

Research Article

Thermal and Photoresponsive Studies of Starch Modified with 2-(5-(4-Dimethylamino-benzylidene)-4-oxo-2-thioxo-thiazolidin-3-yl)acetic Acid

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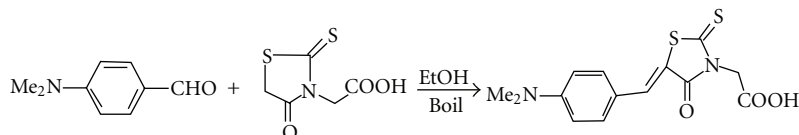
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The present study describes the synthesis of a chromophoric system 2-(5-(4-dimethylamino-benzylidene)-4-oxo-2-thioxo-thiazolidin-3-yl)acetic acid and its incorporation into starch through esterification of the hydroxyl group by the free carboxyl function of the chromophoric system by DCC coupling. The products were characterized by UV-visible, fluorescence, FT-IR, and NMR spectroscopic methods. The newly developed system was subjected to photoresponsive studies such as light absorption, light stabilization and fluorescence emission. The free chromophoric system and the coupled product were also subjected to thermal analysis. The results show that modification enhances the light absorption and light fastening properties of the chromophoric system. Thermal stability of the polymeric system greatly enhances on attaching the chromophoric system. In view of these results the newly developed system is proposed as a nature friendly, green, and photoactive product which could find application in dyes, inks, paints, and so forth.

1. Introduction

Starch is an inexpensive commodity that has been used for food and many nonfood purposes for centuries. Starch, one of the main polysaccharides in the world, has been paid much attention because of its biodegradability and abundance as a renewable resource. It has been widely used as a raw material for biodegradable plastics. The chemical modification of starch is of interest because the modification would not change the fundamental skeleton of starch, would keep the original physicochemical and biochemical properties, and finally would bring new or improved properties. Chemically, starch is composed of two different molecules, amylose and amylopectin. In amylose, the glucose molecules are linked in a “linear” fashion; however, the tetrahedral chemistry of carbon (and the bond angles that result from this chemistry) gives amylose an overall spiral shape. Amylopectin, on the other hand, has a linear arrangement of glucose molecules

which includes, at regular intervals, a different kind of linkage between two adjacent glucoses. This different linkage results in the formation of a branched structure and an overall treelike shape for this molecule. Starch consists of amylose and amylopectin, which are polymers of glucose, linear and branched, respectively. Each glucose unit potentially has three reactive hydroxyl groups that are the basis of all derivatizations. Native starches in its derivative forms open a wide scope in pharmaceutical-, food-, and nonfood based industries. Starch modification is generally achieved through derivatization such as esterification, etherification, cross-linking, acid hydrolysis, enzymatic hydrolysis heat treatment, and grafting of starch [1–7]. The recent report on modified starches and its future scope predicted that total consumption will grow to almost 75 million tons by 2012 and the demand for starch by food and nonfood industries in Asia is likely to grow by 4–6 percent per year in low and middle income countries in this region. Despite numerous



SCHEME 1: Synthesis of 2-(5-(4-dimethylamino-benzylidene)-4-oxo-2-thioxo-thiazolidin-3-yl)acetic acid.

studies that have been undertaken over many years to elucidate the role of modified starch in pharmaceutical-, food-, and nonfood-industry-based application, starch remains an outstanding inscrutable molecule to be explored. Modified starches are utilized in hundreds or even thousands of food, industrial, biofuels, and bioplastic applications [8–13].

In the present study, functional modification of starch has been achieved by DCC coupling. The free hydroxyl group of the biopolymeric core material was esterified with free carboxylic group of the chromophoric system. Thus we could develop a thermo stable and photo responsive system on starch. Modified starches have a very promising industrial prospects on application basis, due to its more biocompatible and environmental friendly nature as compared to synthetic polymers.

2. Experimental

2.1. Materials and Methods: General. Starch was purchased from Merck (Germany). Dimethylaminopyridine (DMAP) and dicyclohexylcarbodiimide (DCC) are commercial samples and are used as purchased from E. Merck India Ltd. *p*-Dimethylaminobenzaldehyde and rhodanine-*N*-acetic acid were purchased from Merck (Germany). The solvents used for the study such as dimethylformamide (DMF) were purified by literature procedure. NMR spectra were recorded on a Bruker 500 MHz NMR instrument. IR spectra were recorded on a Shimadzu FT-IR instrument operating in the range 4000–400 cm^{-1} . UV-visible spectra were recorded on a Shimadzu UV-visible-NIR spectrophotometer operating in the range 200–1100 nm.

