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The Effect of Extraction and Prehydrolysis on the Thermoplasticity and Thermal Stability of Chemically Modified Rice Straw

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ABSTRACT

Rice straw after exraction with organic solvents was subjected to benzylation and acetylation reactions. Products of mentioned reactions were characterized by their FTIR and ^{1}H NMR spectra. Thermal stability of products were evaluated by TGA thermograms and it was observed that the thermal stability of products was higher than that of starting materials. Thermoplastic behaviour of products was characterized by TMA thermograms and it was observed that the thermoplasticity of products was higher than that of starting materials. As a second pretreatment, rice straw was hydrolyzed. Then it was subjected to benzylation and acetylation reactions. FTIR and ^{1}H NMR spectra of products were recorded. TGA and TMA thermograms of products show that they have higher thermal stability and thermplasticity in comparrison with starting materials.

Key Words:
lignocellulosic resources;
benzylation;
acetylation;
rice straw;
delignification;
extraction;
prehydrolysis.

INTRODUCTION

Lignocellulosic resources are useful renewable materials, produced by plants in large quantities throughout the world. Wood and straw of annual plants such as wheat and rice are lignocellulosic materials composed mainly of cellulose while lignin and hemicelluloses are also in substantial amounts.

From mechanical and processing point of view, wood and other lignocellulosic materials differ from the three main material categories, i.e., metals, plastics and glass. These

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materials can be shaped mostly via melt processing which in some cases involve high temperatures, whereas lignocellulosic materials can not be softened or melted. However it is possible by chemical modification, for example, reacting with an alkylating or acylating agent, convert these substances into processable thermoplastic materials.

Although cellulose is a linear biopolymer, it tends to act as a thermoset due to its frequent and strong interchain hydrogen bonds in the crystalline regions. The crystalline melting point of the cellulose is higher than its decomposition temperature, as a result lignucellulosics are decomposed upon heating. However, if the interchain H-bonds are disrupted by the introduction of nonpolar side chains, lignucellulosics can be transformed into processable materials (internal plasticization). Thus provides an opportunity to take advantage of the lignucellulosic wastes by transforming these raw materials into new and useful products.

Chemical modification of wood and other lignocellulosic resources can be defined as a chemical reaction between one of its components and a chemical reagent, leading to the formation of a covalent bond between these two components [1].

In an attempt to bestow thermoplasticity into wood, Shiraishi et al. [2-4] have introduced large substituent groups, such as higher fatty acids into cellulose in non-aqueous conditions (N_2O_4-dimethylformamide). Also, etherification of wood has been carried out by reacting with benzyl chloride and the product has shown good plasticity but poor mechanical properties[5]. Thiebaud group has done solvent-free esterification of wood by fatty acids [6-7].

All of these researches have been conducted on wood residues with no attempt on modification of other lignucellulosic resources. Also the benzylation and acetylation of poplar and beech woods were carried out by the author of this article [8-9]. In this work rice straw was selected as a lignocellulosic raw material to study the effect of extraction and prehydrolysis on its thermoplasticity and thermal stability when chemically modified. Extracted and prehydrolyzed samples of rice straw were subjected to benzylation and acetylation reactions. Thermal stability and thermoplasticity of benzylated and acetylated derivatives were characterized by TGA and TMA analysis methods, respectively. ^{1}H NMR and FTIR spectra of products were also recorded.

EXPERIMENTAL

Materials

Rice straw was used after drying and milling. Benzyl chloride, methanol, acetic acid, acetic anhydride, sulfuric acid, and toluene all were purchased from Merck.

Measurements

FTIR Spectra were recorded on a Shimadzu FTIR-4300 (Tokyo, Japan) as KBr disks. ^{1}H NMR Spectrum was recorded on a Brucker AC-80. Chloroform-d_1 and TMS were used as a solvent and an internal standard, respectively. TMA and TGA thermograms were recorded on a V5.1A Dupont 2000 thermomechanical analyzer. Samples with dimensions of 3×5×5 mm were fabricated by pressing and used for TMA analysis. The temperature increment was 5°C/min and temperature ranges for TMA and TGA, were 20-250°C and 20-700°C, respectively.

