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ORIGINAL RESEARCH

Synthesis and characterization of novel Schiff's bases derived from dialdehyde cellulose-6-phosphate

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Abstract In this study, the effects of replacing a hydroxyl group on C-6 of cellulose by a phosphate group, as in cellulose-6-phosphate, on the aldehyde content and the reactivity of dialdehyde cellulose phosphate were explored. Cellulose-6-phosphate (**1**) was efficiently oxidized by using an aqueous solution of potassium periodate to obtain dialdehyde cellulose phosphate (DACP) (**2**). The condensation of DACP with two aromatic amines, sulfanilamide (**3**) and sulfathiazole (**4**) produced the respective Schiff bases, namely (cellulose-6-phoshate-2,3-bis-[(4-methylene-amino)-benzene-sulfonamide] (**5**) and cellulose-6-phoshate-2,3-bis-[(4-methylene-amino)-*N*-(thiazol-2-yl) benzene sulfonamide] (**6**). Fourier transform infrared spectra, scanning electron microscope (SEM), X-ray diffraction (XRD), and thermal gravimetric analysis (TGA) were used to characterize the synthesized biopolymers. For compounds **2**, **5**, and **6,** the aldehyde content of was found to be 95%, 20.1%, and 11.2%, respectively. The highest reactivity of DACP toward sulfa drugs was displayed due to aldehyde content values. Significant changes in the *d*-spacing with decreasing crystallinity index (46.9%) were observed in the XRD of cellulose-6-phosphate and its Schiff's base. In SEM images, a fibrous structure and a rough surface were observed in the samples with slight variations. The results of TGA showed a delay in the major degradation step for DACP, cellulose-6-phosphate-2,3-bis[(4-methyleneamino)-*N*-(thiazol-2-yl)-benzen sulfonamide] and cellulose-6-phosphate-2,3-bis-[(4-methyleneamino)-benzene sulfonamide] compared to cellulose phosphate.

Keywords Cellulose-6-phosphate · Dialdehyde cellulose phosphate · Schiff's · Base · XRD · TGA

Introduction

Cellulose and its derivatives are used in various biomedical applications, as either unmodified or

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esters, ethers, and as either crosslinked or grafted copolymers (Dumitriu 1996; Keshk and Gouda 2017). Moreover, most of the cellulose derivatives are widely used in the pharmaceutical and food industries for several purposes and they take the advantage of the generally recognized as safe (GRAS) status. The cellulosic materials are hydrophilic, biodegradable, and insoluble in water, dilute acids, alkali solutions, and most of the common organic solvents (Wanrosli et al. 2011). The reactivity of cellulose must be increased by molecular modifications to improve the functionality of cellulose without using any extraneous crosslinking agents (Keshk and Nada 2003; Keshk 2008; Skopinska-Wisniewska et al. 2016). Periodate oxidation is used industrially to incorporate selectively dialdehyde groups into cellulose, starch, and chitosan (Teotia et al. 2012; Keshk et al. 2015, 2016, 2017). In periodate oxidation, an extremely regioselective reaction converts vicinal dihydroxyl (glycol) groups into paired aldehyde groups without any significant side products. A large number of aldehyde groups that are introduced into polysaccharides can be further converted to Schiff bases with primary amines (Keshk et al. 2015, 2016, 2017). Schiff bases make the dialdehyde polyglucan a valuable intermediate for biopolymer-based functional materials, such as adsorbent agents for heavy metals and drug carriers as well as in the separation and analysis of proteins (SuYao et al. 2012). In addition, cellulose phosphate (C_6–O–PO_3H_2, CP) is considered a good biomedical material and used in the treatment of calcium metabolism-related diseases for decades, taking advantage of its high ability to bind calcium ions and efficiency to uptake Pb^{2+}, Cd^{2+}, and Cr^{3+} ions (Misuse et al. 1996; Rungrodnimitchai 2014). CP is used as potential drug carrier, where model drugs like benzocaine and prazosin are coupled to DACP by covalent and ionic linkage, respectively and compressed to tablets (Volkert et al. 2009). In our previous study, dialdehyde cellulose (DAC) was found to be less reactive toward Schiff bases due to hemiacetal formation, which is proved from density function theory and its aldehyde contents (Keshk et al. 2015, 2016). Recently, the synthesis, physicochemical characterization, and functionalization of dialdehyde biopolymer based on microcrystalline cellulose, starch, and chitosan have received great attention. In this context, the condensation of sulfanilamide and sulfathiazole with dialdehyde cellulose was used to synthesize two new cellulose derivatives and Schiff bases (Keshk et al. 2015). DAC was prominently obtained from periodate oxidation of cellulose, and less reactive toward sulfanilamide and sulfathiazole according to the AC values and density functional theory calculation. These results were rationalized with the formation of hemiacetal and high dipole moment in DAC (Keshk et al. 2016, 2017). It is believed that the substitution of an OH group at C-6 (which is responsible for hemiacetal formation either with C-2 and/or C-3 in DAC) by a phosphate group, as in cellulose-6-phosphate, will increase its reactivity toward sulfa drugs. This approach is based on the masking of an OH group by phosphate that prevents the possible formation of hemiacetal. In this context, in order to attain high chemical reactivity toward Schiff base formation, the synthesis and physicochemical characterization of novel 2,3-dialdehyde cellulose-6-phosphate and its Schiff base derivatives with sulfanilamide and sulfathiazole are reported.

