PRAJÑĀ - **Journal of Pure and Applied Sciences Vol. 24 – 25 : 121 – 129 (2017)**
ISSN 0975 - 2595

STUDIES ON ESTERIFICATION OF SUGARCANE BAGASSE (SCB)

JITENDRA K. PARMAR*[1] AND DIPAK K. RAVAL[2]

[1]Government Science College, Idar
[2]Department of Chemistry, Sardar Patel University, Vallabh Vidyanagar-388 120.
Email: aanal.virat@gmail.com

ABSTRACT

The esterification of cellulose has acquired great importance due to the wide applicability of the products for various useful purposes. Esterification is a well known reactions by which polysaccharide can easily be transformed into the modified form. Sugarcane bagasse (SCB) powder was activated by alkali treatment prior to modification. The phthalate, maleate and succinate derivatives of SCB were synthesized by employing respective acid anhydride as the esterifying agent and acetic acid as the solvent. Pyridine was used as the catalyst for preparation of the ester derivatives. The effects of reaction influencing factors like concentration of acid anhydride, amount of pyridine, liquid:solid ratio and reaction period were studied. The products were characterized by determination of ester, IR-Spectroscopy and by thermogravimetry.

Keywords: Esterification, Sugarcane Bagasse (SCB), Phthalate, Maleate, Succinate.

INTRODUCTION

In recent years, there observed an increasing trend towards more efficient utilization of agro-industrial residues such as sugarcane bagasse (generally known as "bagasse"), sugar beet pulp, and coffee pulp. These lingo-cellulosic materials are abundant and renewable, and they are promising to be used as alternatives to fossil resources [1]. Nowadays chemically modified SCB is used to remove water pollutants as its adsorption capacity of metal ions from aqueous solution is excellent [2,3].

Because of the increasing need for high performance biocompatible polymers, new synthetic paths for the defined chemical modification of the polyglucan cellulose were investigated[4]. Cerqueira A. D. et al. [5] reported membrane from cellulose acetate using poly (ethylene glycol) as additive. They used SCB as a cellulosic source for the study. Xie W. et al. [6] reported the chemical modification of corn starch by using ionic liquid as the catalyst. Succinic anhydride or acetic anhydride was employed as an esterifying agent and reaction was carried out using 1-butyl-3-methylimidazolium chloride ([bmim]Cl) as the reaction medium.

Acetylation of SCB was reported using N-bromosuccinimde (NBS) as a catalyst and the resultant product was used for the production of oil sorption-active materials [7,8]. Acetylation of sugarcane bagasse hemicelluloses was also reported under mild reaction conditions by using NBS as the catalyst [9]. Cellulose and cellulignin extracted from SCB was used for the fabrication of composites reinforced with polypropylene and effect of acetylation was also studied on mechanical and thermal properties of the fabricated composites [10]. H. M. Shaikh et al. have fractionated SCB to cellulose, hemicellulose and lignin by a proprietary steam explosion process, followed by downstream purifications. They demonstrated that the residual hemicellulose need not be considered as an impurity; rather it can be used in acetylated form as a plasticizer as well as a biodegradable additive for cellulose acetates from non-wood origin [11]. SCB cellulosic phthalate was prepared using 1-butyl-3-methylinidazolium chloride ionic liquid as an ionic liquid as reaction medium [12]. Cyanoethylation of Psyllium [13], incorporation of casein in urea-formaldehyde and melamine-formaldehyde resins[14,15,16] are reported earlier from our laboratory. Recently we have reported acetylation of Sugarcane Bagasse[17]. Ferreira, B.C.S., et al. has recently reported a solvent-free procedure involving esterification of sugarcane bagasse with Meldrum's acid[18].

From the literature survey, it reveals that very little work is reported on esterification of SCB powder in its native form. We have successfully attempted various SCB esters i.e. acetate, phthalate, maleate and succinate by using SCB powder in its native form in order to get valuable products by following simple protocol. The fractionation step of SCB into cellulose, hemicelluloses and lignin was intentionally circumvented to make the derivatives in the

cost-effective manner. The SCB powder was thus directly employed without any extraction process in order to search for the user friendly process for esterification.

EXPERIMENTAL

SCB was procured from local market. Procured bagasse was washed thoroughly to remove traces of sugar and then dried in sunlight. It was cut into small pieces and was again dried in oven at 60°C for 24 hours. It was then powdered and used for the chemical modification purpose.