REACTIONS

Before modifying reaction , rice straw was subjected to two pretreatments: Extraction and prehydrolysis. After these pretreatments principal reactions, that are, delignification, benzylation and acetylation were carried out.

Extraction of Rice Straw Flour

35 g oven-dried rice straw flour was placed in a 500 mL soxhelet apparatus and extracted with mixture of 350 mL benzene and 350 mL ethanol. After 3 days extraction rice straw was dried and weighted. Loss due to extraction was 8%.

Benzylation of Extracted Rice Straw Flour (Procedure A1).
20 g dried extracted rice straw (ERS) flour was placed in a 1000 mL round-bottomed flask together with 140 mL benzylchloride and 140 mL NaOH solution 40% by weight. The flask was equipped with a condenser and magnetic stirrer and the contents refluxed for 9 h. After this period, the liquor was decanted and solid mass was refluxed twice with methanol (for the removing of unreacted benzyl chloride). The product was washed with hot and cold water successively and then dried at 55°C. As a result, 29.2 g extracted benzylated rice straw (EBRS) was obtained.

Acetylation of Extracted Rice Straw Flour (Procedure A2)
5 g dried ERS flour was placed in a 250 mL Erlenmeyer

flask together with 25 mL glacial acetic acid. The flask was equipped with magnetic stirrer and was placed in a water bath at 50-55°C for 30 min. After this period a mixture of 16 mL acetic anhydride and 0.5 mL concentrated sulfuric acid was added to flask, and the mixture was stirred for 1.5 h at 55°C. After this step, the liquor was decanted and acetylated product was washed several times with water and was stabilized through boiling in 100 mL H_2SO_4 solution 0.01% by weight [10]. The stabilized product was dried in oven at 60°C. As a result, 5.8 g Extracted acetylated rice straw (EARS) was obtained.

Delignification of Extracted Rice Straw Flour with Ethylene Glycol (Procedure A3)

30 g dried extracted rice straw flour was placed in a 1000 mL round-bottomed flask together with 300 mL ethylene glycol and 6 mL NaOH solution 40% by weight. The flask was equipped with condenser and magnetic stirrer and the content was refluxed for 2 h. The temperature during the refluxe was about 150-160°C. After refluxing the extracted delignified rice straw (EDRS) was washed several times with water and was dried. Loss due to delignification was 39%.

Benzylation of EDRS

12 g Dried EDRS was benzylated according to procedure A1 and after purification and drying 16.4 g extracted delignified benzylated rice straw (EDBRS) was obtained.

Acetylation of EDRS

3 g Dried EDRS was acetylated according to procedure A2 and 4 g extracted delignified acetylated rice straw (EDARS) was obtained.

Acetylation of EBRS

10 g Dried EBRS was acetylated according to procedure A2 and 7.7 g extracted benzylated acetylated rice straw (EBARS) was obtained.

Acetylation of EDBRS

6 g of EDBRS was acetylated through procedure A2 and after purification and drying 5.4 g extracted delignified benzylated acetylated rice straw (EDBARS) was obtained.

Prehydrolysis of Rice Straw Flour

100 g oven-dried rice straw flour was placed in a 2L Erlenmeyer flask with sufficient distilled water and was boiled for 2 h. After this period the water decanted and again sufficient distilled water was added and boiled for another 2 h. Weight loss due to prehydrolysis was 20.5%.

Benzylation of Prehydrolyzed Rice Straw

20 g Dried prehydrolyzed rice straw (PRS) flour was benzylated according to procedure A1 and after purification and drying 32.9 g prehydrolyzed benzylated rice straw (PBRS) was obtained.

Acetylation of Prehydrolyzed Rice Straw

5 g Dried PRS flour was acetylated according to procedure A2 and 6.5 g prehydrolyzed acetylated rice straw (PARS) was obtained.

Delignification of Prehydrolyzed Rice Straw

30 g Dried PRS flour was delignified according to procedure A3 and after purification and drying 17.1 g prehydrolyzed delignified rice straw (PDRS) was obtained.