Materials and methods

Chemicals

All chemicals used were of analytical grade and purchased from Sigma-Aldrich© (St. Louis, MO).

Determination of phosphate content and degree of substitution

The phosphorus content in the cellulose 6-phosphate was determined via spectrophotometer using ammonium vanadate-molybdate method (Granja et al. 2001). Where 0.02 g sample of cellulose phosphate was digested in 2 ml of perchloric acid at 165 °C till a colorless clear solution was obtained. The vanadate-molybdate acid solution (10 mL) was added to the digested sample (1 mL). The solution was diluted to 50 mL and the absorbance was measured at 400 nm. The phosphorus content in cellulose phosphate was found to be 12.25%. The degree of substitution was calculated using the following Eq. (1) (Towle and Whistler 1972):

$$DS = \frac{162 * \%P}{3100 - (81 * \%P)} \tag{1}$$

where 162 is the molar mass of anhydro-glucose unit; % P is the percentage of phosphorus content; 3100 is the atomic weight of P multiplied by 100; 81 is the molar mass of the phosphate substituent (H_2PO_3). Therefore, the calculated DS value was almost equal to one.

Preparation of dialdehyde cellulose phosphate (DACP)

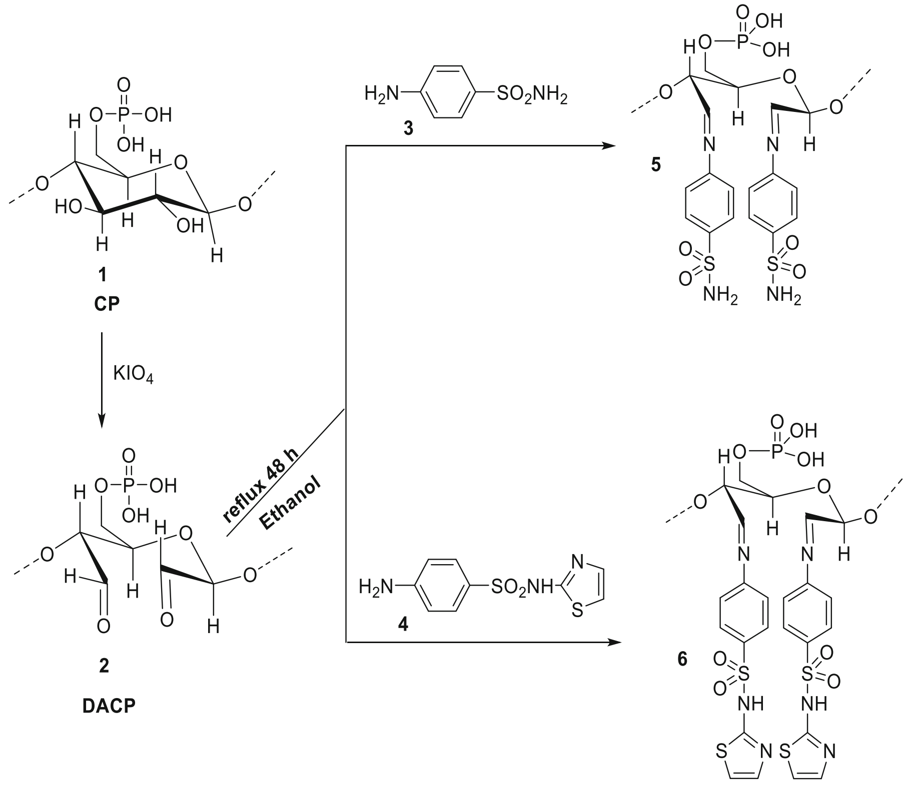
Cellulose phosphate (**1**) (0.68 g, 0.003 mol) was suspended in 50 ml distilled water and kept for 1 h. Then, potassium periodate (1.4 g, 0.006 mol) was slowly added to the mixture, and the mixture was heated at 80 °C for 2 h. Thereafter, the mixture was kept in the dark for 24 h at room temperature. Finally, the product (DACP, **2**) was filtered and promptly washed with distilled water (Scheme 1). The yield of DACP was 96%.