Activation of SCB powder

SCB powder was carefully mixed with 10% aqueous sodium hydroxide solution by controlling the temperature of the reaction flask at 15°C. The reaction mixture was stirred for 1.5 hours at 15°C then neutralized with 10% aqueous acetic acid solution. The powder was then filtered and washed with water until the filtrate became neutral. Finally it was washed with methanol and dried in oven at 60°C for three hours. This dried material was used for further modification.

Preparation of SCB phthalate

2.5 g activated SCB powder was mixed with 3.7 – 10.4 g phthalic anhydride (25 to 70 mmol) and 1- 5 mL pyridine (12.38 to 61.90 mmol) in 10 mL acetic acid. The reaction mass was thoroughly mixed and the homogeneous paste thus obtained was heated at 120°C for different time intervals (2 to 10 hours) in an oil bath. After the completion of reaction, the reaction mixture was cooled to room temperature and was discharged in 200 mL of distilled water. The mixture was then acidified with dilute hydrochloric acid to remove pyridine. This solution was subjected to high speed agitation for the precipitation of product. The solvent mixture was decanted after the product settled down. The whole procedure of precipitation was repeated until the washings became acid free. The solid product was then filtered and dried in oven at 60°C. It was powdered to approximately uniform particle size (100 mesh) through woven wire mesh sieves according to technical requirement ISO 3310-1.

Preparation of SCB maleate and succinate

The maleate and succinate derivatives of SCB were prepared by employing respective acid anhydride as the esterifying agent and acetic acid as the solvent. The synthetic procedure for the esterification by these anhydride was similar to that described above for preparation of SCB phthalate.

Determination of Extent of esterifying group

In the current study, the extent of esterification was determined by evaluation of percentage of esterifying group rather than evaluating degree of substitution. Evaluation is based upon saponification of ester with a measured excess of alcoholic sodium hydroxide solution of known concentration and then back titration of excess sodium hydroxide with standard hydrochloric acid using phenolphthalein indicator [19]. The calculation formula employed for the calculation of percentage of esterifying group of different esters is as follows:

$$\%\ Esterifying\ group = \frac{(BR - SR) \times N_{HCl} \times MW}{W}$$

Where, BR is the volume of hydrochloric acid required for blank determination, SR is the volume of hydrochloric acid required for sample determination, N_{HCl} is the normality of hydrochloric acid solution, MW is the molecular weight of esterfying group (14.9 mol for phthalyl group, 9.9 mol for maleyl group and 10.1 mol succinyl group) and W is the weight of sample (in gram).

RESULTS AND DISCUSSION

Various set of products obtained upon esterification were characterized by determination of Extent of esterifying group, thermogravimetry and infra-red (IR) spectroscopy. The experimental data comprising of the effects of reaction influencing factors are given in Table 1 to 6.

Effect of amount of esterifying agent

Tables 1 to 3 show the dependency of extent of esterification on the amount of esterifying agents in the esterification of SCB. Tables 1-3 represent the effect for phthalate, maleate and succinate derivatives respectively.

In case of succinates, the extent of esterification was found to increase with increase in esterifying agents. While in that of maleates and phthalates, it was found to decrease with increase in amount of esterifying agent. In case of succinates, the maximum esterification was observed upto 62.80% when amount of succinic anhydride was increased from 15 mmol to 60

mmol. With further increase in succinic anhydride from 60 mmol to 75 mmol, 7.76%

Table 1: Effect of amount of phthalic anhydride on formation of SCB Phthalate

Sr. No.	Sample Code	Amount of phthalic anhydride		% Phthaloyl group
		g	mmol	
1	SCBPHPA-25	3.7	25	73.99%
2	SCBPHPA-40	5.9	40	80.63%
3	SCBPHPA-55	8.1	55	63.83%
4	SCBPHPA-70	10.4	70	56.95%