Benzylation of PDRS

10 g Dried PRS straw flour was benzylated according to procedure A1 and after purification and drying 23.4 g prehydrolyzed delignified benzylated rice straw (PDBRS) was obtained.

Acetylation of PDRS

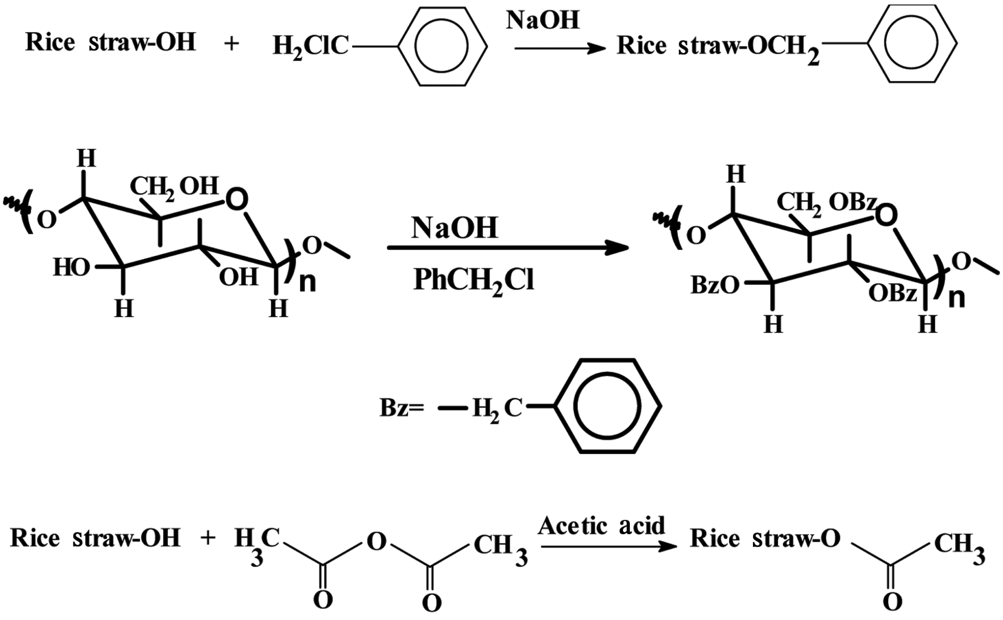
3 g Dried PDRS flour was acetylated according to procedure A2 and 6.4 g prehydrolyzed delignified acetylated rice straw (PDARS) was obtained.

Acetylation of PDBRS

10 g of PDBRS was acetylated through procedure A2 and after purification and drying 4.2 g prehydrolyzed delignified benzylated acetylated rice straw (PDBARS) was obtained.

RESULTS AND DISCUSSION

Each lignocellulosic material usually contain four main constituents: cellulose, lignin, hemicelluloses and extractives. In pulp and paper manufacturing lignin should be removed by pulping processes. By removing lignin, cel-



Scheme I

lulose fibers are released and by forming hydrogen bonds between fibers, structure of paper is formed.

By complete removing of lignin and hemicelluloses, dissolving pulp is formed that is used for manufacturing of cellulose derivatives, such as, cellulose nitrate and cellulose acetate. Derivatization with ester and ether groups is the best method to thermoplasticization of lignocellulosic materials. In this work for derivatization of rice straw benzylation and acetylation reactions were used in which the OH groups of cellulose moiety were converted to OCH_2Ph and $OCOCH_3$ groups, respectively. By this conversion some hydrogen bonds between cellulose chains are broken and thermoplasticity is induced in the material. Scheme I shows the benzylation and acetylation reactions of rice straw and cellulose macromolecule.