Preparation of Schiff's bases

Either sulfanilamide (**3**) (1.03 g, 0.006 mol) or sulfathiazole (**4**) (1.53 g, 0.006 mol) was added to a suspension of DACP (0.67 g, 0.003 mol) in absolute ethanol (20 mL). The mixture was refluxed with stirring for 48 h. Then, the mixture was cooled down to room temperature. Finally, the formed pale-yellow powder was filtered, washed with ethanol, and dried.

Determination of aldehyde content (AC)

Aldehyde content was determined to evaluate the degree of oxidation of cellulose phosphate. Moreover, a reaction with hydroxylamine hydrochloride in an aqueous sodium hydroxide solution was used to convert DACP into an oxime. Then, 25 mL of distilled water was used to dissolve DACP (approximately 0.1 g). Using 0.1 M sodium hydroxide, the pH of the solution was adjusted to 5.0. Subsequently, 20 mL of 0.72 mol/L hydroxylamine hydrochloride at pH 7 was added to the DACP solution. The mixture was stirred



Scheme 1 Synthesis of novel Schiff bases **5**-**6** derived from sulfa drug and dialdehyde cellulose phosphate (DACP)

for 12 h in a water bath at 40 °C, followed by the titration of the released hydrochloric acid with 0.1 M sodium hydroxide. By matching the color of the sample solution with that of the blank, the endpoint was determined. The consumption of the sodium hydroxide solution was denoted by V_C (in milliliters). The consumption of the alkali solution for the blank was denoted by V_b (in milliliters). Therefore, the AC (%) in DAS was calculated using Eq. (2) which is:

$$AC(\%) = [M_{\mathrm{NaOH}}(V_C - V_b)222/m] \times 0.1 \tag{2}$$

where M_{NaOH} = 0.1 mol/L, m is the dry weight (g) of DACP, and 240 g/mol is the molecular weight of the one unit of DACP. The aldehyde content of the synthesized Schiff bases (**5** and **6**) was determined in a similar way. However, the blank was treated using the same weight of Schiff bases in the absence of hydroxylamine hydrochloride taking into consideration any reaction between the sulfonamido group and sodium hydroxide (Hinsberg reaction) under the same conditions (Keshk et al. 2015).

Fourier transform infrared (FTIR) spectroscopy

FTIR spectra of the prepared composites were recoreded using Thermo Scientific Nicolet FTIR spectrometer (Bruker IFS 66). Each sample was carefully grounded, mixed with KBr powder, and then pressed in a form of a disk before analysis.

X-ray diffraction (XRD)

A Shimadzu-Lab-XRD-6000 diffractometer with nickel-filtered Cu-Kα radiation at 40 kV and 50 mA was used to determine the XRD patterns of CP, DACP, and Schiff base derivatives. Crystallinity was calculated from the diffracted intensity data using the method of Segal et al. (1959). The crystallinity index values were obtained using the following Equation:

$$\mathrm{C.I.}(\%) = (I_{200} - I_{am})/I_{200} \times 100 \tag{3}$$

where I_{200} is the maximum intensity at $2\theta = 22.8^{\circ}$ and I_{am} is the intensity of the amorphous background scattering measured at $2\theta = 18^{\circ}$.

Scanning electron microscope (SEM)

Scanning electron microscope was used to examine the surface morphologies of CP, DACP, and the two Schiff bases. The SEM-FEI Quanta 200 model was used to perform SEM analysis, which was equipped with an energy-dispersive X-ray analysis instrument (EDX) giving the elemental composition of the system.

Thermal stability

A Shimadzu TGA-50H thermal analyzer was used to carry out thermal analysis. Approximately 10 mg of the sample was heated in a platinum crucible within the temperature range of 25–600 °C with a heating rate of 10 °C min^{-1} by using the method of controlled nitrogen flow.

Results and discussion

The periodate oxidation of cellulose phosphate produced DACP in a neutral medium. The fact that a cellulosic material is susceptible to oxidation in an acidic medium is well known, which results in the degradation of the polymeric chain (Keshk et al. 2015). In order to determine the efficiency of periodate oxidation of CP, the aldehyde content in DACP was evaluated. The aldehyde content was estimated to be 95%, which is higher than that of dialdehyde cellulose (82.9%; Keshk et al. 2015). The highest reactivity of CP toward oxidation is due to the highest percentage of AC in the DACP chain. The lower degree of molecular order in cellulose phosphate (branched chain), as compared with cellulose (linear chain), is due to the higher reactivity of CP. Cellulose itself is a hydrophilic material; however, its dissolution in an aqueous medium is difficult due to the hydrogen bonds between glucan chains that form a strong network (Biermann et al. 2001). Thus, the cellulose phosphate becomes more reactive as compared to cellulose toward periodate oxidation because of the absence of the hydrogen bonds between the OH on C2 and the C6 oxygen of the hydroxyl group in the neighboring glucose residue (O_2–H–O_6), in addition to the absence of the major intermolecular hydrogen bond between the OH on C6 and the oxygen on C3 (O_6–H–O_3) due to the presence of a phosphate group at C6 position