2.1.1. Synthesis of 2-(5-(4-Dimethylamino-benzylidene)-4-oxo-2-thioxo-thiazolidin-3-yl)acetic Acid. *p*-Dimethylaminobenzaldehyde (1 g) and rhodanine-*N*-acetic acid (1.25 g) were dissolved in ethanol. The mixture was stirred thoroughly for a few minutes. The temperature was raised and the mixture was refluxed for 4 hours with magnetic stirring under an inert atmosphere of argon. The product was filtered, purified by recrystallisation from absolute ethanol, and further purified by column chromatography using silica column and 10 : 3 chloroform-methanol and solvent system, solvent was removed on a vacuum rotary evaporator and characterised by spectroscopic analysis. The yield is noted as 81% [14].

2.1.2. Synthesis of Starch Functionalized with 2-(5-(4-Dimethylamino-benzylidene)-4-oxo-2-thioxo-thiazolidin-3-yl)acetic Acid. 2-(5-(4-dimethylamino-benzylidene)-4-oxo-2-thioxo-thiazolidin-3-yl)acetic acid (2.25 g), starch (1 g), DMAP

(200 mg), and DCC (1 g) were separately dissolved in DMF and mixed together. The mixture was stirred at room temperature for 2 hours and at 80°C for 6 hours. The byproduct dicyclohexyl urea (DCU) was removed by warming-cooling-filtration process and the solvents were removed on a vacuum rotary evaporator and dried. It was purified by column chromatography using silica column and 10 : 2 chloroform-methanol solvent system and dried in vacuum [14]. The product was characterised by spectroscopic analysis.

3. Results and Discussion

Spectroscopic analyses such as UV-visible, FT-IR, and ^1H NMR have been done in order to visualize the chemical changes in the structure of starch. The green, nature friendly starch functionalized with 2-(5-(4-dimethylamino-benzylidene)-4-oxo-2-thioxo-thiazolidin-3-yl)-acetic acid is a novel photoresponsive system and reported in the present paper for the first time.

3.1. Synthesis and Characterisation of 2-(5-(4-Dimethylamino-benzylidene)-4-oxo-2-thioxo-thiazolidin-3-yl)acetic Acid. *p*-Dimethylaminobenzaldehyde and rhodanine-*N*-acetic acid were condensed together at 80°C yielding 2-(5-(4-dimethylamino-benzylidene)-4-oxo-2-thioxo-thiazolidin-3-yl)acetic acid (Scheme 1).

IR spectrum of 2-(5-(4-dimethylamino-benzylidene)-4-oxo-2-thioxo-thiazolidin-3-yl)acetic acid was recorded in the solid state as KBr discs in the operating frequency range 4000–400 cm^{-1} . 3440 cm^{-1} (broad): $\nu_{\text{O-H}}$ (str), 2920 cm^{-1} : $\nu_{\text{C-H}}$ of CH_2 , 1716 cm^{-1} : $\nu_{\text{C=O}}$ (str), 1573 cm^{-1} : $\nu_{\text{C=C}}$ (str), 1379 cm^{-1} : $\nu_{\text{C-N}}$ (str), 1309 cm^{-1} : $\nu_{\text{C=S}}$ (str), 1184 cm^{-1} : $\nu_{\text{C-O}}$ (str), 650 cm^{-1} : $\nu_{\text{C-S}}$ (str) (Figure 1).

The proton NMR spectrum of the product was recorded in chloroform using a 500 MHz ^1H NMR spectrophotometer. ^1H NMR: 10.32 ppm (1H,s: –COOH), 7.42 ppm (2H,d:aromatic proton a), 6.74 ppm (2H,d:aromatic proton b), 4.81 ppm (1H,s: H_c), 3.65 ppm (2H,s: H_d), 3.09 ppm (6H,s: $\text{N}(\text{CH}_3)_2$) (Figure 2).

3.2. Synthesis and Characterisation of Starch Functionalised with 2-(5-(4-Dimethylamino-benzylidene)-4-oxo-2-thioxo-thiazolidin-3-yl)acetic Acid. The end hydroxyl functionalities of starch were esterified with the free carboxyl group of 2-(5-(4-dimethylamino-benzylidene)-4-oxo-2-thioxo-thiazolidin-3-yl)acetic acid through DCC coupling using DMAP as the catalyst (Scheme 2).

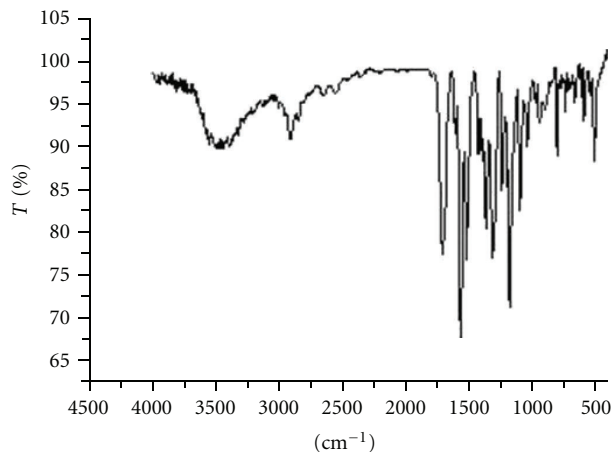


FIGURE 1: IR spectrum of 2-(5-(4-dimethylamino-benzylidene)-4-oxo-2-thioxo-thiazolidin-3-yl)acetic acid.

