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Synthesis, Characterization and Thermal studies on natural Polymers modified with 2-(5-(4-dimethylamino-benzylidin)-4-oxo-2-thioxo-thiazolidin-3-yl) acetic acid

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Abstract

In the present work, 2-(5-(4-dimethylamino-benzylidin)-4-oxo-2-thioxo-thiazolidin-3-yl)acetic acid, a chromophoric system with push-pull electron modulation was synthesized and incorporated onto biopolymers such as lignin, starch and cellulose through esterification by DCC Coupling. The products were characterized by UV-visible, fluorescence, FT-IR and NMR spectroscopic methods. The unmodified natural polymers and the coupled products were subjected to thermal analysis by TG-DTA studies. The results of the studies show that incorporation of the chromophoric system onto the polymeric core enhanced the thermal stability of the chromophoric system and core materials. The thermal data obtained were analysed and compared.

Keywords: 2-(5-(4-dimethylamino-benzylidin)-4-oxo-2-thioxo-thiazolidin-3-yl)acetic acid, biopolymer incorporation, thermal stability, lignin, starch, cellulose.

Introduction

The incorporation of rhodanine based chromophoric system on to biopolymeric core material such as lignin, starch and cellulose presents a series of nature friendly and naturally occurring biopolymers[1]. These system can be used as the ''Green Alternatives'' for photoresponsive materials with excellent applications as photoprobing systems[2].

Lignin is a large, cross-linked macromolecule and is relatively hydrophobic and aromatic in nature. Lignin plays a vital role in plant growth and development by improving water conduction through xylem tracheary elements, enhancing the strength of fibrous tissues, and limiting the spread of pathogens in plant tissues. Lignin restricts the degradation of structural polysaccharides by hydrolytic enzymes, thereby limiting the bioconversion of forages and fibrous crops into animal products or into liquid fuels and other industrial products[3,4]. Lignin is formed by dehydrogenative polymerization of hydroxy cinamyl alcohols of three different types. P-coumaryl alcohol, coniferyl alcohol and sinapyl alcohol. During the polymerization, the mono lignols are oxidized by peroxidases or laccases to form phenoxy radicals that exist in the main mesomeric forms. The most abundant inter unit linkage in all lignins is the beta aryl ether bond. Starch is an abundant, inexpensive, naturally occurring polysaccharide. It is biocompatible biodegradable, and nontoxic, so it can be used as biocompatible implant materials and drug carriers[5,6]. A starch molecule is a polysaccharide assembled from the simple sugar glucose, it can contain anywhere from five hundred to several hundred thousand glucose molecules joined by covalent bonds into a single structure. In addition to its importance in human nutrition, starch has many industrial applications: it is used in the manufacture of paper, textiles, pharmaceuticals, and biodegradable polymers, and it is an additive in foods[7-13]. As the most important skeletal component in plants, the polysaccharide cellulose is an exhaustible polymeric raw material with fascinating structure and properties, formed by the repeated connection of the D-glucose building blocks. Cellulose constitutes approximately a third of all vegetable matter and thus it exist in far greater quantity than any other polysaccharide. It occurs as a principal structural component of the cell walls of mosses and seaweeds, annual plants and trees. Cotton fiber contains 98% cellulose. It is the most abundant natural polymer on earth and an important natural and sustainable resource. Cellulose derivatives have found application in many fields. In the present study, the biopolymers namely lignin, starch and cellulose were functionally modified with photoactive groups with a view to develop a series of nature friendly and naturally occurring biopolymers with high thermal stability and photoresponsive properties[14-20].

Material and Methods

Lignin, starch and cellulose were purchased from Merck (Germany). P-Dimethylamino benzaldehyde, rhodanine-N-acetic acid, dimethylaminopyridine (DMAP) and dicyclohexylcarbodiimide (DCC) are commercial samples and used as purchased from E. Merck India Ltd. The solvents used for the study such as dimethyl formamide (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 4000-400cm^{-1}. UV-Visible spectra were recorded on a Shimadzu UV-visible NIR spectrophotometer operating in the range 200-1100nm.

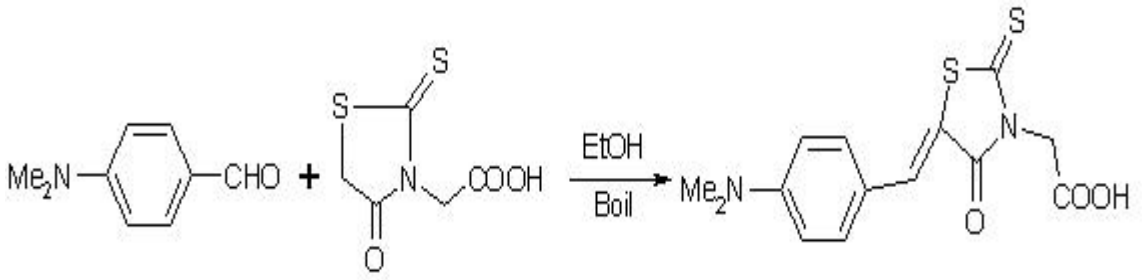
Synthesis of 2-(5-(4-dimethylamino-benzylidin)-4-oxo-2-thioxo-thiazolidin-3-yl) acetic acid: p-Dimethyl amino benzaldehyde (1g) and rhodanin-N- acetic acid (1.25g) were dissolved in 50ml ethanol. The mixture was stirred thoroughly for a few minutes. The temperature was raised to 80^{0}C and the mixture was refluxed for 4 hours. The product was filtered and purified by recrystallisation from absolute ethanol (scheme 1). The yield was noted as 81%. It was further purified by column chromatography using 10:3 hexane-ethyl acetate solvent system and dried in vacuum.