(Gardner and Blackwell 1974; Keshk et al. 2016). Furthermore, the aldehyde content (AC) in the Schiff bases derived from DACP (**5** and **6**) was determined to be 20.1% and 11.2%, respectively, whereas those derived from DAC (**5** and **6**) had an AC of 41.5% and 20.8%, respectively (Keshk et al. 2015). The higher reactivity of DACP toward the condensation reaction with sulfa drugs is supported by AC rather than DAC. The absence of intramolecular hemiacetal formation could contribute to this higher reactivity of DACP (Keshk et al. 2016). The formation of hemiacetal is a reversible reaction that can recover free aldehyde depending on the stability of the ring formation of a hemiacetal (Guthrie 1962). Two characteristic bands for HO–P=O stretching appeared at 1647 and 1710 cm^{-1} in the FTIR spectrum of CP (Fig. 1), while two broad weak bands for P=O stretching appeared at 1371 cm^{-1} and 1164 cm^{-1}. On the other hand, two broad bands for P–O–C stretching appeared at 667 cm^{-1} and 559 cm^{-1} (Simth 1982; Rungrodnimitchai, 2014). The stretching for two secondary hydroxyl groups was observed at 3354 cm^{-1} (Fig. 1). The OH vibrations for the secondary hydroxyl bending appeared at 1430 cm^{-1} and the C–O–C stretching vibration of the glycosidic or β-(1 → 4)-glycosidic bond appeared at 1058 cm^{-1} (Kaputskii and Komar 1988). An absorption band at 1640 cm^{-1} corresponding to the carbonyl group associated with hydrogen bonding was observed in the FTIR spectrum of DACP (Fig. 1), which confirms the effective periodate oxidation of cellulose phosphate. A HO–P=O stretching band and two P=O stretching bands appeared at 1734 cm^{-1}, 1371 cm^{-1} and 1164 cm^{-1}, respectively. In addition, the absorption band at 615 cm^{-1} was associated with the P–O–C stretching vibration (Simth 1982). The broadness and intensity of the DACP peaks are most likely caused by the smaller crystalline size or the orientation effect. The effectiveness of the oxidation using potassium periodate is confirmed by a decrease in the band size of both the secondary hydroxyl group bending (1439 to 1380 cm^{-1}) and the C–O stretching vibration (1064 cm^{-1}). The FTIR spectra of DACP Schiff bases (**5**) and (**6**) (Scheme 1 and Fig. 1) exhibited completely different absorption bands as compared with DACP. On the other hand, the FTIR spectrum of the DACP Schiff base (**5**) (Scheme 1, Fig. 1) displayed a significant absorption band at 1595 cm^{-1} for C=N and two bands at 1327 and 1170 cm^{-1} that corresponded to asymmetric and symmetric stretching vibrations of S=O in SO_2NH_2, respectively (Nakamura et al. 1984).

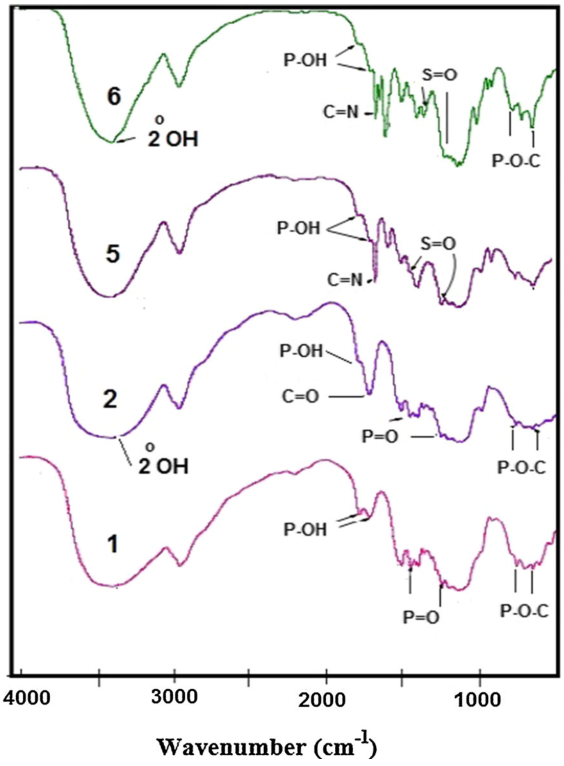


Fig. 1 FT-IR spectra of DACP (**2**) cellulose 6-phoshate-2,3-bis-[(4-methylene-amino)-benzene sulfonamide] (**5**), and cellulose-6-phoshate-2,3-bis[(4-methylene-amino)-*N*-(thiazol-2-yl)-benzene sulfonamide] (**6**)