Rice straw flour as a lignocellulosic resource was extracted by mixture of benzene and ethanol. The yield of extraction was 92%. Extracted rice straw (ERS) was chemically modified by benzylation and acetylation. Figures 1 and 2 show FTIR spectrum of two samples of benzylated and acetylated derivatives, respectively. The characteristic absorption of phenyl moiety of benzyl group appear at 1700-2000 cm^{-1} region for benzylated rice straw (Figure 1). FTIR Spectrum of benzylated acetylated rice straw(BARS) shows that the acetyl carbonyl group appears at 1743 cm^{-1} (Figure 2). Figures 3 and 4 show ^1H NMR spectra of two derivatives.

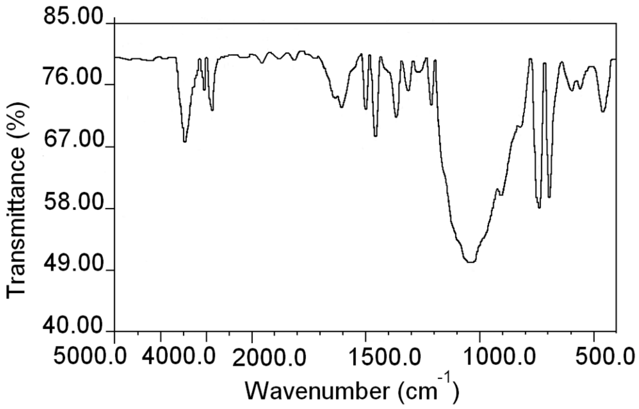


Figure 1. FTIR Spectrum of extracted benzylated rice straw.

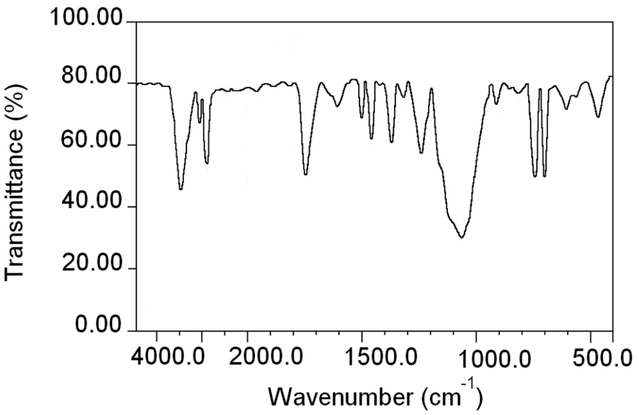


Figure 2. FTIR Spectrum of extracted benzylated acetylated rice straw.

The benzene ring protons appear at δ 7.2 ppm, glucose protons and methylene protons of the benzyl group overlap at δ 3.0-5.0 ppm (Figure 3). The methyl protons of the acetyl moeity appear at about δ 2.1 ppm (Figure 4).

Thermoplastic behaviour of the derivatives can be detected by thermal mechanical analysis (TMA). The raw rice straw, and its delignified product show no observable thermoplastic behaviour because it is softened at temperatures above 240°C. Figures 5 and 6 show TMA thermograms of acetylated and benzylated derivatives. For the evaluating of thermal stability of derivatives, TGA thermogram of samples were recorded. Figures 7 and 8 show the TGA thermograms of rice straw and its benzylated derivative, respectively. As seen by benzylation thermal stability has been increased.

Table 1 shows the results of TGA and TMA analysis of chemically modified extracted rice straw. It is found that the total thermal stability of derivatives are higher than the untreated rice straw. TGA Thermograms shows

