

PREPARATION AND CHARACTERIZATION OF BENZYLATED PRODUCTS FROM RICE STRAW

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In the present study, the pulping process was employed to prepare chemically modified thermoplastics from natural resources. Rice straw is a natural source and the products from this material (pulp and pulping liquor) were separated in this work. The benzylation reaction with benzyl chloride chemically modified the structure of rice straw and its pulping products (pulping liquor and pulp). The final products, except the benzylated pulp, showed thermoplastic behavior. The Fourier transform infrared (FTIR) spectroscopy, tensile and thermal properties analyses, dynamic mechanical thermal analysis (DMTA), rheological analysis, contact angle measurement and SEM were carried out to evaluate the modified rice straw. The FTIR spectra confirmed the benzylation reaction as H groups were substituted by benzyl groups. The differential scanning calorimetry (DSC) showed only a T_g and no T_m was detected for the prepared samples. The benzylated rice straw pulping liquor (BR SPL), which was the main objective of this research, showed the highest tensile strength, maximum elongation at break, maximum thermal stability, continuous morphology, minimum activation energy and the highest hydrophilicity.

Keywords: rice straw, benzylation, pulping, chemical modification, lignocellulosic resources, thermoplastic

INTRODUCTION

Lignocellulosic biomass is among the most abundant raw materials in nature. Every year, billions of tons of these materials are synthesized. Wood and several annual plants are the main sources of lignocellulosic materials.¹ The main macromolecular constituents of these materials are cellulose, lignin and hemicelluloses.^{2,3} Cellulose is highly crystalline, while hemicellulose and lignin are amorphous.⁴ Cellulose is the main macromolecular component of lignocellulose materials since cellulose forms 40% of the dry weight. The main application of cellulose is in paper making, which is obtained by pulping of wood and other lignocellulose in various ways.⁵ Although wood and some lignocellulose materials are composed of macromolecular components, they cannot be processed like synthetic macromolecules, such as

polyethylene and polypropylene. Due to the existence of inter- and intra-chain hydrogen bonding in the cellulose structure and inherent association of cellulose with other components, such as lignin and hemicellulose, lignocellulosic materials would be degraded by heat.⁶ For the extensive use of cellulose with thermoplastic polymers, some of the inter- and intra-chain hydrogen bonding between cellulose chains should be destroyed. To increase the thermoplasticity in cellulose, various substituents and different methods are used. The most important methods are esterification and etherification of cellulose.⁷ Inorganic (*e.g.* nitro cellulose) and organic ester types of cellulose (*e.g.* cellulose acetate) have been manufactured.^{7,8} Cellulose ethers (*e.g.* methyl cellulose, ethyl cellulose, *etc.*), as well as cellulose esters, were

prepared with numerous industrial applications.^{9,10} Lignin and hemicellulose, which are the major macromolecular components of wood and other lignocellulosic materials, have numerous hydroxyl groups in their backbones.¹¹ These macromolecules have been mostly used in esterification or etherification reactions without separation from each other, so the whole lignocellulosic material turned into thermoplastic. One of the efforts in this area was the benzylation of wood flour. Wood flour was benzylated by Honma *et al.* and converted into a thermoplastic material.¹² All the fiber straw composites were studied by Chen *et al.* The benzylated rice straw and the raw straw material were mixed together and the properties of the prepared composites were studied.¹³ The main components of rice straw were determined to be 40.09% cellulose, 26.8% hemicellulose, 18.9% lignin and 10.76% ash (94% silica).¹⁴ In our previous works, wood and other lignocellulosic materials were also benzylated.^{7,15,16}

In the present research, in order to achieve novel thermoplastic materials and to improve the properties of benzylated products, the whole rice straw flour and its pulp and pulping liquor were benzylated, separately. For the preparation of rice straw, pulp and pulping liquor, the rice straw was pulped by 10% NaOH solution in the atmospheric pressure. The spectral properties (FTIR-ATR spectra) of benzylated products were studied. The mechanical, thermal, rheological and morphological properties of benzylated products were evaluated by tensile, DMTA, DSC, TGA, rheometry, contact angle measurements and SEM, respectively. The main objective of this study is to obtain cost-effective natural thermoplastic fillers from natural resources. Raw rice straw and fractions, such as pulp (cellulose-rich) and pulping liquor (lignin-rich), were studied separately, and the benzylated product of pulping liquor extracted from the rice straw (BRSP) showed good improvement after benzylation. All the benzylated components, especially BRSP, proved to have the ability to be used in polymer composites and their applications can be further studied.