The N–H stretching vibrations appeared at 3360 cm^{-1} and overlapped with the O–H stretching vibration at 3394 cm^{-1}. Unexpectedly, the high reactivity of sulfanilamide (**3**) toward DACP (**2**) compared to DAC is indicated by the absence of a weak absorption band at 1640 cm^{-1} corresponding to the C=O in compound (**5**) (Keshk et al. 2015).

In the X-ray diffraction pattern, CP showed two distinguishable peaks at $2\theta = 15.97°$ and $22.74°$ corresponding to the merged peaks involving both the (1–10) and (110) reflections and (200) planes of CP, in addition to the phosphorous plane (211) that interfered with cellulose plane (004) at $2\theta = 34.76°$. The crystallinity index was determined to be 85% (French 2014; Keshk and Salah 2014). In the XRD pattern of DACP, the crystallinity index (83%) decreased due to a loss in the packing order of glucopyranose rings (Fig. 2). The XRD patterns of cellulose-6-phosphate Schiff base (**5**) were found

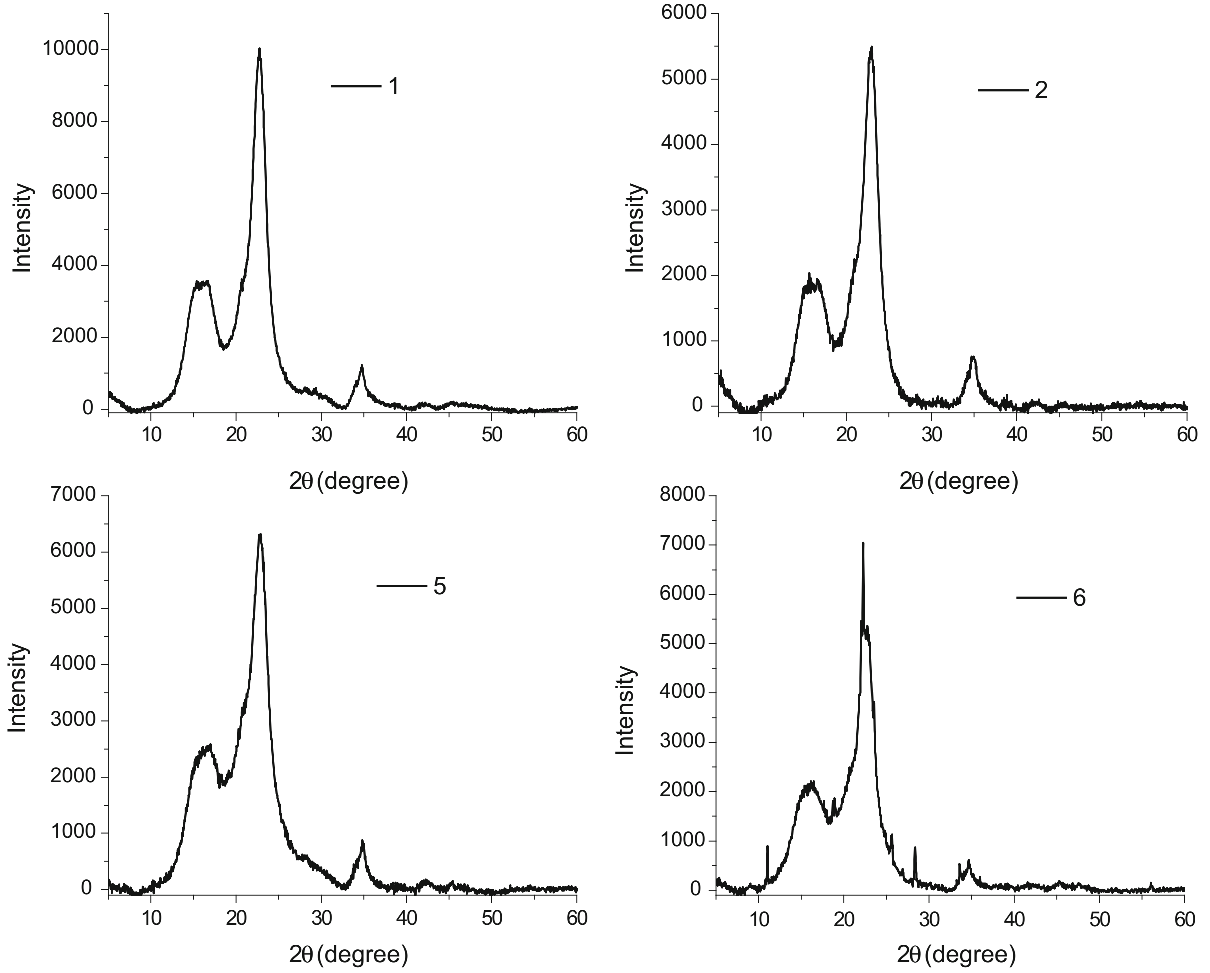


Fig. 2 X-ray Pattern of CP (1), DACP (2), cellulose-6-phosphate-2,3-bis-[(4-methyleneamino)-benzenesulfonamide] (5), cellulose-6-phosphate-2,3-bis [(4 methylene amino)-*N*-(thiazol-2-yl)-benzensulfonamide] (6)