Synthesis of natural polymer functonalised with 2-(5-(4-dimethylamino-benzylidin)-4-oxo-2-thioxo-hiazolidin-3-yl) acetic acid: General Procedure: 2-(5-(4-dimethylamino-benzylidin)-4-oxo-2-thioxo-thiazolidin-3-yl)acetic acid and the natural polymers such as lignin, starch and cellulose (in molar ratio), DMAP(200mg), and DCC(1g) were separately dissolved in DMF and mixed together. The mixture was stirred at room temperature for 2 hours and at 80^{0}C for 6 hours. The by-product dicyclohexyl urea (DCU) was removed by warming-cooling-filtration process and the solvents were removed on a vacuum rotory evaporator and dried. It was purified by column chromatography and the product was characterised by spectroscopic analysis.

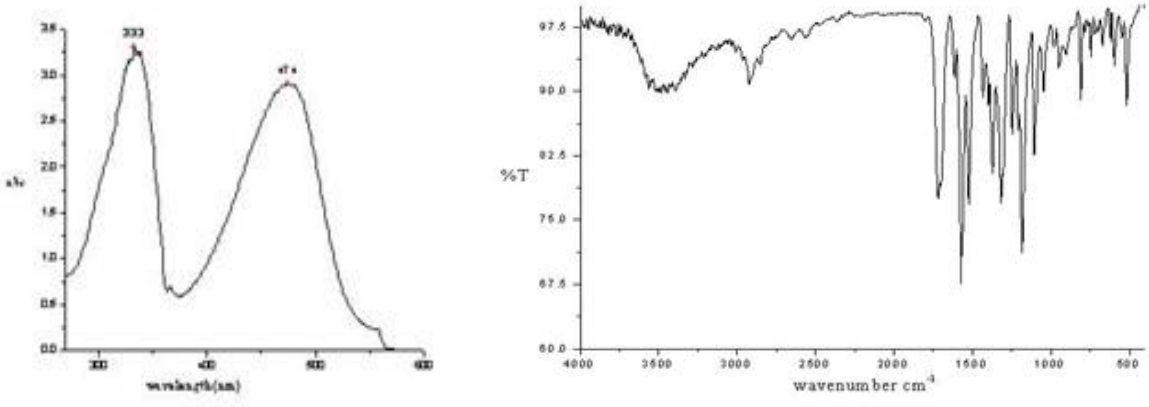
Results and Discussion

Synthesis and characterisation of 2-(5-(4-dimethylamino-benzylidin)-4-oxo-2-thioxo-thiazolidin-3-yl)acetic acid: *p*-dimethyl amino benzaldehyde and rhodanin-*N*- acetic acid were condensed together at 80 ^{0} C yielding 2-(5-(4-dimethylamino-benzylidin)-4-oxo-2-thioxo-thiazolidin-3-yl) acetic acid (scheme1).

IR spectrum of 2-(5-(4-dimethylamino-benzylidin)-4-oxo-2-thioxo-thiazolidin-3-yl)acetic acid was recorded in the solid state as KBr discs in the operating frequency range 4000-400cm^{-1}. IR(KBr): 3300-3500 cm^{-1} (broad):ν_{O-H}(str), 2920 cm^{-1}: ν_{C-H} of CH_2 , 1716 cm^{-1}: $\nu_{C=O}$(str), 1608 $\nu_{C=C}$(str), 1573cm^{-1}: $\nu_{N=N}$(str), 1373 cm^{-1}: ν_{C-N}(str), 1319 cm^{-1}: $\nu_{C=S}$(str), 1184 cm^{-1}: ν_{C-O}(str). The UV-visible spectrum shows λ max at 474 nm (figure 1).



Scheme-1
Synthesis of 2-(5-(4-dimethylamino-benzylidin)-4-oxo-2-thioxo-thiazolidin-3-yl) acetic acid



(a) (b)

Figure-1
(a) UV-visible and (b) IR spectra of 2-(5-(4-dimethylamino-benzylidin)-4-oxo-2-thioxo-thiazolidin-3- yl)acetic acid

The proton NMR spectrum of 2-(5-(4-dimethylamino-benzylidin)-4-oxo-2-thioxo-thia zolidin-3-yl)acetic acid was recorded in chloroform using a 500 MHz ^{1}H NMR spectrophotometer. ^{1}H NMR: 10.32 ppm(1H,s:-COOH), 7.42ppm (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:N(CH_3)$_2$(figure 2).

Synthesis and characterisation of biopolymer functionalised with 2-(5-(4-dimethylamino-benzylidin)-4-oxo-2-thioxo-thiazolidin-3-yl)acetic acid: Functional modification of the free hydroxyl groups of lignin, starch and cellulose with the free carboxyl functions of the photo responsive system was acheived through esterification by DCC Coupling (scheme 2).

The products were characterized by FT-IR, NMR and UV-visible spectroscopic studies. The spectral results of the lignin functionalised with 2-[5-(4- dimethyl amino-benzylidine-4-oxo-2-thioxo thiozolidine-3-yl] acetic acid are summarized below.