[*SCB: 2.0 g; Pyridine: 2 mL; Acetic acid: 25 mL; Reaction Time: 2 hrs; Reaction Temperature: 120°C*]

decrease was observed in esterification. For phthalates and maleates, the maximum percentage esterification was found upto 80.63% and 41.28% when amount of respective anhydride was increased from 25–40 mmol and 15.29–45.89 mmol respectively. Further increase in amount of respective anhydrides from 40–70 mmol and 45.89–76.48 mmol resulted in makeable decrease in percentage of esterification from 80.63% to 56.95% for phthalation and 41.28% to 34.64% for maleation. Any increase in the percentage esterification with increasing the anhydride group is obvious in the sense that esterification, an equilibrium process, can be shifted more towards the ester formation by using an excess of reagent. The enhanced availability of the anhydride molecules in the immediate environment of the SCB molecules, which are kept in the fixed concentration throughout the series, may be considered responsible for the increments. All the three esters attained a maximum level for extent of esterification within the concentration range of anhydrides under question. The leveling-off was observed at 80.63%, 41.28% and 62.80% respectively for phthalate, maleate and succinate. This is evident from Table 1 to Table 3. About 1.67 and 7.76 times increase in maleic anhydride and succinic anhydride (i.e. from 45.89 to 76.48 mmol and 60 to 75 mmol respectively) affects the percent esterification value to an extent of only 6.64% and 7.76%. The saturation in the degree of reaction may be ascribed to the reversibility of the reaction which is not driven only in the forward direction due to the formation of water in the product mixture. The dominance of the reverse reaction, acid catalyzed hydrolysis of ester, may be considered responsible for the abnormal development observed for phthalates and maleates beyond 40 mmol and 45.89 mmol of corresponding anhydrides respectively (Tables 1-3).

Table 2: Effect of amount of maleic anhydride on formation of SCB Maleate

Sr. No.	Sample Code	Amount of maleic anhydride		% Maleic group
		g	mmol	
1	SCBMAMA-1.5	1.5	15.29	37.77%
2	SCBMAMA-3.0	3.0	30.59	37.11%
3	SCBMAMA-4.5	4.5	45.89	41.28%
4	SCBMAMA-6.0	6.0	61.19	35.95%
5	SCBMAMA-7.5	7.5	76.48	34.64%

[*SCB: 2.0 g; Pyridine: 2 mL; Acetic acid: 25 mL; Reaction Time: 4 hrs; Reaction Temperature: 120°C*]

Table 3: Effect of amount of succinic anhydride on on formation of SCB Succinate

Sr. No.	Sample Code	Amount of succinic anhydride		% Succinoyl group
		g	mmol	
1	SCBSASA-15	1.5	15	31.12%
2	SCBSASA-30	3.0	30	37.91%
3	SCBSASA-45	4.5	45	58.32%
4	SCBSASA-60	6.0	60	62.80%
5	SCBSASA-75	7.5	75	55.04%

[*SCB: 2.0 g; Pyridine: 2 mL; Acetic acid: 25 mL; Reaction Time: 4 hrs; Reaction Temperature: 120°C*]

Effect of amount of Pyridine concentration

The effect of the concentration of pyridine as a catalyst on percentage esterification of various esters is depicted in Tables 4 to 6 respectively for phthalate, maleate and succinate. The retarding effect of pyridine was observed in phthalate and maleate esters. A fivefold increase in pyridine concentration brought about ~1.3 times decrease in esterification values in case of maleate. While 2.5 times increase in pyridine concentration brought about ~1.5 times decrease in that of phthalate. A decrease in the amount of anhydride actually available for the reaction enhances the difference between the moles of anhydride taken and used-up for the purpose. This results into lowering ratio of moles of

anhydride bound to the substrate to the moles of anhydride initially taken into the reaction mixture.

The above results may be viewed as enhanced intermolecular interaction between pyridine and anhydride molecules upon increasing pyridine concentration. The acylpyridinium cation is in equilibrium with the pyridine to anhydride complex ratio. More the concentration of the pyridine more will be the complex formation and more will be the active concentration of acylpyridinium cation.

Table 4: Effect of amount of pyridine on formation of SCB Phthalate

Sr. No.	Sample Code	Amount of pyridine		Phthalic anhydride: pyridine mole ratio	% Phthaloyl group
		mL	mmol		
1	SCBPHPy-1	1	12.38	3.23	71.49%
2	SCBPHPy-2	2	24.76	1.62	80.63%
3	SCBPHPy-3	3	37.14	1.08	74.48%
4	SCBPHPy-4	4	49.52	0.81	61.94%
5	SCBPHPy-5	5	61.90	0.65	52.17%

[*SCB: 2.0 g; Amount of phthalic anhydride: 5.9 g (40 mmol); Acetic acid: 25 mL; Reaction Time: 2 hrs; Reaction Temperature: 120°C*]

However, in phthalic anhydride and maleic anhydride, the presence of π-bond in conjugation with partial positive charge on carbonyl carbon of the cation may be considered responsible for the decreased reactivity towards the esterification. The higher electron density of the π-cloud will be attracted towards the carbonyl carbon, and thereby neutralizing the positive charge on it in part.

