Spectrophotometric and calorimetric measurements.

2 Materials and Methods

Cotton linter (DP= 900-920) and corn starch from Sigma were used.

^aCorresponding author.
E-mail: keshksherif@gmail.com.

2.1 Extraction of Cellulose from Paper Garbage

Cellulose was extracted by swelling paper in water for 12 h, and then refluxed with an appropriate aliquot of sodium hydroxide for 4h. The resultant paste was washed well till neutralization, and then dried at room temperature.

2.2. Starch and Composite Preparation

Corn starch was dispersed in de-ionized water and stirred for 24 h at room temperature before use.

Extracted cellulose and corn starch were immersed into a NaOH/polyethylene glycol solution (8g ethylene glycol with 7 g NaOH in 100 ml H₂O). Then, the mixture was stirred for 12 h at 100°C. The blend was washed well till neutralization and finally dried under reduced pressure. The preparation procedure was repeated for different starch to cellulose ratio (1:1, 2:1 and 3:1) at 100°C.

2.3 X-ray Diffractometry

The thick sample was prepared according to Kai & Keshk²². Diffractogram of the sample was recorded at room temperature with RIGAKU PRINT 2200V series using Ni-filtered CuK_α radiation ($\lambda = 1.54 \text{ \AA}$). The operating voltage and current were 40 kV and 30 mA respectively. Crystallinity index (C.I.) was calculated from the reflected intensity data using the Segal *et al.* method²³, as given below:

$$C.I. = (I_{020} - I_{am}) / I_{020} \quad \dots (1)$$

where I_{020} and I_{am} represent the maximum intensity of the lattice diffraction and the intensity at $2\theta = 18^\circ$ respectively.

2.4 Measurement of UPF and Thermal Stability

AS/NZ 4399 was used to determine the Ultraviolet Protection Factor (UPF) of a clothing material as an in vitro test method²⁴.

The calorimetric measurements were carried out in Setaram (DSC 131 Evo) with an accuracy of $\pm 0.1 \text{ }^\circ\text{C}$. Temperature and energy calibrations of the instrument were performed using the well-known melting temperatures and melting enthalpies of high purity indium and zinc. For non-isothermal experiments, the prepared sample (10 mg) was sealed in an aluminum pan and tempered at 15 K/S from 30 °C to 500 °C. An empty aluminum pan was used as reference and in all cases flow of nitrogen was maintained at 60 mL/min in order to extract the gases emitted by the reaction, which are highly corrosive to the sensory equipment installed in the DSC 131 Evo furnace.

3 Results and Discussion

3.1 X-ray Diffraction

The X-ray diffractograms (XRD) of cellulose, starch and the prepared composites in different ratios are shown in Fig. 1. The native starch diffraction peaks are related to its A-type crystalline structure while the peaks observed for cellulose reveal its B-type structure²⁵. The diffractive angle ($2\theta^\circ$) and d-spacing of the corresponding planes are presented in Table 1. Composite processed using 1:1 ratio at 100°C shows no change in a diffraction plane of (020) while a diffraction plane of (1 $\bar{1}$ 0) appears at a lower angle side ($2\theta^\circ = 12.2$) with broader d-spacing (7.27) rather than those of native starch (14.8° and 5.97). A diffraction plane of (110) appears at higher angle ($2\theta^\circ = 19.92$) with narrow d-spacing (4.55) than those in native starch (16.9° and 5.22). These results could be attributed to greater insertion of cellulose via (1 $\bar{1}$ 0) and (110) planes of starch. The d-spacing of (1 $\bar{1}$ 0) plane expands and the d-spacing of the (110) plane contracts, these are accompanied with a higher angle shift and a lower diffraction intensity. The intermolecular hydrogen bonding and the crystallinity index of starch/cellulose composite might be increased compared to that of native starch. This can be explained by the strong interaction and good close packing between cellulose fibre and starch at 100°C. In case of higher amount of cellulose, the diffraction intensity of (0 2 0) plane increases with a smaller angle shift owing to the little inclusion of cellulose in (1 $\bar{1}$ 0) and (1 1 0) planes of starch. Moreover, the steric effect of cellulose size decreases the affinity of cellulose towards starch chains.