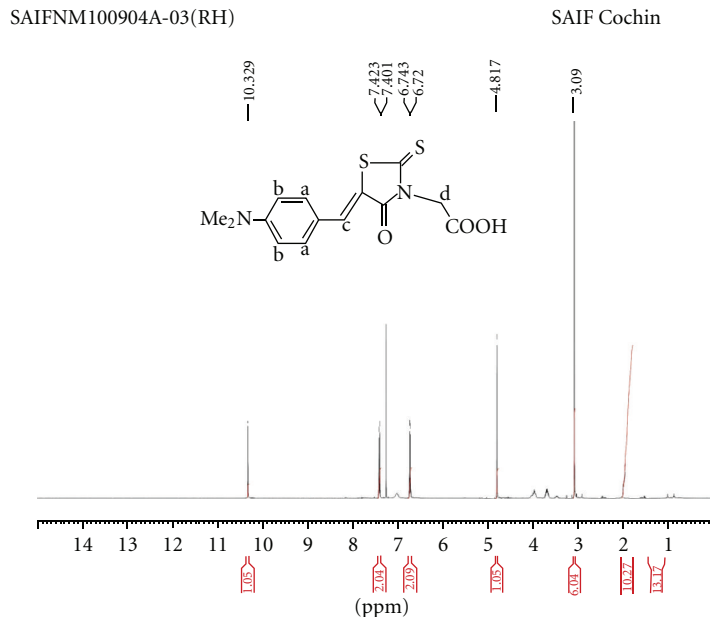


FIGURE 2: ^1H NMR spectrum of 2-(5-(4-dimethylamino-benzylidene)-4-oxo-2-thioxo-thiazolidin-3-yl)acetic acid.

IR spectrum was recorded in the operating frequency range $4000\text{--}400\text{ cm}^{-1}$. IR(KBr): 3326 cm^{-1} (broad): $\nu_{\text{O-H}}$ (str), 2927 cm^{-1} : $\nu_{\text{C-H}}$ of CH_2 , 1706 cm^{-1} : $\nu_{\text{C=O}}$ (str), 1627 cm^{-1} (tightly bound H-O-H present in starch), 1579 cm^{-1} : $\nu_{\text{C=C}}$ (str), 1334 cm^{-1} : $\nu_{\text{C-N}}$ (str), 1375 cm^{-1} : $\nu_{\text{C=S}}$ (str), 811 cm^{-1} : $\nu_{\text{C-S}}$ (str) (Figure 3).

The proton NMR spectrum of the product was recorded in chloroform using a 500 MHz ^1H NMR spectrophotometer. ^1H NMR: 7.75 ppm (2H,d:Ha), 6.75 ppm (2H,d:Hb), 5.0 ppm (1H,s: OH group unreacted), 4.90 ppm (1H,s:Hc), 3.55 ppm (2H,s:Hd), 3.09 ppm (6H,s:N(CH₃)₂), 1.37–2.17 ppm (m: aliphatic protons of starch). The signal corresponding to COOH proton observed in the proton NMR spectrum of the dye was absent here (Figure 4).

3.3. Light Absorption Properties of Starch Modified with 2-(5-(4-Dimethylamino-benzylidene)-4-oxo-2-thioxo-thiazolidin-3-yl)acetic Acid. The UV-visible spectra of the chromophoric system 2-[5-(4-dimethylamino-benzylidene)-4-oxo-2-thioxo-thiazolidine-3-yl]acetic acid and starch modified with 2-[5-(4-dimethylamino-benzylidene)-4-oxo-2-thioxo-thiazolidine-3-yl]acetic acid were recorded in chloroform. UV-visible spectra showed an intense band at 474 nm for the chromophoric system and a band centred at 503 nm for the coupled product. The λ_{max} showed a notable red shift of 29 nm on attaching the dye to the starch core (from 474 nm to 503 nm). The HOMO-LUMO energy gap of the conjugated π system is notably reduced on attaching the chromophore onto the core material, and this was