In maleic anhydride, the effect is observed to be more pronounced. This may be due to the additional repelling force exerted by carboxylate anion on the π-cloud which results into more shifting of π-electrons towards carbonyl dipole. The retarding effect may also be viewed as the consumption of acylpyridinium ions by the increased number of pyridine molecules in the medium to form similar ions through acyl shift. Thus the setting up of an equilibrium process, between pyridine and acylpyridinium ion, lower the chances for availability of such active cations for the desired purpose.

The succinate esters (Table 6) are observed to be increased in the extent of esterification value with increase in pyridine within the concentration range studied.

With increase in pyridine concentration from 12.38 mmol to 61.90 mmol, the value of percent esterification increases from 58.85% to 72.29%. i.e. with 5 times increase in the concentration of pyridine, the increase in percent esterification value of about ~1.2 times is observed.

Effect of liquid:solid ratio

Table 7, 8 and 9 depict the effect of liquid:solid

Table 5: Effect of amount of pyridine on formation of SCB Maleate

Sr. No.	Sample Code	Amount of pyridine		Maleic anhydride: pyridine mole ratio	% Maleic group
		mL	mmol		
1	SCBMAPy-1	1	12.38	3.71	45.59%
2	SCBMAPy-2	2	24.76	1.85	41.28%
3	SCBMAPy-3	3	37.14	1.24	37.51%
4	SCBMAPy-4	4	49.52	0.93	36.17%
5	SCBMAPy-5	5	61.90	0.74	35.12%

[*SCB: 2.0 g; Amount of maleic anhydride: 4.5 g (45.89 mmol); Acetic acid: 25 mL; Reaction Time: 4 hrs; Reaction Temperature: 120°C*]

Table 6: Effect of amount of pyridine on formation of SCB Succinate

Sr. No.	Sample Code	Amount of pyridine		Succinic Anhydride :pyridine mole ratio	% Succinoyl group
		mL	mmol		
1	SCBSAPy-1	1	12.38	4.85	58.85%
2	SCBSAPy-2	2	24.76	2.42	62.80%
3	SCBSAPy-3	3	37.14	1.62	66.19%
4	SCBSAPy-4	4	49.52	1.21	66.87%
5	SCBSAPy-5	5	61.90	0.97	72.29%

[*SCB: 2.0 g; Amount of succinic anhydride: 6.0 g (60 mmol); Acetic acid: 25 mL; Reaction Time: 4 hrs; Reaction Temperature: 120°C*]

ratio on the extent of phthalate, maleate and succinate formation respectively. The results for phthalate ester formation as furnished in Table 7 shows an initial increase followed by a rapid decrease in the extent of ester formation values with increase in the liquid:solid ratio. A maximum value of 80.63% is achieved at the ratio of 3.42. Then after nearly ~1.4 times increase in the liquid content decreases the percent values to 44.69 %. i.e. 1.8 times lower percent esterification is observed. In case of

succinates, a similar trend is observed. A maximum value of 72.29% is found at the ratio of 3.75. Further increase in liquid content to about ~1.5 times, ~3.4 times decrease in percent esterification is observed. This trend could be explained on the ground of the magnitude of the association of the reagents with cellulose molecules and their collision probability. At low values of the liquid:solid ratio, these parameters are more pronounced. An increase in the liquid content of the reaction mass decreases the chances of collision between reagent molecules and cellulose molecules. However, lower extent of esterification obtained at extreme lower ratios in each case may be due to the trapping of the reagent molecules within the cellulose matrix below the optimum level of the reaction medium required for the maximum collisions between the reagent and substrate molecules. The optimum level of liquid:solid ratio were found out to be 3.42, 6.31 and 3.75 respectively for phthalate, maleate and succinate series.