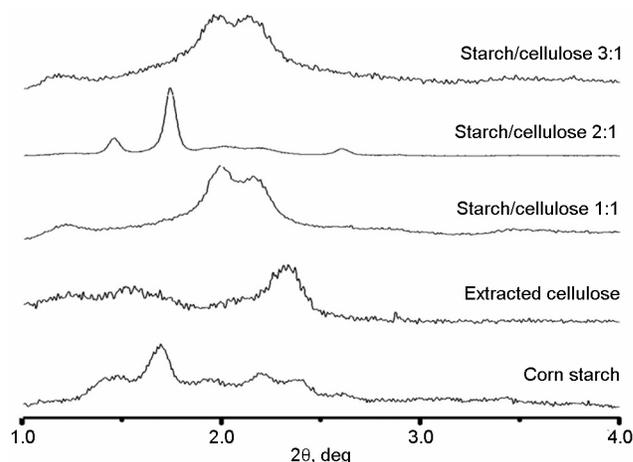


Fig. 1—X-ray diffractogram of starch, cellulose and their composite samples

Table 1—Reflective angle, d-spacing and crystallinity index (C.I.) of the cellulose, corn starch and their composite

Materials	C.I. %	2θ, deg d(11̄0)	2θ, deg d(110)	2θ, deg d(020)
Cellulose	62	12.32 (7.179)	16.92 (5.237)	23.38 (3.802)
Corn starch	51	14.80 (5.976)	16.96 (5.226)	21.88 (3.802)
Starch/cellulose 1:1	76	12.16 (7.274)	19.92 (4.455)	21.60 (4.113)
Starch/cellulose 2:1	83	14.60 (6.065)	19.94 (4.500)	21.92 (4.052)
Starch/cellulose 3:1	69	11.80 (7.500)	19.60 (4.526)	21.30 (4.186)

3.2 Optical Spectra Analysis

The nature of optical transition involved in the starch/cellulose blend can be determined on the basis of the absorption coefficient (α) of the photon energy ($h\nu$). Herein, the absorption shifts in the series starch/cellulose 3:1 → 2:1 → 1:1 from the UV spectral region to the highest wavelengths of the visible region (Fig.2). The potential of UV radiation to cause skin damage rises exponentially with decreasing wavelength. UV light at 280 nm is 1000 times more damaging than the light at 340 nm, hence a fabric ability to block UV-B is the most important factor in preventing the negative side effects of sun exposure. The optical absorption coefficient [$\alpha(\nu)$] in the optical region shows an exponential dependence on the photon energy ($h\nu$) and matched with the following Urbach equation ²⁶:

$$\alpha(\nu) = \alpha_0 \exp(h\nu / E) \quad \dots (2)$$

where ν is the frequency of radiation; α_0 is a constant; and E is related to the tail width of localized states in the band gap.

The physical origin of E can be attributed to the phonon-assisted indirect electronic transitions. The exponential variation of α with $h\nu$ is due to transitions between localized states and will depend on the types of material²⁷. These data are matched to the optical band gap (E_{opt}) through the following general relationship proposed for materials:

$$\alpha(\nu) = \frac{B(h\nu - E_{opt})^r}{h\nu} \quad \dots (3)$$

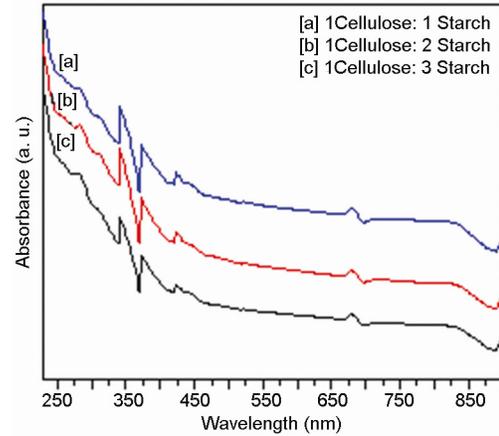


Fig. 2—UV and VIS absorbance spectra of cellulose / starch composite in 1:1, 1:2 and 1:3 ratios