UV-visible: λ max: 498 nm (figure 3). IR(KBr): 3743 cm^{-1}(broad):ν_{O-H}(str), 2927 cm^{-1} ν_{C-H} of CH_2 aromatic,1747 cm^{-1}: $\nu_{C=O(str),}$ 1535 cm^{-1}: $\nu_{C=C}$(str), 1315 cm^{-1}: ν_{C-N}(str),1186cm^{-1}: ν_{C-O}(str), 665 cm^{-1}: ν_{C-S}(str) (figure 3). ^{1}H NMR: 7.70 ppm (2H,d:H_a),7.45 ppm (2H,d:H_b), 6.74 ppm (m:aromatic protons in lignin), 5.05 ppm (1H,s:unreacted OH in lignin), 4.81ppm (2H,s:aliphatic proton c), 3.65 ppm(2H,s:H_d), 3.09 ppm (6H,s:N(CH_3)$_2$), 2.22 ppm (2H,s:aliphatic proton c), 1-2 ppm (aliphatic protons of lignin core) (figure 4).

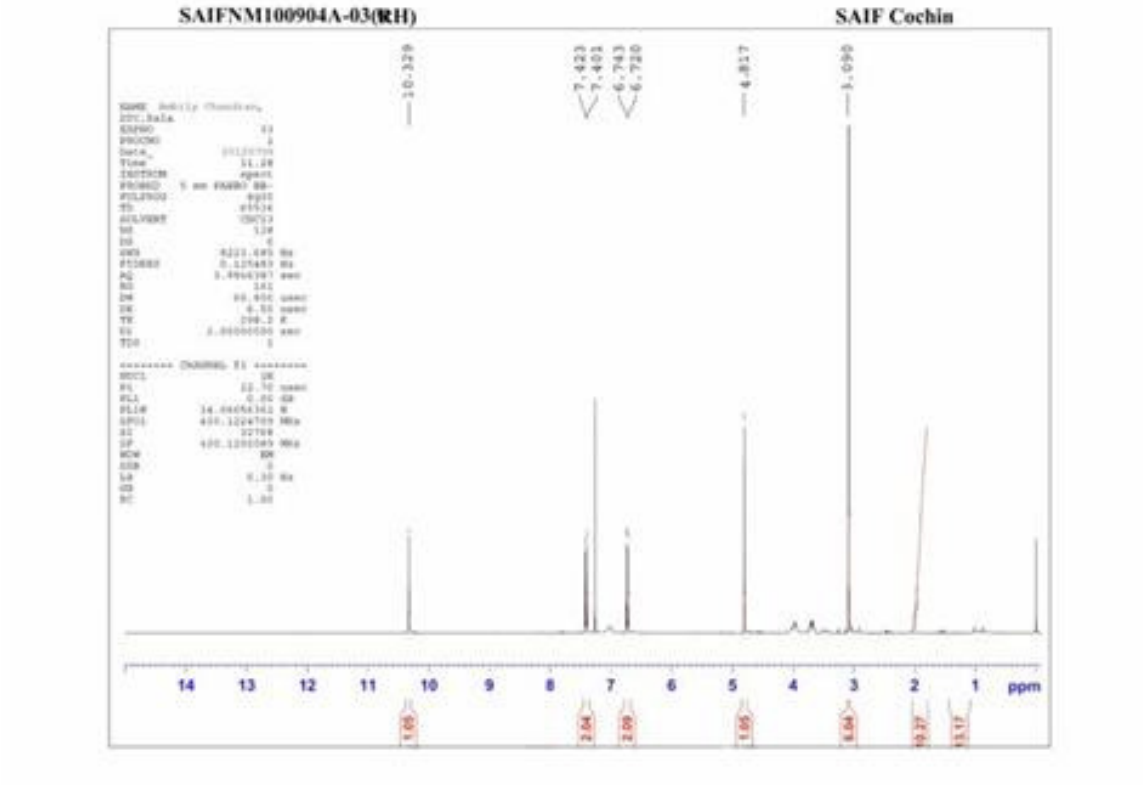
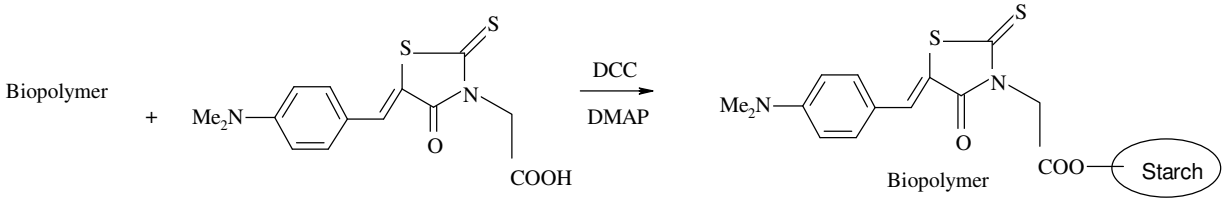


Figure-2
^{1}H NMR spectrum of 2-(5-(4-dimethylamino-benzylidin)-4-oxo-2-thioxo- thiazolidin-3-yl) acetic acid



Scheme-2
Functional modification of biopolymer with 2-(5-(4-dimethylamino-benzylidin)-4-oxo-2-thioxo-thiazolidin-3-yl)acetic acid