similar to those of DACP with a low intensity and crystallinity index (83%) and with some significant changes in the *d*-spacing (Table 1). The high affinity of sulfanilamide (**3**) to DACP is confirmed by these results which contradict our previous results on dialdehyde cellulose (Keshk et al. 2015).

The XRD patterns of cellulose-6-phosphate Schiff base (**6**) showed completely different results from those observed for DACP with large differences in the values of *d*-spacing (Table 1). Four sharp peaks (as spikes) were observed in the diffractogram of Schiff's base (**6**) at $2\theta \cong 11.04°$, 18.98°, 22.34°, 25.67° and 28.36° corresponding to sulfathiazole (Hu et al. 2013). These results indicated that sulfathiazole (**4**) reacted effectively with DACP. In addition, the projection of the Schiff bases along the C=N axis was associated

Table 1 The X-ray diffraction data of CP (**1**), DACP (**2**), cellulose-6-phoshate -2,3-bis-[(4-methyleneamino)-benzenesulfonamide] **5**), cellulose-6-phoshate-2,3-bis[(4-methyleneamino)-*N* (thiazol -2-yl)-benzensulfonamide] **(6)**

Samples	2θ/d (110)	2θ/d (200)	C.I. (%)
1	15.97 (5.54)	22.74 (3.91)	85
2	16.03 (5.52)	23.00 (3.86)	83
5	16.10 (5.46)	22.84 (3.92)	71
6	16.48 (5.37)	22.27 (4.00)	74