Table 7: Effect of liquid:solid ratio on formation of SCB Phthalate

Sr. No.	Sample Code	Amount of acetic acid		Liquid: solid ratio	% Phthaloyl group
		mL	mmol		
1	SCBPHAC-20	20	338.98	2.78	69.63%
2	SCBPHAC-25	25	423.73	3.42	80.63%
3	SCBPHAC-30	30	508.47	4.05	63.22%
4	SCBPHAC-35	35	593.22	4.68	44.69%

[*SCB: 2.0 g; Amount of phthalic anhydride: 5.9 g (40 mmol); Pyiridine: 2 mL; Reaction Time: 2 hrs; Reaction Temperature: 120°C*]

Table 9 represents the similar result for the formation of succinate derivatives. The astonishing behavior is marked for the maleate formation as depicted in Table 8. It shows that with increase in amount of acetic acid from 338.98 mmol to 677.96 mmol in the reaction matrix, the extent of ester formation was also slowly found to increase within the range studied respectively for phthalate, maleate and succinate derivatives.

Tables 10-12 show the effect of reaction time on extent of esterification respectively for phthalate, maleate and succinate derivatives. The extent of values of percent esterification were found to increase with prolonging the reaction period from 2 to 10 hours for phthalylation and

Table 8: Effect of liquid:solid ratio on formation of SCB Maleate

Sr. No.	Sample Code	Amount of acetic acid		Liquid: solid ratio	% Maleic group
		mL	mmol		
1	SCBMAAC-20	20	338.98	3.23	43.90%
2	SCBMAAC-25	25	423.73	4.00	45.59%
3	SCBMAAC-30	30	508.47	4.77	53.47%
4	SCBMAAC-35	35	593.22	5.54	59.69%
5	SCBMAAC-40	40	677.96	6.31	64.51%

[*SCB: 2.0 g; Amount of maleic anhydride: 4.5 g (45.89 mmol); Pyridine: 1 mL; Reaction Time: 4 hrs; Reaction Temperature: 120°C*]

Table 9: Effect of liquid:solid ratio on formation of SCB Succinate

Sr. No.	Sample Code	Amount of acetic acid		Liquid: solid ratio	% Succinoyl group
		mL	mmol		
1	SCBSAAC-20	20	338.98	3.13	55.29%
2	SCBSAAC-25	25	423.73	3.75	72.29%
3	SCBSAAC-30	30	508.47	4.38	24.44%
4	SCBSAAC-35	35	593.22	5.00	22.36%
5	SCBSAAC-40	40	677.96	5.63	21.50%

[*SCB: 2.0 g; Amount of succinic anhydride: 6.0 g (60 mmol); Pyridine: 5 mL; Reaction Time: 4 hrs; Reaction Temperature: 120°C*]

succinylation while 2 to 8 hours for maleation. In case of maleate and phthalate derivatives, the extent of esterification was found to decrease up to ~1.5 and ~1.7 times with increasing the reaction time from 4 to 8 hours for maleate and 4 to 10 hours for succinates. While in case of phthalate, with increase in reaction time from 2 to 10 hours, it was found to decrease in extent of esterification in the linear pattern from 80.63% to 45.02%.

Table 10: Effect of Reaction Time on formation of SCB Phthalate

Sr. No.	Sample Code	Reaction Time (hrs)	% Phthaloyl group
1	SCBPHRT-2	2	80.63%
2	SCBPHRT-4	4	68.62%
3	SCBPHRT-6	6	55.23%
4	SCBPHRT-8	8	49.74%
5	SCBPHRT-10	10	45.02%

[*SCB: 2.0 g; Amount of phthalic anhydride: 5.9 g (40 mmol); Pyiridine: 2 mL; Acetic acid: 25 mL; Reaction Temperature: 120°C*]

It can be concluded, from the time variation study, that a maximum level of esterification of SCB was reached by continuing the reaction for

Table 11: Effect of Reaction Time on formation of SCB Maleate

Sr. No.	Sample Code	Reaction Time (hrs)	% Maleic group
1	SCBMART-2	2	39.44%
2	SCBMART-4	4	64.51%
3	SCBMART-6	6	58.20%
4	SCBMART-7	7	49.08%
5	SCBMART-8	8	43.44%

[*SCB: 2.0 g; Amount of maleic anhydride: 4.5 g (45.89 mmol); Acetic acid: 40 mL; Pyridine: 1 mL; Reaction Temperature: 120°C*]

Table 12: Effect of Reaction Time on formation of SCB Succinate

Sr. No.	Sample Code	Reaction Time (hrs)	% Succinoyl group
1	SCBSART-2	2	36.19%
2	SCBSART-4	4	72.29%
3	SCBSART-6	6	47.18%
4	SCBSART-8	8	44.46%
5	SCBSART-10	10	41.91%