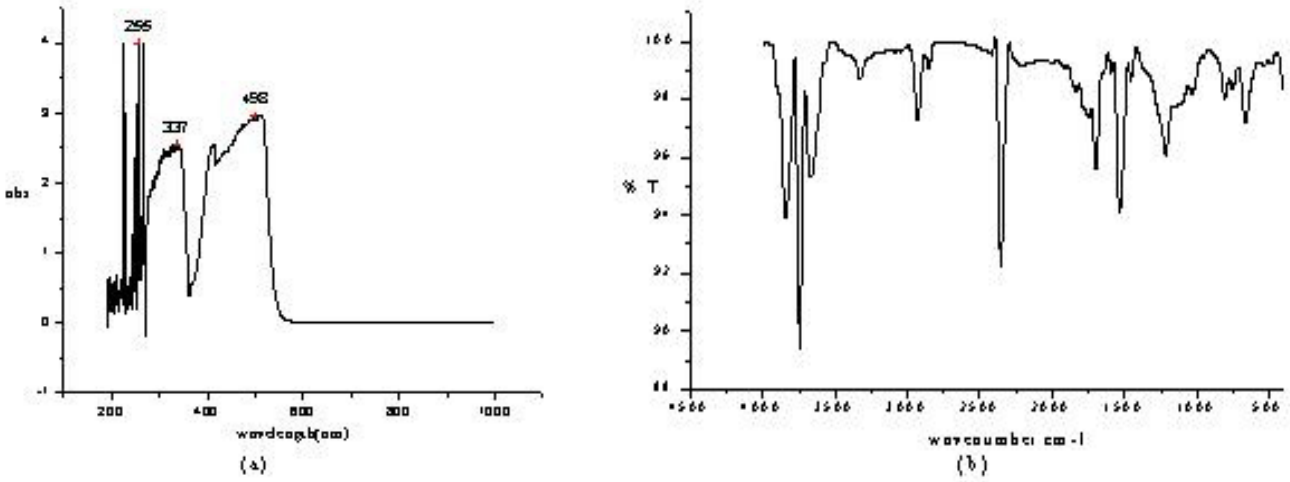


Figure-3
(a)UV-visible and (b) IR spectra of lignin modified with 2-(5-(4-dimethylamino- benzylidin)-4-oxo-2- thioxo-thiazolidin-3-yl) acetic acid

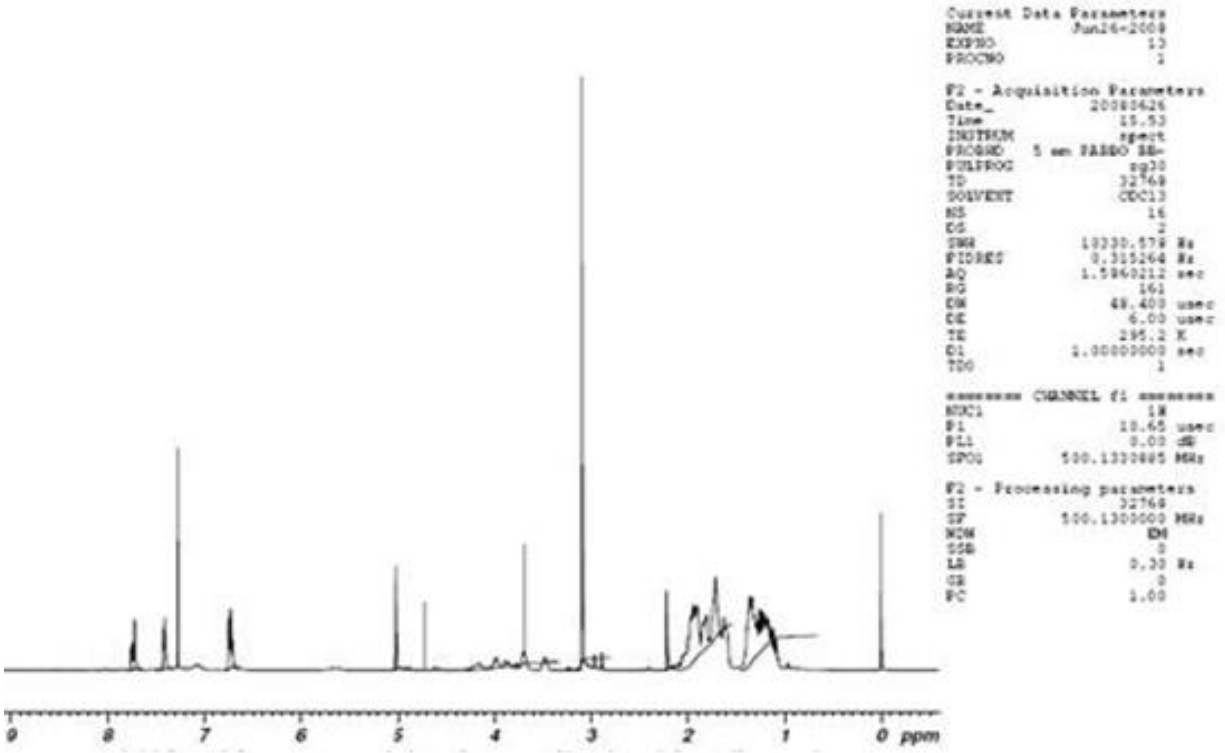


Figure-4
^{1}H NMR spectrum of lignin modified with 2-(5-(4-dimethylamino-benzylidin)-4-oxo-2-thioxo-thiazolidin-3-yl) acetic acid

The photoactive rhodanine based dye was introduced into the biopolymer core of starch by DCC coupling and characterized by FT-IR, UV-visible and 1H NMR spectral analysis. The results are summarized below. UV-visible: λ max: 503 nm (figure 5).IR(KBr): 3326cm^{-1}(broad):ν_{O-H}(str), 2927 cm^{-1}: ν_{C-H} of CH_2, 1706 cm^{-1}: $\nu_{C=O}$(str), 1579 cm^{-1}: $\nu_{C=C}$(str), 1334cm^{-1}: ν_{C-N}(str), 1375cm^{-1}: $\nu_{C=S}$(str), 811 cm^{-1}: ν_{C-S}(str) (figure 5). ^{1}H NMR: 7. 75 ppm (2H,d:Ha), 6.75 ppm (2H,d:Hb), 5.0 ppm (1H,S: OH group unreacted), 4.11 ppm (1H,s:Hc), 3.71 ppm (2H,s:Hd), 3.09 ppm (6H,S:N(CH_3)$_2$), 2.35 ppm (2H,s:Hd), 1.37-2.17ppm (m: aliphatic protons of starch) (figure 6).