EXPERIMENTAL

Materials

Rice straw was supplied by a local mill (Guilan, Paresar). The particle size of the rice straw was 70-80 in mesh numbers. The rice straw flour was dried at 110 °C for 24 h in order to set the moisture content within

1-2%, and then, it was stored over desiccant in some sealed containers. All the chemicals and solvents were of reagent grade from Merck (Darmstadt, Germany).

Benzylation of whole rice straw flour

An amount of 20 g of oven dried whole rice straw flour was placed in a 500 mL round-bottomed flask together with 140 mL benzyl chloride and 140 mL 40% NaOH solution (wt%). The flask was equipped with a condenser and a mechanical stirrer and the contents were refluxed for 4 h at 110 °C. After a period of time, two phases were separated and the organic phase was washed twice, once with water and once with methanol. They were then dissolved in chloroform and precipitated in methanol. For better purification, the dissolution and precipitation were repeated and the product was dried in a vacuum oven at 110 °C for 24 h. As a result, 45 g of benzylated whole rice straw (BWRS) was obtained.

Pulping of rice straw with 10% NaOH solution

An amount of 100 g of oven dried rice straw flour was placed in a 2000 mL round-bottomed flask with 1000 mL of 10% NaOH solution (wt%). The mixture was refluxed for 1 h at 120 °C and agitated manually. Afterwards, the liquor was separated from the pulp using filters and the resulting pulp was washed with water a few times. After drying in an oven at 105 °C, 38.5 g of pulp was obtained. The liquor, which contains other components of rice straw (mainly lignin, hemicelluloses and silica), was heated up at 100 °C for 2 h in the atmospheric pressure to get to a volume of 200 mL, suitable for the benzylation reaction.

Benzylation of rice straw pulp

An amount of 20 g of oven dried rice straw pulp was placed in a 500 mL round-bottomed flask together with 140 mL of benzyl chloride and 140 mL of 40% NaOH solution. The same method as that used for benzylation of whole rice straw flour was used in this stage, and 49 g of benzylated rice straw pulp (BRSP) was obtained. Sodium hydroxide is important in this process, because a charged intermediate species is formed, which allows for faster nucleophilic addition of benzyl chloride.¹⁷

Benzylation of rice straw pulping liquor

An amount of 35 g of pulping liquor after evaporation was placed in a 500 mL round-bottomed flask together with 200 mL benzyl chloride. The flask was equipped with a condenser and a mechanical mixer and the contents were refluxed for 4 h at 110 °C. Like the previous benzylation stages, two phases separated and the organic phase was washed twice, once with water and once with methanol. Afterwards, they dissolved in chloroform and precipitated in methanol. This process was repeated a couple of times for better purification. Finally, the product was dried in a vacuum oven at 110 °C for 24 h. As a result, 70 g of

benzylated rice straw pulping liquor (BRSPL) was obtained.