[*SCB: 2.0 g; Amount of succinic anhydride: 6.0 g (60 mmol); Acetic acid: 25 mL; Pyridine: 5 mL; Reaction Temperature: 120°C*]

the optimum time period under the set of reaction condition studied. After acquiring the optimum extent of esterification, the cellulose molecule did not undergo further electrophilic displacement with the acylpyridinium complex. Thus the leveling-off in the esterification value may be viewed as the establishment of equilibrium between the products and the reactants under the chosen set of reaction conditions. The maximum values achieved for the percent esterification after the optimum time duration of the reaction were 80.63%, 64.51% and 72.29% respectively for phthalate, maleate and succinate. The optimum time duration of the reaction was found to be 2 hours, 4 hours and 4 hours respectively for phthalate, maleate and succinate derivatives.

CHARACTERIZATION BY INFRA-RED (IR) SPECTROSCOPY

The spectral data of unmodified SCB and its derivatives are shown in the Table 13. The spectra were recorded on "PerkinElmer USA Spectrum GX" spectrophotometer using KBr pellets. The most striking evidence for the presence of >C=O group [20] shows the band at 1750 – 1735 cm-1. A new band was observed in each derivative at this region of IR spectrum. It was observed at 1722, 1735 & 1734 respectively for phthalate, maleate and succinate derivatives. Table 13 represents IR characteristics vibrations for unmodified SCB, SCB phthalate, SCB maleate and SCB succinate respectively. The band observed in the range of 1605–1638 cm-1 corresponds to the bending mode of the absorbed water [21,22,23,24] and is found in all the cases. The O–H bending vibration of the hydroxyl in plane deformation is characterized by the band at about 1380 cm-1. A series of peaks in all the spectra over the range 3750–3000 cm-1 may be considered as a broad band due to –OH absorption. In all the spectra, the band observed at about 1160 cm-1 may be assigned to the C–O–C asymmetrical stretching in the glucopyranose ring of cellulose [23]. The band observed at around 1050 cm-1 may be due to C–O stretching in C–O–C linkages. The sharp band at 897 cm-1 is originated from the β-glucosidic linkages between the sugar units [21].

Table 13: Main features observed from IR studies for the prepared esters of SCB

Unmodified SCB cm^{-1}	SCB Phthalate cm^{-1}	SCB Maleate cm^{-1}	SCB Succinate cm^{-1}
3425	3428	3424	3428
2920	2900	2924	2922
---	---	---	1784
---	1722	1735	1734
1638	1609	1631	1605
---	---	1401	1420
1377	1375	1377	1372
1163	1163	1165	1163
1060	1061	1057	1056
897	894	898	917

The strong and broad band extending from 1200-950 cm^{-1} consisting of several close bands which are typical of all cellulosic fibers has been found to change to a relatively transparent region and having only a few individual weaker bands [25].

CHARACTERIZATION BY THERMO-GRAVIMETRIC ANALYSIS (TGA)

Thermal behavior of prepared ester derivatives of SCB with different substitutions was studied.

PerkinElmer model Pyris 1 Thermo-gravimetric analyzer was employed to study the thermal behavior of prepared derivatives of SCB. The thermobalance consists of furnace, sample holder, glass enclosure and recording balance mechanism. The samples were powdered to the same average mesh size and dried carefully in vacuum desiccator. 10 mg of exact weight of sample was taken for each Thermo Gravimetric Analysis (TGA). Tables 14 to 16 show thermal behavior of prepared derivatives.

Table 14: Thermal parameters of SCB phthalate.

Sample code	Unmodified	SCBPH Py-5	SCBPH PA-55	SCBPH PA-40
% Substitution	-	52.17	63.83	80.63
Ti °C	162	210	213	219
T_{10} °C	223	253	255	261
T_{50} °C	298	328	327	329
T_{max} °C	303	322	321	327
IPDT °C	441.52	574.84	593.06	584.91
E kJmol^{-1}	65.67	34.76	39.28	49.13
% Char	19.83	29.2	20.74	22.86

Ti, initial decomposition temperature, was found to increase from 162°C (for native SCB) to 219°C, 178°C and 228°C respectively for phthalate, maleate and succinate i.e. the values of Ti was found to increase with the maximum possible substitution of esterifying group. The observed increase in the thermal stability may be due to the reduced reactivity of the hydroxyl group by its esterification [26].