The cellulose-dye ester was characterized by FT-IR, UV-visible and ^{1}H NMR spectral analysis. The results are: UV-visible: λ max: 496 nm (figure 7).IR(KBr):3431-3321cm^{-1}(broad):ν_{O-H}(str), 2925 cm^{-1}: ν_{C-H}(str), 1622 cm^{-1}: $\nu_{C=O}$(str), 1581 cm^{-1}: $\nu_{C=C}$(str), 1529 cm^{-1}: $\nu_{C=S}$(str), 1380 ν_{O-H}(bend), 1309 cm^{-1}: ν_{C-N}(str), 1188 cm^{-1}: ν_{C-O}(str) in esters (figure 7). ^{1}H NMR: 7.75 ppm (2H,d:aromatic proton a),7.5 ppm (2H,d:aromatic proton b), 5.0 ppm (OH protons), 4.10 ppm (1H,s:Hc), 3.6 ppm (2H,s:Hd),3.01 ppm (6H,s:N(CH_3)$_2$), 1-2 ppm (cellulosic aliphatic protons) (figure 8).

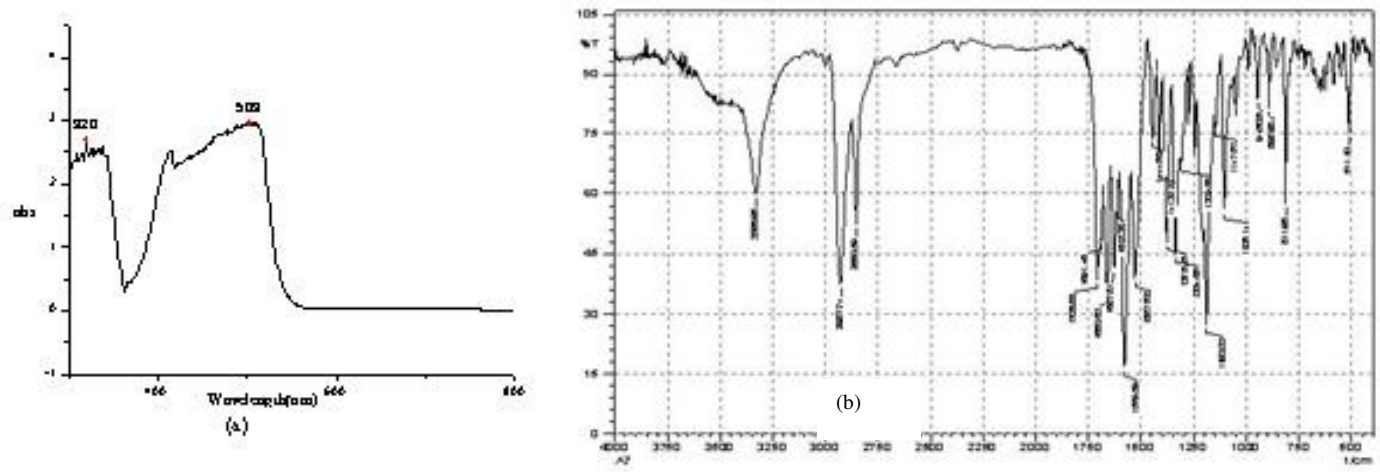


Figure-5
(a) UV-visible and (b) IR spectra of starch modified with 2-(5-(4-dimethylamino-benzylidin)-4-oxo-2-thioxo-thiazolidin-3-yl) acetic acid