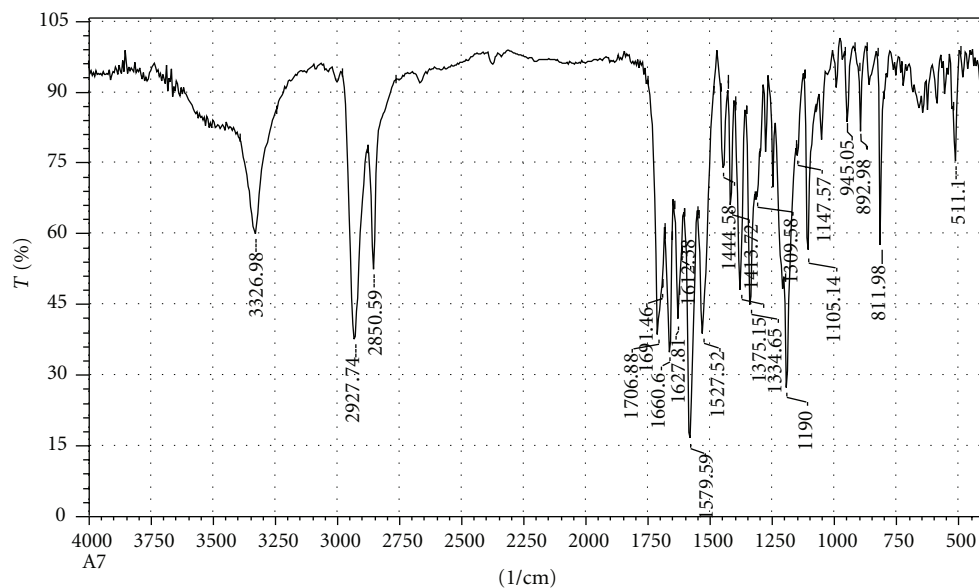


FIGURE 3: IR spectrum of starch modified with 2-(5-(4-dimethylamino-benzylidene)-4-oxo-2-thioxo-thiazolidin-3-yl)acetic acid.

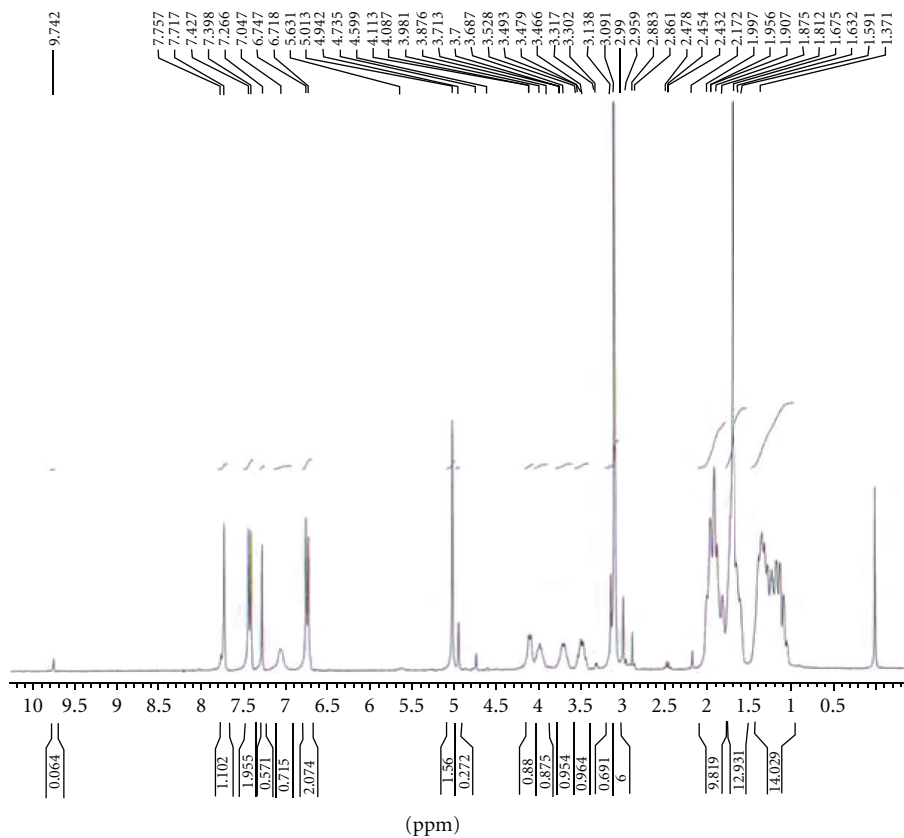


FIGURE 4: ¹H NMR spectrum of starch modified with 2-(5-(4-dimethylamino-benzylidene)-4-oxo-2-thioxo-thiazolidin-3-yl)acetic acid.