T_{10} values observed for the derivatives were found to increase as compared to native SCB. This indicates that modification retards the rate of thermal degradation up to first 10% weight loss. T_{50} values for the prepared derivatives were found to be improved. T_{max} values observed for the different derivatives were found to increase as compared to the native SCB. IPDT values have been greatly influenced by modification of bagasses. For the prepared derivatives, it was observed almost 50°C to 150°C higher as compared to native SCB (i.e. 441°C). Activation energy values were found to decrease for all the derivatives covered under the thermal study as compared to native SCB.

Table 15: Thermal parameters of SCB maleate

Sample code	Unmodi-fied	SCBMA MA-7.5	SCBMA AC-30	SCBMA AC-40
% Substi-tution	-	34.64	53.47	64.51
Ti °C	162	178.32	172.13	164.33
T_{10} °C	222.89	237.79	238.89	235.07
T_{50} °C	297.93	334.58	334.62	319.05
T_{max} °C	303.18	312	321	311
IPDT °C	441.52	579.43	570.51	558.78
E kJmol^{-1}	65.67	34.33	31.38	28.19
% Char	19.9	15.8	31.7	12.76

Table 16: Thermal parameters of SCB succinate.

Sample code	Unmodi-fied	SCBSA AC-30	SCBSA SA-45	SCBSA Py-4
% Substitution	-	24.44	58.32	66.87
Ti °C	162	221.31	224.39	227.55
T_{10} °C	222.89	264.92	269.89	257.93
T_{50} °C	297.93	334.41	406.02	363.18
T_{max} °C	303.18	329	333	330
IPDT °C	441.52	590.8	581.51	561.82
E kJmol^{-1}	65.67	45.36	32.49	27.82
% Char	19.9	29.38	38.57	36.11

CONCLUSION

Treatment of Sugarcane Bagasse with alkali leads to remove lignin. This modification provided a very good method for esterification. Further, all the esterification processes were studied by varying amount of esterifying agents, pyridine concentration, liquid to solid ratio in reaction mixture and reaction time. By this, optimum reaction condition was found out which may help for further study in all aspect of science. Further, the cost and time is also reduced by direct use of Sugarcane Bagasse for the modification. So far as the industrial processes are concerned, we have just initiated a small step for modification of Sugarcane Bagasse without any need of extraction process.

AKNOWLEDGEMENTS

The authors are thankful to University Grants Commission, Government of India, New Delhi for the UGC-CEAP Research Fellowship to Jitendra Parmar.

REFERENCES

[1] Rowell, R. M., Keany, F. M. (1991) Fiberboards made from acetylated bagasse fiber. *Wood Fiber Sci.*, **23:** 15-22.

[2] Salwa, A. A., El-Roudi, A. M. and Alaa A. A. S. (2015) Removal of Mn(II) from Ground Water by Solid Wastes of Sugar Industry. Journal of Environmental Science and Technology, 8: 338-351.

[3] Gurgel, L. V. A., et al (2012) Application of succinylated sugarcane bagasse as adsorbent to remove methylene blue and gentian violet from aqueous solutions e Kinetic and equilibrium studies. Dyes and Pigments, 92: 967-974.

[4] Liebert, T. F. and Heinze T. (2005) Tailored Cellulose Esters: Synthesis and Structure Determination. Biomacromolecules, 6: 333-340.

[5] Cerqueira, A. D., Filho, R. G., De Assuncao, R. M. N., Da Silva, M. C., Toledo, C. L., Zeni, M., Mello, K. and Duarte, J. (2008) Characterization of cellulose triacetate membranes, produced from sugarcane bagasse, using PEG 600 as additive; Polym. Bull. 60: 397-404.

[6] Xie, W., Shao, L. and Liu, Y. (2010) Synthesis of starch esters in ionic liquids. J. Appl. Polym. Sci. 116: 218-24.

[7] Sun, X.F, Sun, R.C, Sun, J.X. (2004) Acetylation of sugarcane bagasse using NBS as a catalyst under mild reaction conditions for the production of oil sorption-active materials. Bioresource Technology, 95: 343–350.

[8] Sun, X.F, Sun, R.C, Sun, J.X. (2003) A convenient acetylation of sugarcane bagasse using NBS as a catalyst for the preparation of oil sorption-active materials. Journal of Materials Science, 38: 3915-3923.