Characterization

Infrared spectroscopy was performed using FTIR-ATR (Bruker, Equinox 55LS 101 series, Germany) with a resolution of 4 cm^{-1} (averaging 50 scans) for determining functional groups. Stress-strain measurements were carried out by means of a Gotech Universal AI-7000-LA (Taiwan) according to ASTM D638. The measurements were conducted at room temperature ($25\text{ }^{\circ}\text{C}$) with the cross-head speed of 5 mm/min for three test specimens of each sample. Thermogravimetric analysis (TGA) was performed using a TGA, Mettler Star SW 10.00 from room temperature to $600\text{ }^{\circ}\text{C}$, at a heating rate of $10\text{ }^{\circ}\text{C/min}$ under nitrogen atmosphere. Differential scanning calorimetry (DSC) was carried out using a Mettler Toledo (USA) DSC 1 Star system equipped with a low-temperature accessory. The temperature scale was calibrated by the high-purity standards. The DSC measurements were performed at a heating rate of $10\text{ }^{\circ}\text{C/min}$, under nitrogen atmosphere and within a temperature range from 0 to $300\text{ }^{\circ}\text{C}$. The glass transition temperatures (T_g) were obtained at the midpoint of the stepwise specific heat increment. Repeated heating scans were performed in order to verify the reproducibility of the results according to ASTM D3418. Dynamic mechanical measurements were carried out on the film samples using an Exstar SII DMS6100 (Japan) in the tensile mode using a pre-tensioning force of 0.4 N , a heating rate of $5^{\circ}/\text{min}$ and various frequencies from 2 - 10 Hz in the temperature range from $0\text{ }^{\circ}\text{C}$ up to $180\text{ }^{\circ}\text{C}$ for each sample. The exact dimensions of each sample were measured before the scan. The rheological properties of the samples were measured at $180\text{ }^{\circ}\text{C}$ using an Anton Paar Physica MCR102 (Austria) with parallel-plate geometry according to ASTM D4440-07 under air atmosphere. Dynamic experiments were performed in an oscillatory shear mode with dimensions of 25 mm (diameter) and 0.5 mm (gap). Frequency sweep tests were carried out from 0.1 to 100 rad/s . Before the rheological measurements, the strain sweep tests at various frequencies were carried out to ensure the applied strain did not exceed the limit of linear viscoelasticity. Time sweep tests were carried out to ensure the physical properties during the frequency sweep have not been changed. The hydrophilic properties have been measured through contact angle measurement using a Kruss G10 by repeating every measurement three times. The average of the measurement data was taken and reported. The SEM micrographs were obtained with KYKY-EM3200,

China, on the fracture surface of samples in liquid N_2 to observe the morphology of the fracture surfaces.

RESULTS AND DISCUSSION

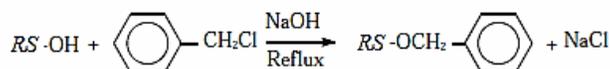
Benylation reaction

Once the benzylation reactions for whole rice straw, rice straw pulp and rice straw pulping liquor are in progress, the substitution of the OH groups in the structures by benzyl nonpolar groups occurs. The raw materials of the benzylation reaction are thermoset-like polymers because of their inter-chain hydrogen bonds. This reaction by substitution leads to thermoplasticity of the feedstock.⁶

According to the reaction shown in Scheme 1, small H atoms were replaced by large benzyl groups. It results in a weight gain after the reaction. The weight gain percent was obtained by Equation 1, where W and W_0 are the weight of the product and the weight of the initial material, respectively:

$$Wt\% = \frac{W - W_0}{W_0} \times 100 \quad (1)$$

Table 1 shows the percent of weight gain for each sample. According to the results, BRSP has the highest weight gain among the samples. This could be explained by the fact that BRSP, which mainly consists of benzylated cellulose, has a higher degree of crystallinity, compared with BWRS or BRSPL. It has to be mentioned that BWRS consists of cellulose, hemicellulose and lignin, and as it has been mentioned earlier, cellulose is crystalline, while lignin and hemicellulose are amorphous, so there is a smaller proportion of accessible OH groups for benzylation at the lower yields available. Finally, BRSPL is a completely amorphous material and, based on L. Ma's report, polysaccharides play an important role in benzylation and lignin has less priority and less contribution to the substitution.¹⁸ Moreover, according to Borysiak *et al.* and Ma, the accessible OH groups in benzylated cellulose, and hemicellulose, non-linearly decreased with an increase in the degree of substitution due to the benzyl group substitution.^{18,19}



Scheme 1: Benzylation reaction of rice straw using benzyl chloride

Table 1
Weight gain percent of BWRS, BRSPL and BRSP

Sample	BWRS	BRSPL	BRSP
Weight gain (%)	125	100	145

Table 2
Tensile properties of BWRS, BRSPL and BRSP sheets

Sample	BWRS	BRSPL	BRSP
Tensile strength (MPa)	24.92	50.69	18.66
Elongation at break (%)	3.08	19.53	1.37
Elastic modulus (GPa)	3.96	3.01	3.4