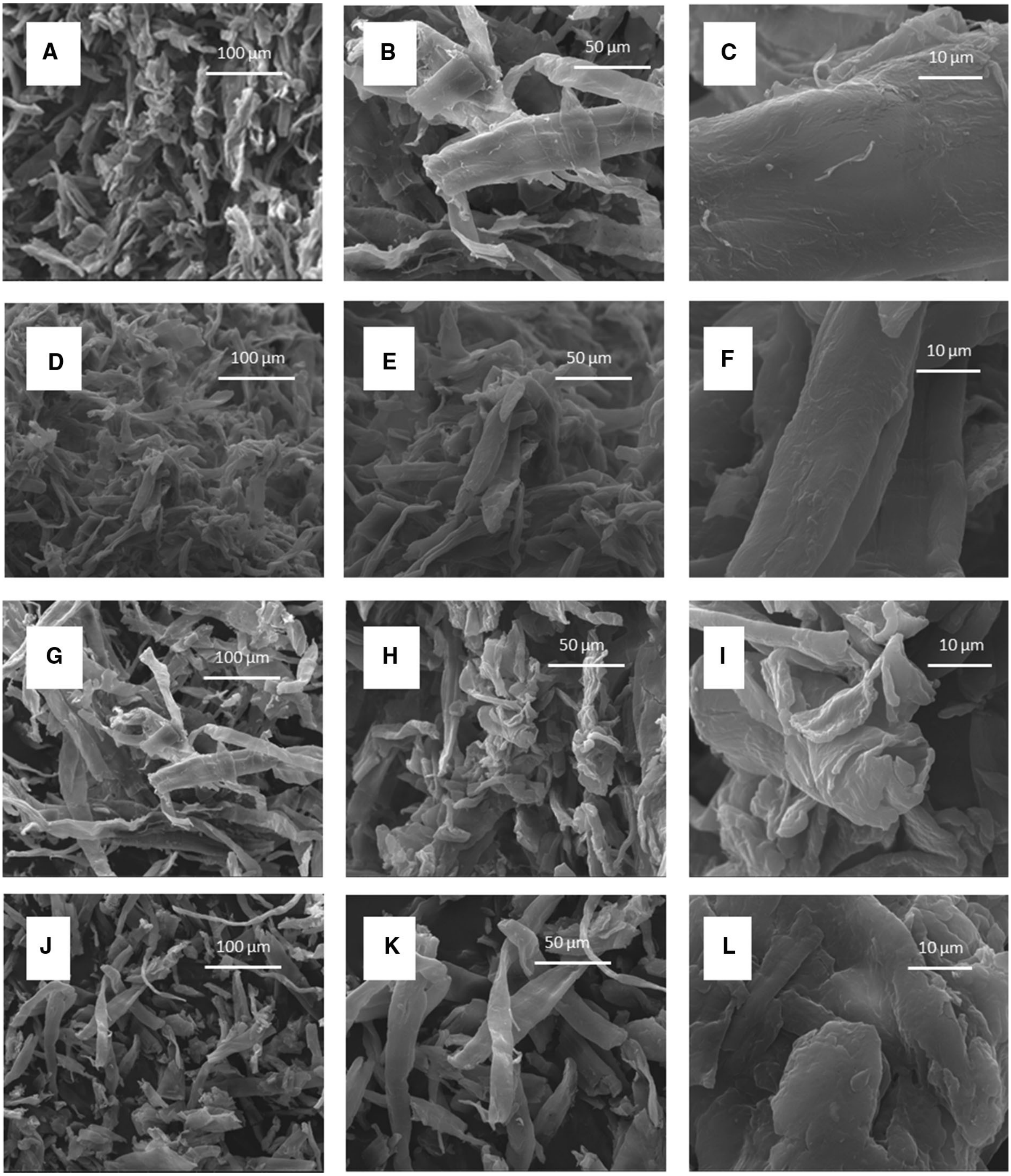


Fig. 3 SEM micrographs of different magnifications for CP (A-C), DACP (D-F), cellulose-6-phosphate–2,3-bis-[(4-methyleneamino) benzene sulfonamide] (G-I), and cellulose-6-phosphate -2,3-bis[(4-methyleneamino)-*N*-(thiazol-2-yl)-benzensulfonamide] (J-L)

with an increase in the interfibrillar distance (Table 1). However, these four sharp peaks were invisible in DACP and cellulose Schiff base. In addition, these results confirmed the high affinity of sulfathiazole (4) rather than sulfanilamide (**3**) toward DACP. This affinity may be due to the breaking of the

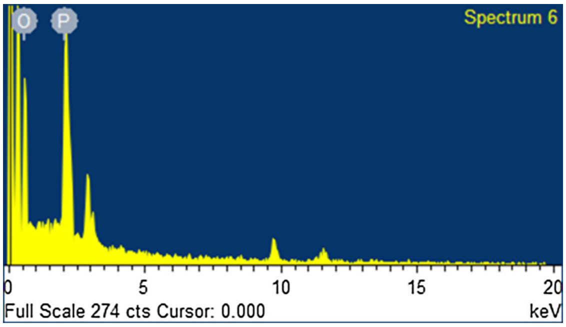


Fig. 4 EDX of cellulose 6-phoshate

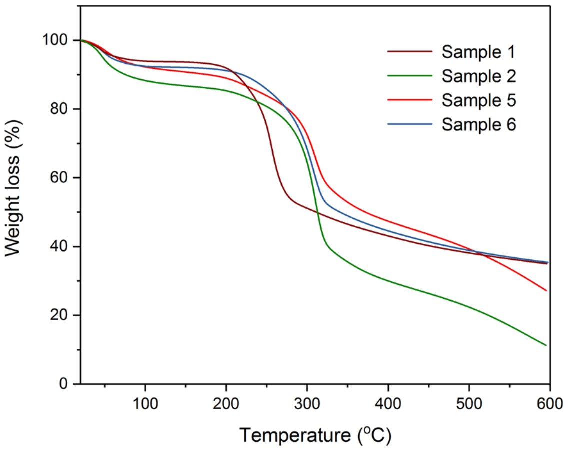


Fig. 5 TGA plots of CP (1), DACP (2), cellulose-6-phosphate-2,3-bis-[(4-methyleneamino)-benzenesulfonamide] (5), cellulose-6-phosphate-2,3-bis [(4 methylene amino)-*N*-(thiazol-2-yl)-benzensulfonamide] (6)