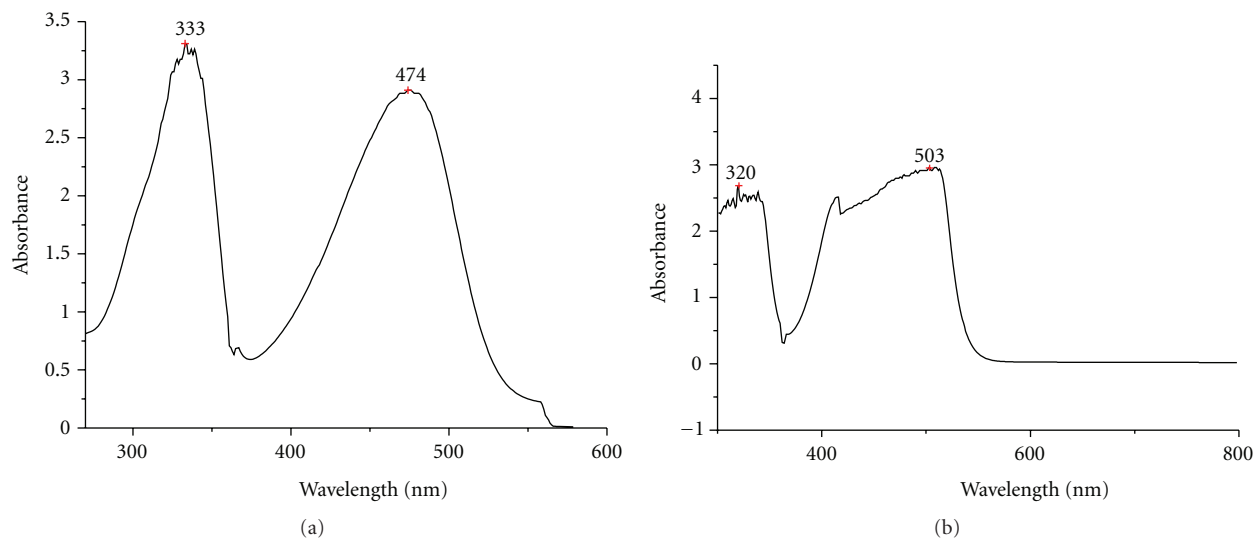


FIGURE 5: UV-visible spectra of (a) 2-[5-4-dimethylamino-benzylidene-4-oxo-2-thioxo-thiazolidine-3-yl]acetic acid and (b) starch modified with 2-[5-4-dimethylamino-benzylidene-4-oxo-2-thioxo-thiazolidine-3-yl]acetic acid.

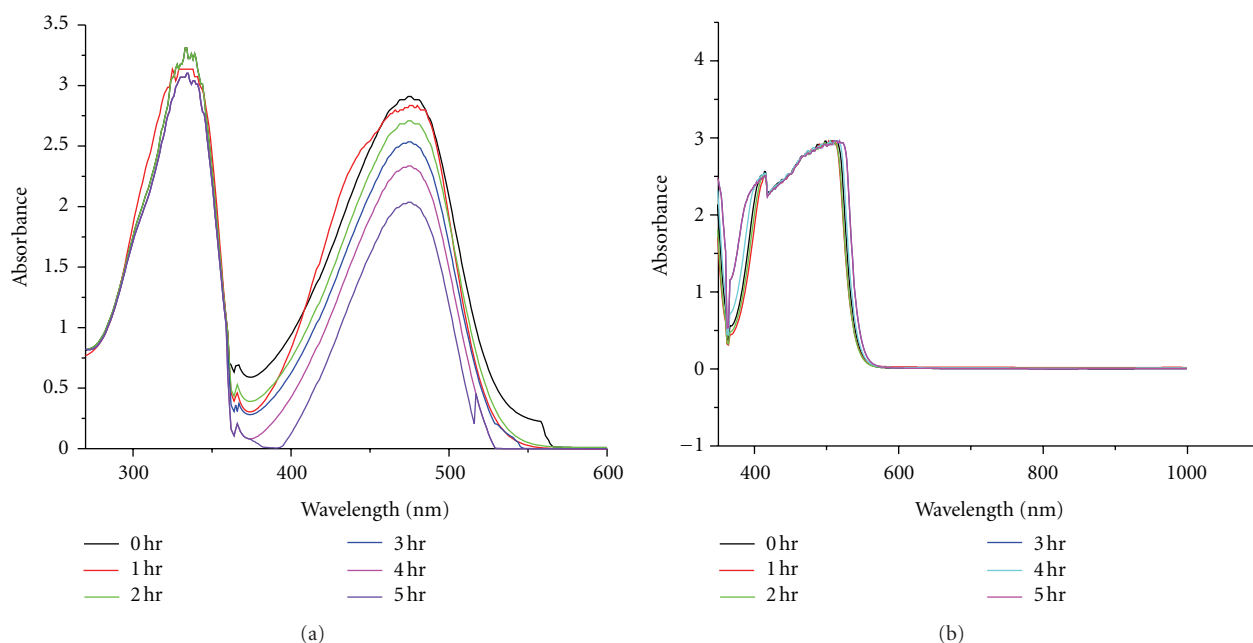


FIGURE 6: Irradiation studies of (a) 2-[5-4-dimethylamino-benzylidene-4-oxo-2-thioxo-thiazolidine-3-yl]acetic acid and (b) starch modified with 2-[5-4-dimethylamino-benzylidene-4-oxo-2-thioxo-thiazolidine-3-yl]acetic acid.

evident from the remarkable red shift noted on attaching the dye to the core material (Figure 5).