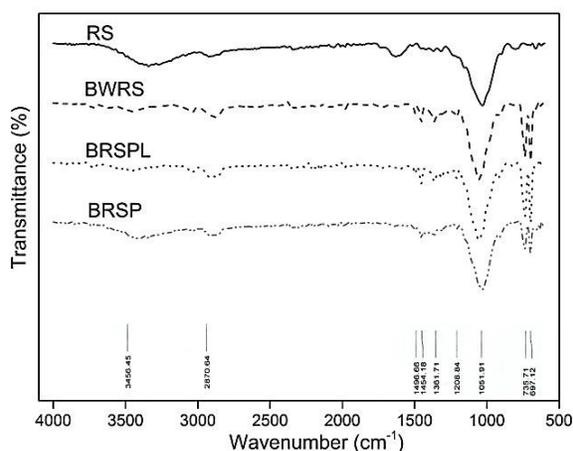


Figure 1: FTIR spectra of rice straw (RS), BWRS, BRSPL and BRSP

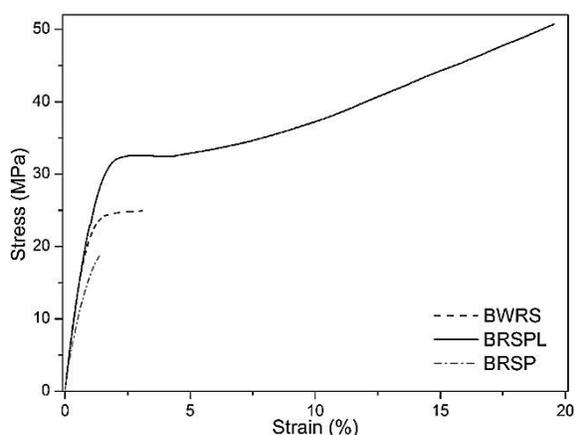


Figure 2: Stress-strain of BWRS, BRSPL and BRSP sheets

FTIR spectroscopy results

Figure 1 shows the FTIR-ATR spectra of rice straw, BWRS, BRSPL and BRSP. A reduction in the peak of OH groups (about 3450 cm^{-1}) is observed in all the benzylated samples, showing the reduction of OH groups by benzylation. The appearance of peaks at 697 cm^{-1} (aromatic C-C angular deformation), 736 cm^{-1} (aromatic C-H out-of-plane bending, mono-substitution) and 1452 cm^{-1} (aromatic C-C axial deformations) confirms the benzylation reaction and substitution of benzyl groups during the reaction. The introduction of bulky substituents interferes with the inter- and intra-molecular hydrogen bonding, resulting in a less crystalline structure or the decrystallization effect. Cellulose shows the greatest loss in crystallinity as a result of benzylation, which is in accordance with previous reports.¹⁸ The results clearly reveal the reduction of OH groups and relative cellulose crystallinity, as well as an increase in aromatic bands and benzyl groups.

Tensile properties

Tensile properties of BWRS, BRSPL and BRSP are available in Table 2. According to the results, the tensile strength of BWRS is lower than that of BRSPL. The weight gain results indicate that some of the lignin molecules are not reacted with benzyl chloride in the BRSPL sample. The amount of lignin may play the role of a paste between the benzylated molecules of lignin and hemicellulose, increasing the tensile strength, compared to that of sole systems.²⁰ Although there is some unreacted lignin in the BWRS sample, it is clear that the mass ratio of lignin in BWRS is lower than in BRSPL, because the cellulose molecules also exist. The tensile strength of BRSP is lower than that of other samples and this is due to lack of lignin in BRSP, and its chains are not completely interacted. Lignin also shows plasticization effects and the presence of this material in polymers can decrease their stiffness.^{21,22} This is observed in the elongation at break of the samples. The lignin