intermolecular hydrogen bonds and inclusion of sulfathiazole (**4**) between the DACP planes. In addition, sulfathiazole (**4**) is sparingly soluble in absolute ethanol, which facilitates attack of the DACP linkage. These domino effects approve our previous results (Keshk et al. 2015), which indicated at a lower solubility, the affinity towards cellulose is higher. It is also plausible that the cellulose chain packing is better in Schiff base (**6**) due to better interaction between the hydrophobic blocks, which improved the organization of cellulose Schiff base (**6**). Thus, Schiff base (**6**) showed higher crystallinity index than that of Schiff base (**5**) because of the efficient crosslinking between sulfathiazole (**4**) and DACP (**2**) as shown in the diffractogram and its *d*-spacing values that changed from 5.52 in DACP to 5.46 and 5.37 in Schiff's bases. The values of *d*-spacing of DACP (5.52) and its Schiff's bases (5.46 & 5.37) indicated that sulfa drugs (**3** & **4**) effectively reacted with DACP. This affinity may be caused by the replacement of OH at the C6 position in cellulose by the phosphate group that hindered the formation of hemiacetal as reported previously by Keshk et al. (2016). In addition, the cellulose chain packing in DACP is better for Schiff base (**6**) as compared to Schiff base (**5**) because of the better interaction between the *N*-thiazole ring and the hydroxyl of the phosphate group in DACP. The FTIR spectrum of Schiff base (**6**) (Fig. 1) revealed a low-frequency shift from 1540 cm^{-1} (attributed to the C=N stretching vibration of the thiazole ring) to 1485 cm^{-1} appearing in the DACP that validates the assumption mentioned above (Chufan et al. 1997). The surface microstructures of CP, DACP, cellulose-6-phosphate-2,3-bis-[(4-methyleneamino)-benzenesulfonamide] (5), and cellulose-6-phosphate-2,3-bis[(4-methyleneamino)-*N*-(thiazol-2-yl)-benzensulfonamide] (6) samples were analyzed by SEM (Fig. 3). The CP sample possessed a larger and smoother morphological structure with fibrous appearance and a rough surface (Fig. 3).

The elemental analysis conducted by EDX confirmed the presence of phosphorous with a 12.3% which confirms the DS = 1 value cellulose phosphate (Fig. 4). The comparison of the DACP images with those of the two Schiff bases at high magnifications indicate that the surfaces DACP particles are smoother and coagulate as compared with those of the two Schiff base particles (see Scheme 1).

Moreover, it is worth noting that Schiff bases morphologies were controlled by using different preparation methods, which result in different morphological structures compared to the starting DACP (see Scheme 1).

Figure 5 represents the TGA curves of the CP and its derivatives in the temperature range between 20 and 600 °C, and the data are summarized in Table 2. The general mode of the TGA curves indicates that the four samples exhibited a homogenous composition. The first weight loss was observed below 100 °C and can be assigned for the loss of adsorbed moisture, dephosphorylation, and dehydration of cellulose. At this temperature range (up to 100 °C), a higher weight loss for was detected for DACP as compared with the other samples which indicates that the Schiff bases were exhibiting low moisture content and dehydration (Table 2).

Table 2 Weight loss (%) in TGA during the thermal degradation of CP (**1**), DACP (**2**), cellulose-6-phoshate -2,3-bis-[(4-methyleneamino)-benzenesulfonamide] **5**), cellulose-6-phoshate-2,3-bis[(4-methyleneamino)-*N* (thiazol -2-yl)-benzensulfonamide] (**6**)

Sample	Water evaporation (20–100 °C)	Thermal degradation (200–340 °C)	Residue at 600 °C
1	6.1	44.5	35.0
2	11.8	48.5	11.2
5	7.8	33.4	27.1
6	7.7	41.1	34.9

The second weight loss for the samples step started at about 200–235 °C. In this step, the thermal degradation involved the formation of carboxyl and carbonyl groups, the evolution of CO and CO_2, and the formation of carbonaceous residues. The highest weight loss at 600 °C was obtained for DACP (89%), and then cellulose-6-phosphate-2,3-bis [(4-methylene amino)-*N*-(thiazol-2-yl)-benzene sulfonamide] (73%). While the lowest weight loss at 600 °C was recorded for both CP and cellulose-6-phosphate–2,3-bis- [(4-methylene amino)-benzenesulfonamide (65%), which indicates a higher thermal stability for these materials as compared with DACP and cellulose-6-phosphate-2,3-bis[(4-methyleneamino)-*N*-(thiazol-2-yl)-benzensulfonamide. It is worth noting that the prepared Schiff bases were more stable than the starting DACP at 600 °C.

Conclusion

In this study, a simple and efficient method for the preparation of dialdehyde cellulose phosphate and its Schiff bases with sulfanilamide and sulfathiazole was reported. The synthesized polymer was characterized and the chemical reactivity of DACP toward two sulfa drugs was analyzed. The results proved that the presence of a phosphate group at C-6 of cellulose hindered the formation of hemiacetal either with C-2 or C-3 in DACP, which enhanced both AC and the chemical reactivity of DACP toward sulfa drugs. The X-ray analysis confirmed that the conversion of cellulose phosphate to DACP increased the crystallinity, while the transformation of DACP to Schiff bases **5** and **6** decreased the crystallinity. The prepared polymers **3**, **5**, and **6** also exhibited good thermal properties.

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