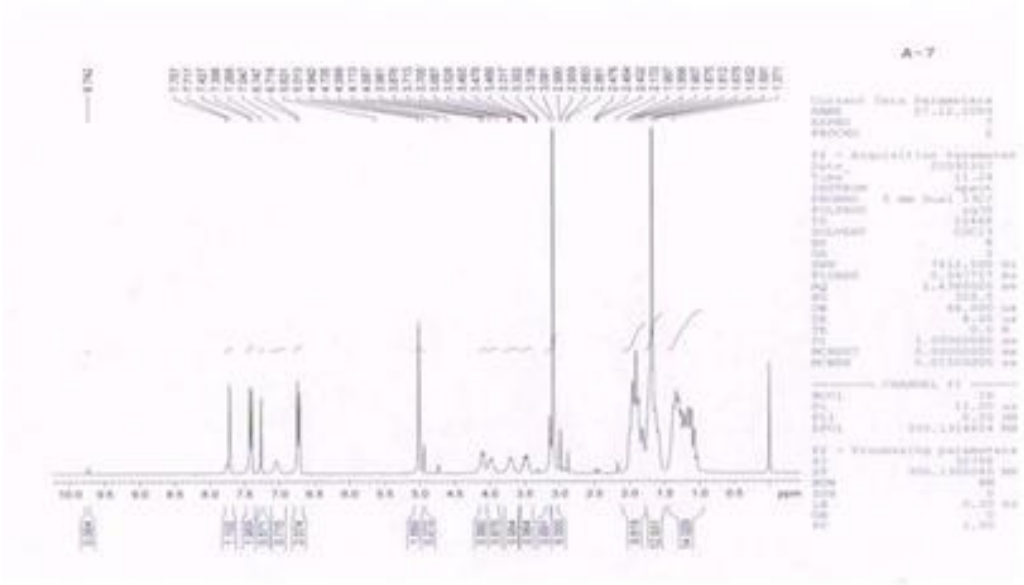


Figure-6
^{1}H NMR spectrum of starch modified with 2-(5-(4-dimethylamino-benzylidin)-4-oxo- 2-thioxo-thiazolidin-3-yl) acetic acid

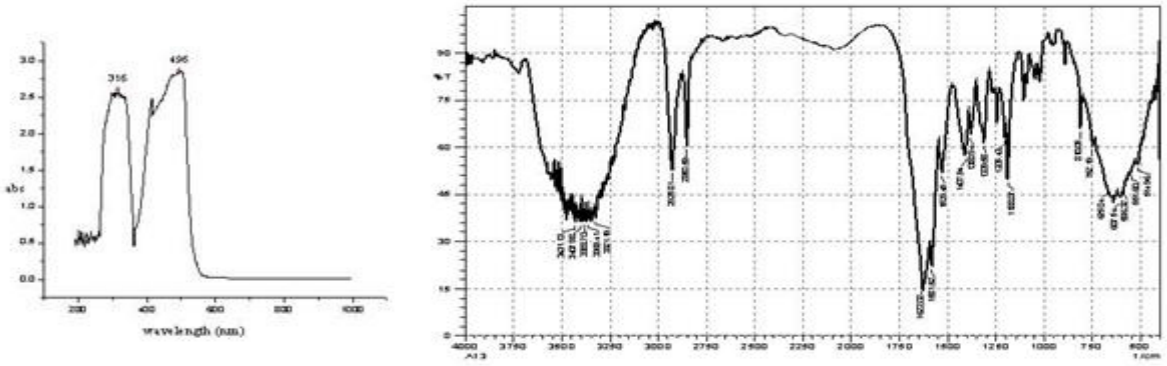


Figure-7

(a) UV-visible and (b) IR spectra of cellulose modified with 2-(5-(4-dimethylamino- benzylidin)-4-oxo-2- thioxo-thiazolidin-3-yl)acetic acid

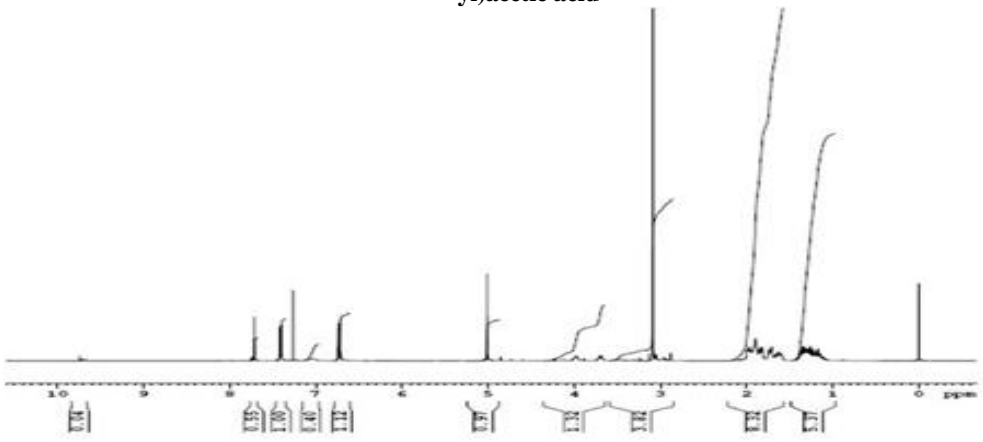


Figure-8

^{1}H NMR spectrum of cellulose modified with 2-(5-(4-dimethylamino-benzylidin)-4-oxo-2-thioxo-thia zolidin-3-yl) acetic acid

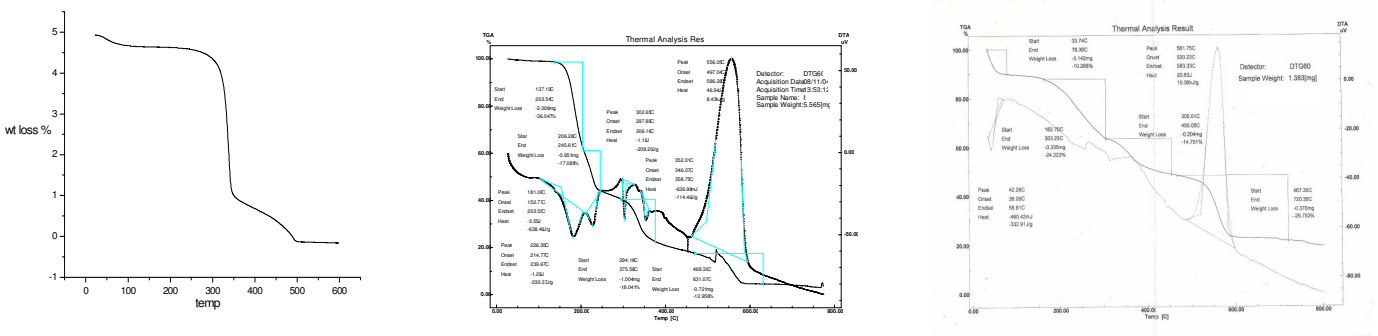


Figure-9

TG-DTA curve of (a) lignin (b) 2-(5-(4-dimethylamino-benzylidin)-4-oxo-2-thioxo thiazolidin-3-yl) acetic acid and (c) lignin modified with 2-(5-(4-dimethylamino- benzylidin)-4-oxo-2-thioxo-thiazolidin-3-yl) acetic acid