4. Light Fastening Studies

The low molecular chromophoric system 2-[5-4-dimethylamino-benzylidene-4-oxo-2-thioxo-thiazolidine-3-yl]acetic acid and its polymer-bound analogue were subjected to light fastening studies. Solutions of the two systems were prepared

in chloroform with same molar concentrations. These solutions were subjected to irradiation under visible radiant energy. The changes in the UV-visible absorption spectra as a function of time of irradiation were noted. A sudden, but gradual, decrease in intensity was noted on irradiating the low molecular chromophoric system under visible radiant energy. The intensity of absorption was 2.75 at zero time and this was decreased to 1.8 on prolonged irradiation for 5 hours. The starch modified with 2-[5-4-dimethylamino-benzylidene-4-oxo-2-thioxo-thiazolidine-3-yl]acetic

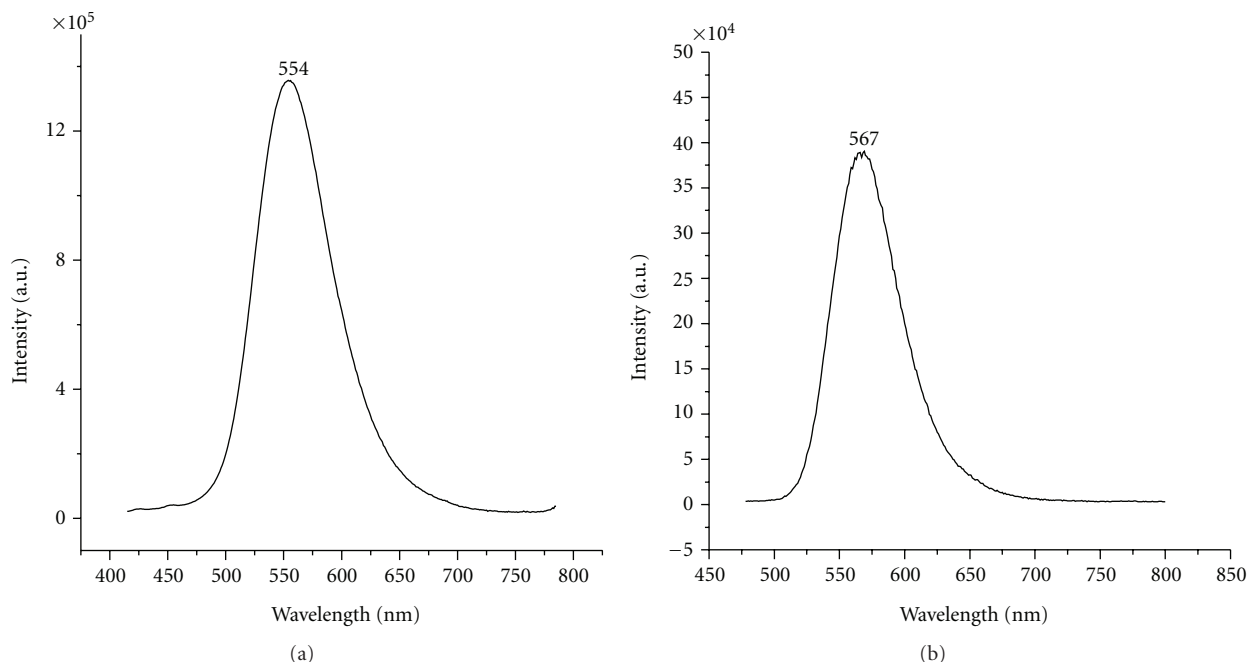


FIGURE 7: Fluorescence spectra of (a) 2-[5-4-dimethylamino-benzylidene-4-oxo-2-thioxo-thiazolidine-3-yl]acetic acid and (b) starch modified with 2-[5-4-dimethylamino-benzylidene-4-oxo-2-thioxo-thiazolidine-3-yl]acetic acid.

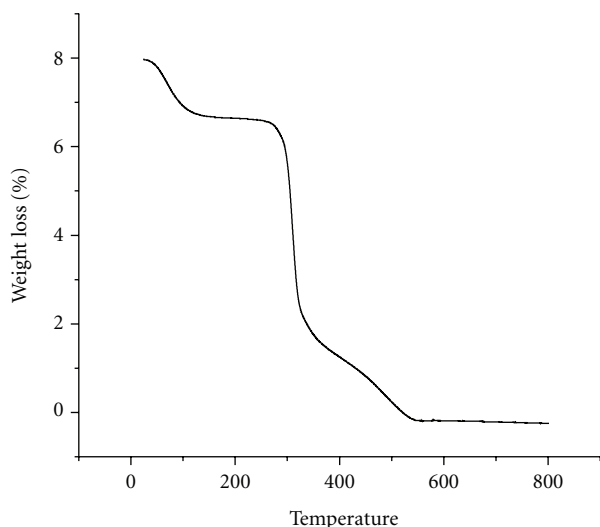


FIGURE 8: TG-DTA curve of starch.

acid showed high stability even after prolonged irradiation. The intensity of absorption was recorded as 3.2 at zero time. This remained nearly the same on irradiation for 5 hours. This shows the efficient light fastening property of the polymer anchored chromophoric system. The irradiation results are shown in Figure 6.