content in BWRS is lower than in BRSP and results in a very low elongation at break for BWRS. In the case of BRSP, lack of lignin may result in a very low elongation at break, due to the existence of more silica in BRSP.²³ As a matter of fact, the elongation at break of the samples was decreased by increasing silica content. The increase in silica content was detected by the TGA thermograms and will be discussed later. BWRS has higher elastic modulus, compared with BRSP and BRSP, which is correlated with the lower lignin content in BWRS. As discussed before, the plasticizer lignin may decrease the stiffness of chemically modified lignocellulosic materials. BRSP shows larger elastic modulus, compared to BRSP, due to the lignin plasticization effect. Between BRSP and BWRS, a lower elastic modulus for BRSP was observed. In fact, lignin drives an opposing effect and its pasting effect has a higher influence in BWRS compared to BRSP.²³ The stress-strain curves of benzylated samples are shown in Figure 2. The curves can completely confirm that BRSP has a more plastic behavior than BWRS and BRSP. The onset of necking and high tensile strength is obvious for BRSP. For BWRS and BRSP, the onset of necking disappeared, but for BWRS a high tensile strength appears, which is comparable to ductile polymers. BRSP presents a low elongation at break and can be compared to brittle polymers.²⁴

Thermal properties

TGA and DTGA thermograms

TGA and DTGA thermograms of BWRS, BRSP and BRSP are presented in Figure 3. By conducting this measurement, the onset temperature of degradation (T_i) and the final

temperature of degradation (T_f) are obtained. The DTGA curves derived from the TGA also help to find out the maximum degradation temperature (T_{max}). The TGA thermograms show high thermal stability for BRSP, as it shows higher T_i and T_{max} compared with the other samples studied here. T_i is the same for all samples, which means they completely degrade at the same temperature; however, the ash content is different. Both BRSP and BWRS show their maximum degradation temperature (T_{max}) at 351 °C, which means their peak of degradation is similar, but the degradation initiation temperature (T_i) of BWRS is higher than that of BRSP, and it degrades at higher temperatures, since it contains lignin. BWRS shows a double peak at T_{max} , which is attributed to the degradation of cellulose, lignin at 351 °C and other extractives at 334 °C. The pulping liquor has the highest lignin content amongst the samples, leading to the highest thermal stability. This may be due to the lignin's cement shape properties, making chains more stable against temperature.²⁵ The thermal degradation pattern of BWRS and BRSP are similar to those of cellulose and lignin, respectively. It is observed that the thermal degradation behavior of modified materials is similar to that of their source materials because of the existence of sources in small amounts in the modified samples. BRSP has a more similar pattern of degradation to that of cellulose as most of the BRSP content is made up by cellulose. The main component in the ash for all samples is silica^{7,15,16} and the ash content of BRSP is higher than the others. It could be referred to the larger silica content in the BRSP sample, affecting its mechanical and thermal properties.

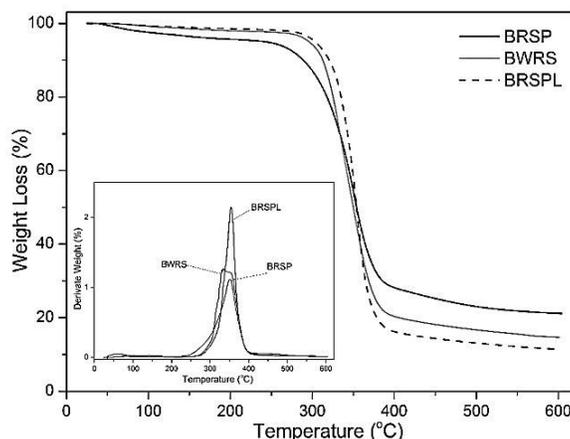


Figure 3: TGA thermograms of BWRS, BRSP and BRSP

Table 3
Important temperatures obtained from DSC and TGA tests

Sample	BWRS	BRSPL	BRSP
T_g (°C)	166	162	119
T_I (°C)	295	303	242
T_f (°C)	424	424	424
T_{max} (°C)	334,351	354	351
Ash content (%)	14.71	11.42	21.15