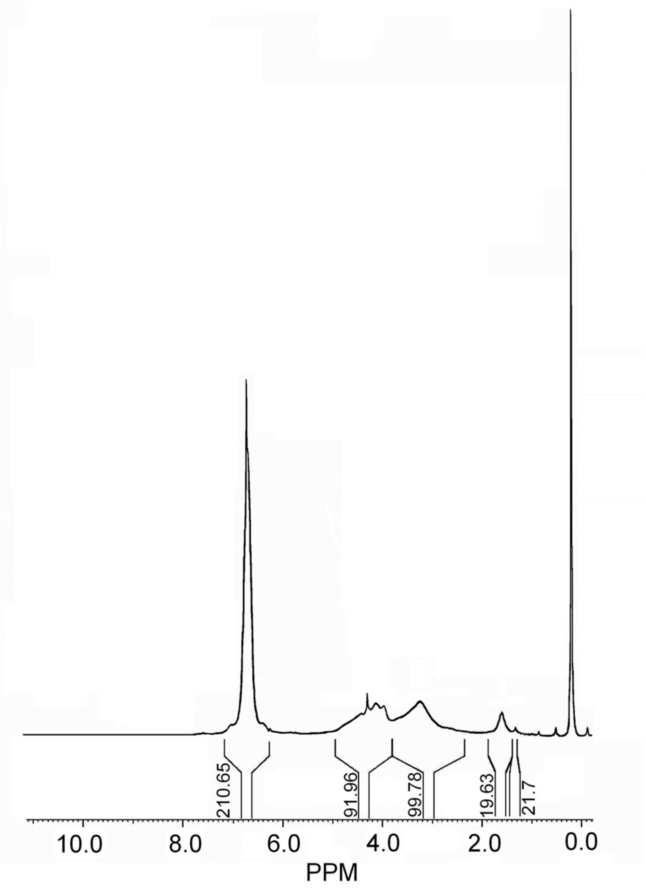


Figure 3. ^{1}H NMR Spectrum of extracted delignified benzylated rice straw.

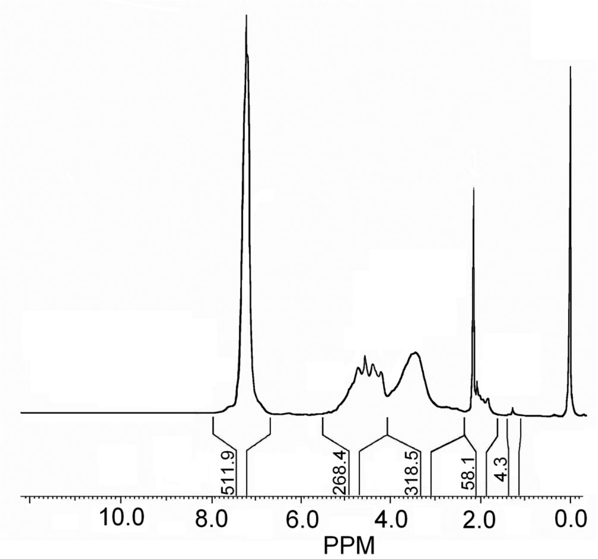


Figure 4. ^{1}H NMR Spectrum of extracted delignified benzylated acetylated rice straw.

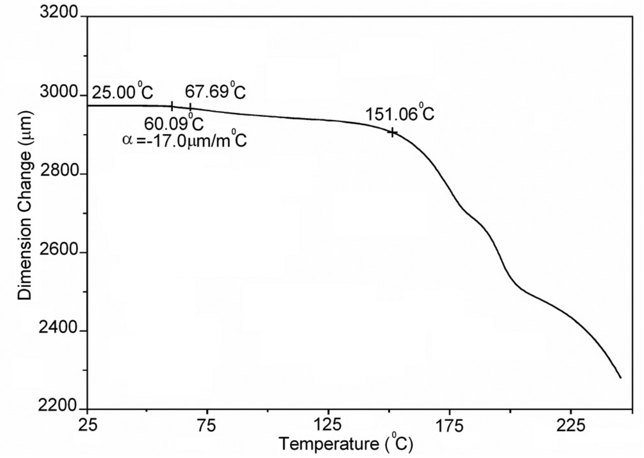


Figure 5. TMA Thermogram of prehydrolyzed delignified acetylated rice straw.