[9] Sun, X.F, Sun, R.C, Zhao, L and Sun, J.X. (2004) Acetylation of sugarcane bagasse hemicelluloses under mild reaction conditions by using NBS as a catalyst. J Appl Polym Sci, 92: 53–61.

[10] Luz, S. M., Del Tio, J., Rocha, G. J. M., Gonçalves, A.R. and Del'Arco Jr., A. P. (2008) Cellulose and cellulignin from sugarcane bagasse reinforced polypropylene composites: Effect of acetylation on mechanical and thermal properties. Composites Part A: Applied Science and Manufacturing, 39: 1362-1369.

[11] Shaikh, H. M., Pandare, K. V., Nair, G. and Varma, A. J. (2009) Utilization of sugarcane bagasse cellulose for producing cellulose acetates: Novel use of residual hemicellulose as plasticizer. Carbohydrate Polymers, 76: 23–29.

[12] Liu, C. F., Sun, R. C., Zhang, A. P. and Ren, J. L. (2007) Preparation of sugarcane bagasse cellulosic phthalate using an ionic liquid as reaction medium. Carbohydrate Polymers, 68: 17–25.

[13] Raval, D. K., Parmar, J. K., Patel, J. P. and Prajapati, M. R. (2009) Studies on cyanoethylation of Plantago Ovata Seed Husks(Psyllium). PRAJNA-Jour. Pure & Appl. Sci., 17: 094-098.

[14] Raval, D. K., Narola, B. N. and Patel, A. J. (2005) Preparation, Characterization and composites form low formaldehyde emission urea-formaldehyde-casein copolymer J Appl Polym Sci, 98: 531.

[15] Raval, D. K., Patel, A. J. and Narola, B. N. (2005) Synthesis, Characterization & composites from resorcinol-urea-formaldehyde-casein resin Iran Polym J, 14: 775.

[16] Raval, D. K., Patel, A. J. and Narola, B. N. (2006) A study on composites from casein modified melamine-formaldehyde resin Polym Plast Technol Eng, 45: 293.

[17] Vyas, S.K., Parmar, J.K. and Raval, D.K. (2010) A study on composites from phenol-formaldehyde -casein resin, J.Appl.Polym.Sci., 115:2838–2846.

[18] Raval, D. K., and Parmar, J. K. (2016) A study on acetylation of Sugarcane Bagasse(SCB), International Journal of Scientific Development and Research (IJSDR), 1: 209-217.

[19] Ferreira, B. C. S., Teodoro, F. S., Mageste, A. B., Gil, L. F., Freitas, R. P. and Gurgel, L. V. A. (2015) Application of a new carboxylate-functionalized sugarcane bagassefor adsorptive removal of crystal violet from aqueous solution:Kinetic, equilibrium and thermodynamic studies. Ind. Crops Prod., 65: 521-534.

[20] Critchfield F. E. (1963) "International Series of Monographs on Analytical Chemistry", vol 8, Pergamon Press, p.141.

[21] Ehrhardt, A., Bui, H. M., Duelli, H. and Bechtold, T. (2010) NaOH/urea aqueous solutions improving properties of regenerated-cellulosic fabrics. J. Appl. Polym. Sci., 115: 2865-2874.

[22] Sun, X. F., Sun, R. C. and Sun, J. X. (2003) A convenient acetylation of sugarcane bagasse using NBS as a catalyst for the preparation of oil sorption-active materials; J. Mater. Sci., 38: 3915-3923.

[23] Liu, C. F., Sun, R. C., Zhang, A. P. and Ren, J. L. (2007) Preparation of sugarcane bagasse cellulosic phthalate using an ionic liquid as reaction medium. Carbohydr. Polym., 68: 17–25.

[24] Mulinari, D. R., Voorwald, H. J. C., Cioffi, M. O. H., da Silva, M. L. C. P. and Luz, S. M.

(2009) Preparation and properties of HDPE/sugarcane bagasse cellulose composites obtained for thermokinetic mixer. Carbohydr. Polym., 75: 317-321.

[25] Sun, R. C., Sun, X. F. and Tomkinson, J. (2004a) Hemicelluloses and their derivatives; ACS Symposium Series 864: 2–22.

[26] Kruger, L. M. and Rutenberg, M. W. (1967) "Starch Chemistry and Technology", vol. 2, Academic Press, New York, p.369.

[27] Desai, D. H., Patel, C. K. and Patel, R. D. (1976) Thermal Properties of Amylose and Its Derivatives. Part I; Starch 28: 377-381.