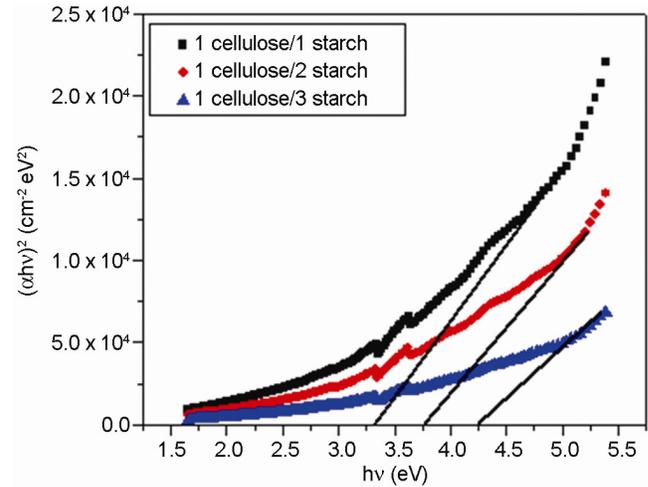


Fig. 3— $(\alpha h\nu)^2$ as a function of $h\nu$ of the prepared cellulose / starch composite in 1:1, 1:2 and 1:3 ratios

where r is an index that has different values depending on the mechanism of inter-band transition; B , a constant; and $h\nu$, the photon energy of incident photon.

Equation (2) depicts a straight line for $r = 2$ and it is found associated with indirectly allowed transitions in most starch/cellulose composites. Figure 3 represents the Tauc's plot $(\alpha h\nu)^{1/2}$ vs. $(h\nu)$ for different composite ratios. The E_{opt} has been estimated from the linear regions of the curves by extrapolating it to meet the $h\nu$ axis at $(\alpha h\nu)^{1/2} = 0$.

The optical energy gap in the range 3.30-4.25 eV shows an increase with increase in starch ratios. The existence and variation of optical energy gap E_{opt} may be explained by the occurrence of local crosslinking within amorphous phase of starch/cellulose composite

that increases the degree of ordering in these parts. The molar volume (R_u) and molar refractivity (V_u) of prepared composite can be calculated using following equation:

$$\sqrt{E_{opt}} = 4.472 \left[1 - \frac{R_u}{V_u} \right] \quad \dots (4)$$

where R_u/V_u is the ratio between molar volume and molar refractivity that is related to refractive index (n), as shown by the following equation:

$$\frac{R_u}{V_u} = \frac{n^2 - 1}{n^2 + 2} \quad \dots (5)$$

Refractive index is dependent on both the chemical structure and the polarization mechanisms. The magnitude of the dielectric constant is dependent on the ability of polarizable units present in the polymer to orient themselves fast enough to keep up with the oscillations of an alternating electric field. The data of optical energy (E_{opt}), refractive index, (n), and dielectric constant (ϵ) are summarized in Table 2. The refractive index value decreases from 1.437 to 1.08 and consequently the dielectric constant value decreases from 2.07 to 1.16 with increasing the starch ratios from 1 to 3. Hence, the electronic polarizability of starch/cellulose composite decreases with the increase in ratio of starch. Starch/cellulose (3:1) ratio has the smallest values of refractive index and dielectric constant.