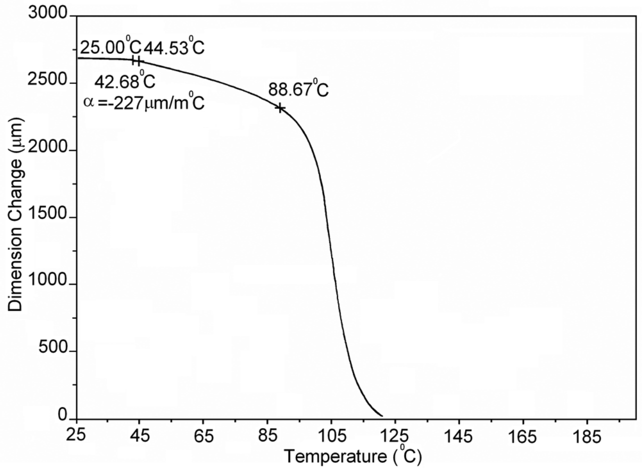


Figure 6. TMA Thermogram of prehydrolyzed delignified benzylatedacetylated rice straw.

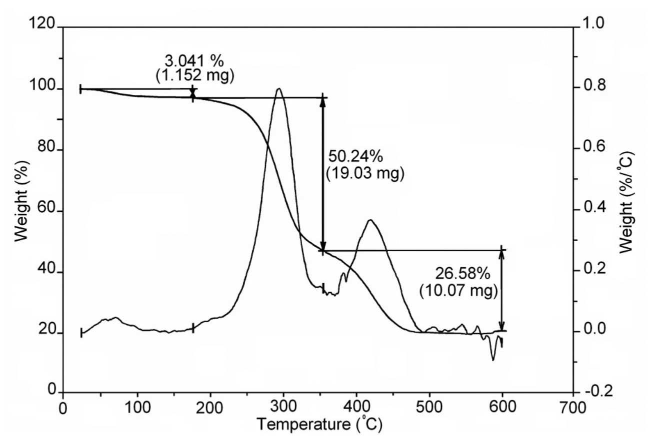


Figure 7. TGA Thermogram of rice straw.

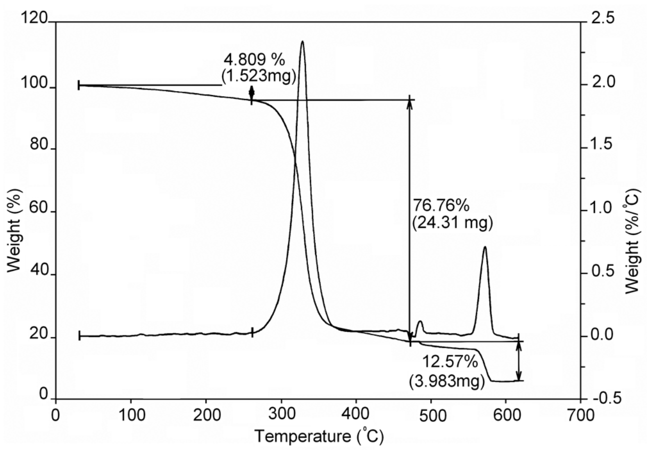


Figure 8. TGA Thermogram of benzylated rice straw.

that the beginning of weight loss of rice straw is 295^{o}C but, for benzylated and acetylated derivatives of rice straw it is 332-362^{o}C. The acetylated derivative has high thermal stability. Thermomechanical analysis is a tool for the monitoring thermoplasticity of the material. Rice straw and all native lignocellulosic resources have not any thermoplastic behaviour because of the high inter-chain hydrogen bonding between cellulose molecules. But with derivatization nearly all the hydrogen bondings among cellulose chains were broken and some thermoplasticity is induced in the material.

It is found from Table 1 that the actylation or ben-

Table 1. Results of TGA and TMA analysis of Extracted rice sraw and its derivatives.

Sample	Temperature (^{o}C) (TGA analysis)	Weight loss (%) (TGA analysis)	Softening point (^{o}C) (TMA analysis)
Rice straw	295	50.2	-
	420	27	
EBRS	346	76.8	86-200
	575	12.6	
EDBRS	330	84	97-200
	650	6.2	
EARS	362	53	71-150
	575	13.3	
EDARS	350	72	-
	570	7.6	
EBARS	356	56	59-110
	562	11	
EDBARS	332	66.8	149-200
	575	8.1	

EBRS : Extracted Benzylated Rice Straw, EDBRS: Extracted Delignified Benzylated Rice Straw, EARS: Extracted Acetylated Rice Straw, EDARS: Extracted Delignified Acetylated Rice Straw, EBARS: Extracted Benzylated Acetylated Rice Straw, EDBARS: Extracted Delignified Benzylated Acetylated Rice Straw.