The fluorescence emission spectra of 2-[5-4-dimethylamino-benzylidene-4-oxo-2-thioxo-thiazolidine-3-yl]acetic acid and starch coupled with 2-[5-4-dimethylamino-benzylidene-4-oxo-2-thioxo-thiazolidine-3-yl]acetic acid were recorded in chloroform. The excitation wavelength was

TABLE 1: Thermal analysis data (TG) of starch.

Mass %	Start temp.	End temp.	Weight loss %
80–100	104.53	261.75	10
60–20	277.74	350.70	80

400 nm. The emission maximum for the free chromophoric system was observed at 554 nm and the coupled product was observed at 567 nm. Compared to the pure chromophoric system, the coupled product shows appreciable increase in emission maximum. The intensity of fluorescence emission was also greatly enhanced on attaching to the polymer. The fluorescence spectra of modified as well as pure chromophoric system are shown in Figure 7.

5. Thermal Studies

In the case of the TG curve of starch, a sudden degradation with 90% weight loss occurs at 350°C. The first thermal event occurs at a weight loss of 15%; this is due to the dehydroxylation taking place in the core system (see Table 1). The sudden change at 350°C is due to the degradation of side chains present in the polymer core (Figure 8).

TG of chromophoric system shows four mass loss steps. In the first thermal event between 137–203°C, 36 mass % loss was observed (see Table 2). The higher mass loss above 30 mass % is a consequence of degradation of aromatic chain present in the chromophoric system. In the second mass loss event between 206–245°C, the loss is 17%. This is due to the escape of sulphur group present in the chromophoric system (Figure 9).

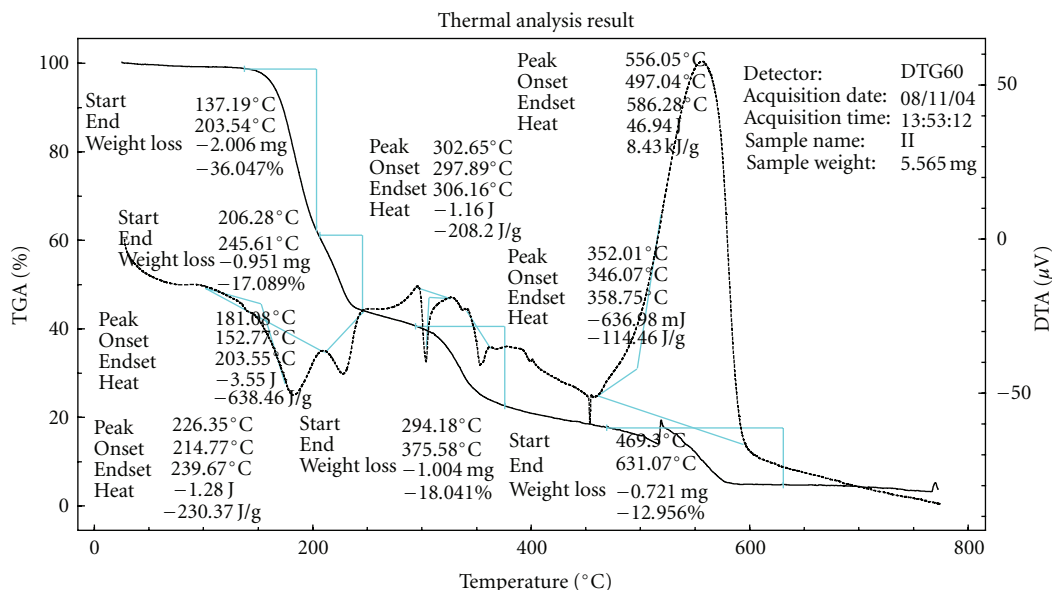


FIGURE 9: TG-DTA curve of 2-(5-(4-dimethylamino-benzylidene)-4-oxo-2-thioxo-thiazolidin-3-yl)acetic acid.