3.3 Differential Scanning Calorimetric (DSC)

DSC is one the most convenient methods to determine the miscibility and thermal properties of the composite. Figure 4 shows the DSC curves of starch/cellulose composite in different ratios (1:1, 2:1 and 3:1). From the DSC curves, the glass transition temperature (T_g), melting temperature (T_m) and the

width of heat capacity (ΔC_p) have been obtained. The first endothermic peak denotes glass temperature (T_g) and second endothermic peak denotes the melting temperature. The increase in T_g usually means that a rigid network composite is increased. Here in our samples, the T_g increases from 107 °C to 115 °C in the series direction of starch/cellulose ratio 1:1 < 2:1 < 3: 1. Hence, the increase in T_g usually means a closer network composite and consequently, starch/cellulose (3:1) has the highest value of T_g = (115 °C). Moreover, we found that the starch/cellulose (3:1) has the highest value of melting point (T_m = 356 °C) and heat capacity (ΔC_p = 57 μ V). It may be attributed to the increase in starch ratio that leads to the increase in local cross link density in starch/cellulose composite network. Hence, the starch/cellulose (3:1) ratio has the highest thermal stability.

Table 2—Optical energy (E_{opt}) refractive index (n) and dielectric (ϵ) of prepared composite

Sample	E_{opt} eV	R_u/V_u mol^{-1}	n	ϵ
Starch: cellulose (1 :1)	3.3	0.262	1.437	2.07
Starch: cellulose (2 :1)	3.75	0.162	1.257	1.58
Starch: cellulose (3:1)	4.25	0.05	1.08	1.16

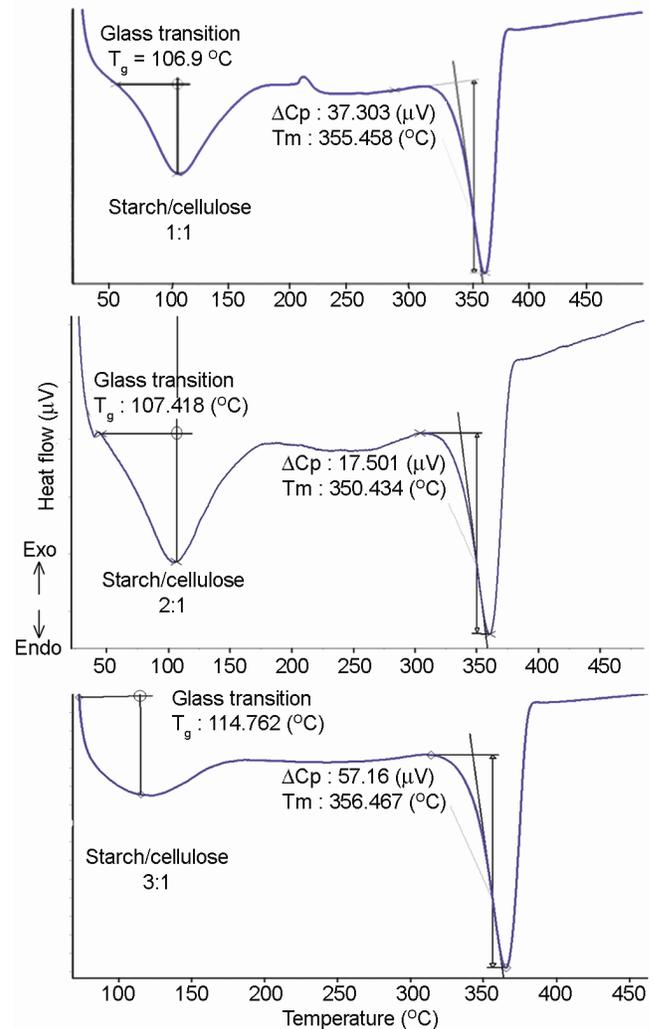


Fig. 4—DSC profiles starch/cellulose using heating rate ($\beta=15$ in $k s^{-1}$).

4 Conclusion

The composite from starch/cellulose has been prepared. Our results prove that the starch/ cellulose composite prepared in 3:1 ratio is the best among other ratios. This starch/ cellulose composite has the lowest thermal expansion with the highest thermal stability owing to the highest crystallinity index. Moreover, the refractive index and dielectric constant decrease with the increase in ratio of starch.

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