Thermal analysis of lignin modified with 2-[5-(4-dimethyl amino-benzylidine-4-oxo-2-thioxo-thiozolidine-3-yl]acetic acid: Thermo gravimetric analysis was conducted on the polymer core and the polymer supported chromophoric systems. In the case of pure lignin almost 80-90% weight loss occurs at 350^{0}c (table 1). The weight loss is due to degradation of aromatic side chains present in the polymer core. The weight loss at 360^{0}C is due to the degradation of phenolic hydroxyl group present in lignin (figure 9).

TG of chromophoric system shows four mass loss steps. In the first thermal event between 137-203^{0}C, 36 mass% loss is observed. 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^{0}C, the loss is 17%. This is due to the escape of sulphur group present in the chromophoric system.

To assess the thermal stability of lignin functionalised with 2-(5-(4-dimethylamino-benzylidin)-4-oxo-2-thioxo-thiazolidin-3-yl)acetic acid, TG analysis was carried out using DTG-60 detector (table 1). It was noted that TG of modified lignin shows four mass loss steps as shown in the curve (figure 9). In the case of modified system the first thermal degradation occurs at 33-78^{0}C. The weight loss is 10.28%. This is due to the escape of moisture. Second thermal event occurs at 162-303^{0}C. The weight loss is 24.22%. This due to the degradation of phenolic hydroxyl side chain present in the lignin core. The mass loss at 305-455^{0}C is 14.75. This is due to dehydroxylation taking place in the core system. The degradation ends at 467-720^{0}C (table 1)

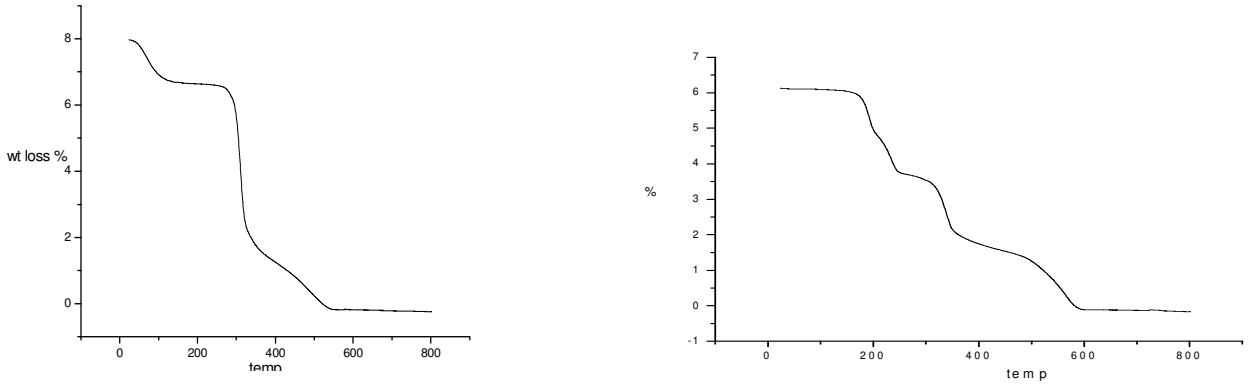
The thermo gravimetric analysis of modified polymer, chromophoric system and core material were compared. The analysis shows that the degradation temperature is increased in the case of lignin modified with2-(5-(4-dimethylamino-benzylidin)-4-oxo-2-thioxo-thiazolidin-3-yl)acetic acid compared to the core or the low molecular chromophoric system. And the overall thermal stability of polymer is also enhanced. The peak value of derivative of the weight change was 360^{0}C for unmodified lignin and 720^{0}C for modified lignin. This indicated that the modified lignin has increased thermo stability compared to unmodified lignin.

Thermal analysis of starch modified with 2-[5-(4-dimethyl amino-benzylidine-4-oxo-2-thioxo-thiozolidine-3-yl] acetic acid: In the case of TG curve of starch a sudden degradation with 90% weight loss occurs at 350^{0}C. The first thermal event occurs at a weight loss of 15%, this is due to the dehydroxylation taking place in the core system. The sudden change at 350^{0}C is due to the degradation of side chains present in the polymer core (figure 10, table 2).

To assess the thermal stability of modified starch TG analysis was carried out using DTG-60 detector. At 10% weight loss the decomposition temperature of modified starch fraction occurred at 200^{0}C. The small weight loss may be due to the escape of moisture. After 200^{0}C thermal degradation took place gradually and ends at 600^{0}C. This is due to the degradation of side chains present in the core system. The TG-DTA curve of modified starch is shown in figure 10.