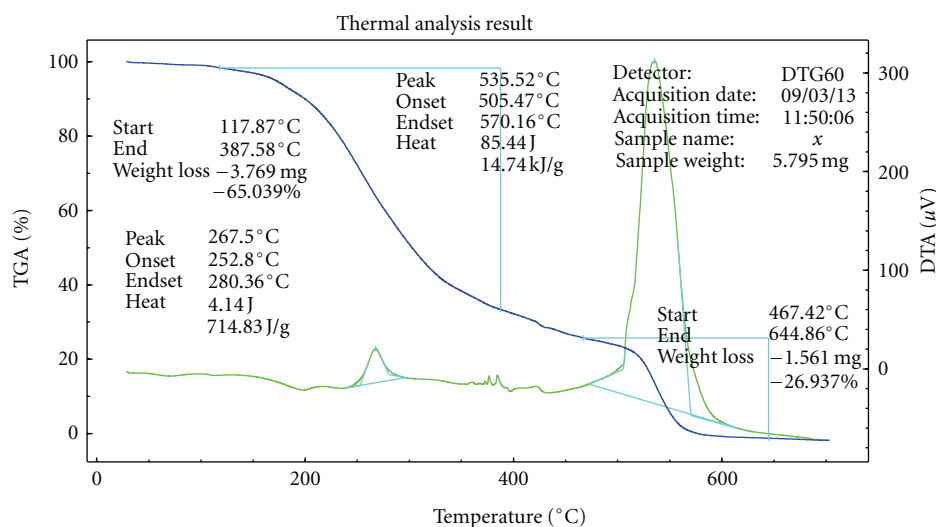


FIGURE 10: TG-DTA curve of starch modified with 2-(5-(4-dimethylamino-benzylidene)-4-oxo-2-thioxo-thiazolidin-3-yl)acetic acid.

TABLE 2: Thermal analysis data (TG) of 2-(5-(4-dimethylamino-benzylidene)-4-oxo-2-thioxo-thiazolidin-3-yl)acetic acid.

Mass %	Start temp.	End temp.	Weight loss %
60–100	137.19	203.54	36.04
40–60	206.28	245.61	17.086
20–40	294.18	375.58	18.04

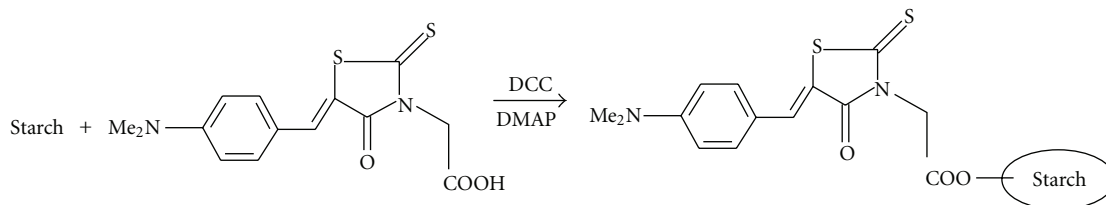
TABLE 3: Thermal analysis data (TG) of starch functionalised 2-(5-(4-dimethylamino-benzylidene)-4-oxo-2-thioxo-thiazolidin-3-yl)acetic acid.

Mass %	Start temp	End temp	Weight loss %
100–40	117.87	387.58	65.03
40–20	467.42	644.86	26.37

It was noted that TG of modified starch shows two mass loss steps as shown in the curve. In the first thermal event 117–387°C, 65.03% mass loss is observed (see Table 3). The higher mass loss is due to the dehydration of neighbouring OH groups in the glucose ring [15]. In the second mass loss

event between 467–644°C, a 26.37 mass % loss is observed (Figure 10).

The thermogravimetric analysis of modified polymer, chromophoric system, and core material were compared. The analysis shows that the degradation temperature was



SCHEME 2: Functional modification of starch with 2-(5-(4-dimethylamino-benzylidene)-4-oxo-2-thioxo-thiazolidin-3-yl)acetic acid.

increased in the case of starch modified with 2-(5-(4-dimethylamino-benzylidene)-4-oxo-2-thioxo-thiazolidin-3-yl)acetic acid compared to the core or the low molecular chromophoric system. The overall thermal stability of polymer was also enhanced upon functional modification with the chromophoric system.

6. Conclusion

In the present study the environment friendly natural polymeric system such as starch was used as the core material for developing nature friendly, “green” photoactive system based on polymeric systems. Modified starches have very promising industrial prospects on application basis, due to its more biocompatible and environment friendly nature as compared to synthetic polymers. The paper reports the development of photoactive, thermostable starch moiety. Starch was modified with chromophoric system, namely, 2-(5-(4-dimethylamino-benzylidene)-4-oxo-2-thioxo-thiazolidin-3-yl)acetic acid by DCC coupling between the carboxyl function of chromophoric system and hydroxyl functionalities of starch. The modified products were characterised and compared by spectroscopic techniques. The modified starch shows remarkable red shift and increase in intensity of absorption and emission. Light irradiation studies of the 2-(5-(4-dimethylamino-benzylidene)-4-oxo-2-thioxo-thiazolidin-3-yl)acetic acid and starch modified with 2-(5-(4-dimethylamino-benzylidene)-4-oxo-2-thioxo-thiazolidin-3-yl)acetic acid were compared. The modified system shows excellent light fastening properties. The fluorescence emission maximum of starch coupled with 2-[5-(4-dimethylamino-benzylidene)-4-oxo-2-thioxo-thiazolidin-3-yl]acetic acid was observed at 567 nm. TGA studies were conducted to determine the effect of esterification on the thermal stability of starch. The results indicated that modified starch has increased thermostability compared to the unmodified starches.

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