Table 2. TGA and TMA results of benzylated and acetylated derivatives of prehydrolyzed rice straw.

Sample	Temperature (^oC) (TGA analysis)	Weight loss (%) (TGA analysis)	Softening point (^oC) (TMA analysis)
PRS	305	58.4	-
	412	24.5	
DRS	322	54	-
	450	25	
PDRS	325	62	-
	445	16.5	
PBRS	335	70	66-225
	565	2.8	
PARS	353	63	96-225
	565	13	
PDBRS	333	65	89-140
	568	5	
PDARS	330	59	151-250
	570	7.8	
PDBARS	196	26.3	88-120
	341	41.8	
	554	10.6	

PRS : Prehydrolyzed Rice Straw, DRS: Delignified Rice Straw, PDRS: Prehydrolyzed Delignified Rice Straw, PBRS: Prehydrolyzed Benzylated Rice Straw, PARS: Prehydrolyzed Acetylated Rice Straw, PDBRS: Prehydrolyzed Delignified Benzylated Rice Straw. PDARS: Prehydrolyzed Delignified Acetylated Rice Straw, PDBARS: Prehydrolyzed Delignified Benzylated Acetylated Rice Straw.

zylation reaction lowers the softening point but the acetylation effect is higher. Also, when extracted rice straw was doubly derivatized, i.e., first benzylated and then acetylated, the thermoplasticization is higher. This effect is probably due to the higher amorphousity of the material.

Probably during acetylation reaction because of the acidic condition some degradation occurs in the macromolecules of rice straw and the weight of the products after purification are less than that of the reactants.

In order to understanding the effect of hemicelluloses on thermoplasticity, the rice straw first hydrolyzed and approximately all of its hemicelluloses were removed. Then it was subjected to benzylation and acetylation reactions. Benzylation is an etherification reaction and Substitution of large benzyl groups leads to formation of products with higher molecular weights. The percentage of weight increase can be measured by the following equation:

$$\text{Weight gain percentage} = \frac{W - W_0}{W_0} \times 100$$

Where, W and W_0 are the weight of product and the weight of initial rice straw flour, respectively. The weight gain percentage for extracted rice straw was 46% but for prehydrolyzed rice straw it was 64% . This data shows that hemicelluloses were reacted to a lesser extent with respect to cellulose.

Table 2 shows the TGA and TMA results of benzylated and acetylated derivatives of prehydrolyzed rice straw. Also similar to extracted rice straw derivatives, the acetylated derivatives show higher thermal stability. Probably due to the conversion of high polar OH groups of cellulose chains to low polar groups of, benzyl and acetyl, via the benzylation and acetylation reactions, respectively. With increasing temperature, degradation of rice straw macromolecules are fastened in the presence of polar groups. Comparison of the TMA results of Table 1 and 2 show that the prehydrolyzed rice straw derivatives have higher softening temperatures in comparision with extracted rice straw derivatives. This is due to the fact that in prehydrolyzed rice straw the hemicelluloses were removed and thus, the hemicelluloses derivatives are absent in the material. Therefore, there is not any induced thermoplasticity relevant to hemicelluloses.

CONCLUSION

Extracted and prehydrolyzed rice straw can be benzylated by benzyl chloride and acetylated by a mixture of acetic acid and acetic anhydride, respectively. TGA Analysis of derivatives show that their thermal stabilities are higher than that of the native rice straw. Probably the low polarity of substituents in derivatives increase the thermalstability of derivatives with respect to unreacted rice straw that has polar OH groups. TMA analysis showed that all derivatives have thermoplastic behaviour and the prehydrolyzed derivatives have higher softening temperatures and therefore, lower thermoplasticity. In prehydrolyzed rice straw the hemicelluloses were removed and the induced thermoplasticity relevant to its derivatives was absent.

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