Table-1
Thermal analysis data (TG) of lignin, 2-(5-(4-dimethylamino-benzylidin)-4-oxo-2-thioxo-thiazolidin-3-yl) acetic acid and lignin modified with 2-(5-(4-dimethylamino- benzylidin)-4-oxo-2-thioxo-thiazolidin-3-yl)acetic acid

System	Mass %	Start temp	End temp	Weight loss%
Lignin	90-100	93.17	284.84	8
	90-20	296.50	353.39	80
Dye	60-100	137.19	203.54	36.04%
	40-60	206.28	245.61	17.086%
	20-40	294.18	375.58	18.04%
Lignin-Dye	80-100	33	78	10.28
	60-80	162	303	24.22
	40-60	305	455	14.75
	20-40	467	720	26.75



(a) (b)

Figure-10
TG-DTA curve of (a) starch (b) starch modified with 2-(5-(4-dimethylamino- benzylidin)-4-oxo-2-thioxo-thiazolidin-3-yl) acetic acid

On comparing the thermo gravimetric results of starch, chromophoric system and functionally modified starch, the degradation was found to be slow in the case of modified system. This is due to the strong interaction of chromophoric system to the polymer. TGA experiment showed that degradation of the unmodified starch almost completes at 350^0C whereas in the case of modified system degradation ends at 600^0C. The greater thermal stability is evident from this experimental data.

In the case of TG curve of cellulose a sudden degradation with 80% weight loss occurs at 350^0C. The first thermal event occurs at a weight loss of 15%, this is due to the dehydroxylation taking place in the core system. The sudden change at 350^0C is due to the degradation of side chains present in the polymer core.

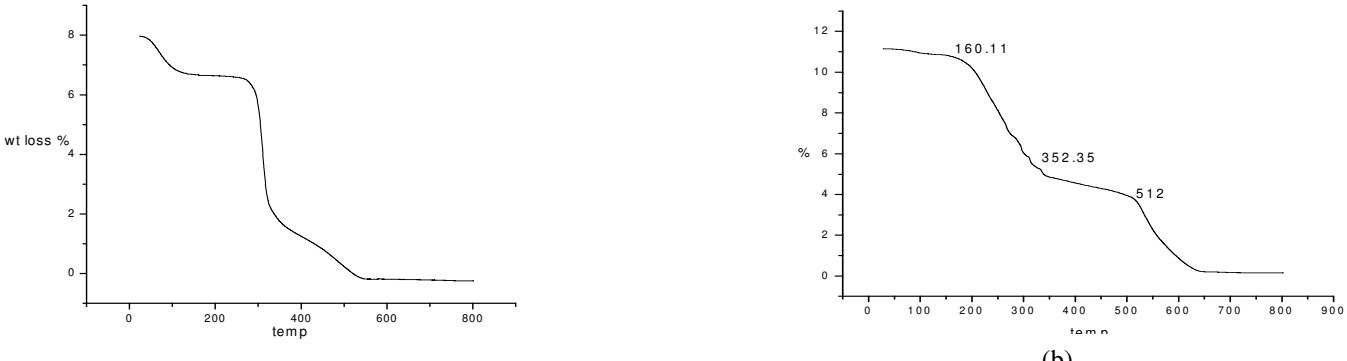
To assess the thermal stability of modified cellulose, TG analysis was carried out using DTG-60 detector. At 60% weight loss the decomposition temperature of modified starch fraction occurred at 352^0C. 60% mass loss is due to degradation of side chain present in the system. 10% weight loss was observed at 325-512^0C and the thermal degradation took place at 512^0C. After 350^0C, it showed high stability (table 3). On comparing the pure chromophoric system and modified system, it was found that the modified system showed greater thermal stability (figure 11).

Conclusion

In conclusion, it seems obvious that the technological potential and industrial utility of biopolymer gets multiplied by several folds by suitable modification. Natural polymers were functionally modified with a chromophoric system 2-(5-(4-dimethylamino-benzylidin)-4-oxo-2-thioxo-thiazolidin-3-yl)acetic acid by DCC coupling between the free carboxyl function of the chromophoric system and the end hydroxyl functionalities of biopolymers such as lignin, starch and cellulose. The products were characterized by spectroscopic methods. The thermal properties of the coupled products were compared with chromophoric system and core materials. The modified systems show an increase in degradation temperature compared to free polymer or the dye system. Overall thermal stability of polymeric system greatly enhances on attaching to the chromophoric system. Due to the natural polymer incorporation in chromophoric system an increase in the thermal stability was observed. Functionally modified lignin shows greater thermal stability than the other two coupled system. This is due to the stable aromatic ring system present in the core material. These thermally stable natural polymer-based photoactive systems are suggested as the green alternatives of conventional polymer-bound coating materials, dyes, printing inks etc. The excellent photo-responsive properties of these materials have been established by conducting light absorption, light stabilisationa and fluorescence emission studies[21].

Table-2
Thermal analysis data (TG) of starch, Starch-Dye ester

System	Mass %	Start temp	End temp	Weight loss%
Starch	80-100	104.53	261.75	10
	60-20	277.74	350.70	80
Starch-Dye	80-100	166.48	254.76	10
	60-20	272.41	354.36	65
	20-10	405.66	584.87	10



(a) (b)

Figure-11
TG-DTA curve of cellulose and cellulose modified with 2-(5-(4-dimethylamino-benzylidin)-4-oxo-2-thioxo-thiazolidin-3-yl) acetic acid

Table-3
Thermal analysis data (TG) of Cellulose, Cellulose-Dye ester

System	**Mass %**	**Start temp**	**End temp**	**Weight loss%**
Cellulose	80-100	104.53	259.09	15
	80-20	283.74	350	80
Cellulose-Dye	60-100	160.11	296.20	60
	60-20	352.35	512.55	10

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