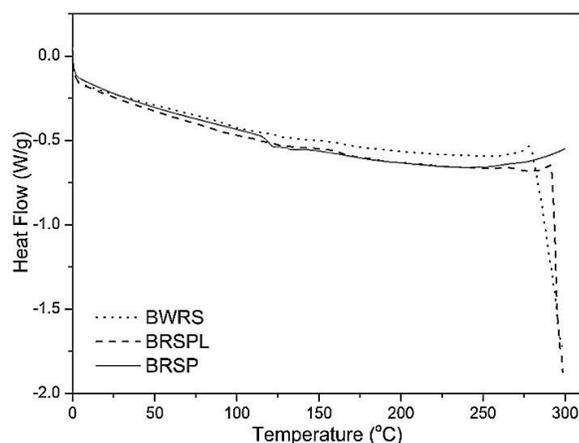


Figure 4: DSC thermograms of BWRS, BRSPL and BRSP

After the pulping process, most of the silica is in the pulp and this is always a problem for the pulp and paper process.²⁶ In the current work, the silica content has an important role and its existence not only represents no problem, but also it interestingly acts as a modifier of properties in many cases. The weight loss and degradation temperatures have been reported in Table 3.

DSC analysis

To investigate the thermal behavior of the synthesized samples, DSC analysis was carried out and the results are depicted in Figure 4. According to the DSC thermograms, the samples show only glass transition temperatures with no melting peaks. This is due to the amorphous structure of the samples, the bulkiness of the benzyl group and the inability of the cellulosic derivatives to form an ordered microstructure.¹⁶ The T_g values of the samples are reported in Table 3. It is clear that BWRS shows the highest T_g amongst the benzylated materials, probably due to its large silica content. The role of silica as filler in the samples is to reduce the polymer chains mobility.²³ On the other hand, BRSPL has a lower T_g than BWRS does due to the lignin presence, making it more plasticized than BWRS and reducing the glass transition temperature.²⁷ BRSP

shows a smaller T_g among the investigated samples. Large amounts of lignin could also increase the T_g due to the pasting effect, reducing the mobility of the polymer. The lack of this material in the sample causes their chains to move freely at lower temperatures.²³

Dynamic mechanical thermal analysis (DMTA)

The prepared samples were studied by DMTA at temperatures near to the glass transition temperature. Here, the maximum of $\tan\delta$ (ratio of storage and loss modulus) represents the T_g of the samples. The $\tan\delta$ plots for each sample are presented in Figure 5. According to the results, the glass transition temperatures (T_g) for BWRS, BRSPL and BRSP are near to the temperatures measured by the DSC at a frequency of 2Hz. Upon an increase in frequency, T_g is increased. The glass transition is a kinetic transition, which is strongly influenced by the frequency (rate) of testing. The glass transition is a molecular relaxation that involves cooperative segmental motion whose rate is dependent on temperature. Therefore, as the frequency of the test is increased, the molecular relaxations may only occur at higher temperatures and, as a consequence, the T_g would be increased with increasing frequency.²⁸ The upper $\tan\delta$ shows

liquid-like behavior at high temperatures.²⁹ BWRS shows the largest $\tan\delta$ among the systems studied, followed by BRSP and BRSP. As expected, the mixture of cellulose, lignin and hemicellulose has the largest glass transition temperature among all the systems studied here, as the mobility of chains is influenced by the benzylation reaction. However, cellulose and lignin show smaller values for T_g , compared to the other systems. This pattern is completely similar to the weight gain of samples in the benzylation reaction; therefore, the weight gain of the samples in the modification reaction may be compared with the maxima of $\tan\delta$.

In the low-temperature region of each DMTA thermogram, the elastic moduli (E') of BWRS and BRSP are slightly decreased with increasing temperature, as expected. They undergo an abrupt drop of nearly two orders of magnitude. However, for BRSP, due to the extraction of lignin and

hemicellulose, the elastic modulus starts to decrease with a larger rate at lower temperatures. The length of the plateau observed in E' is dependent on molecular weight, polymer entanglement and the degree of crystallinity.¹⁸ Due to the lignin removal, there are few benzylation sites for BRSP, so it presents a small value for the modulus, as one would expect. The results of the DMTA study of BWRS and BRSP completely follow and support the present theories. As can be seen in Figure 5a, both show thermoplastic behavior. In relation to the modulus, the plot of $\tan\delta$ displays a relaxation peak, where the maximum temperatures (T_α) of the samples in different frequencies are reported in Table 4. The comparison of T_α from DMTA with T_g data from DSC shows that, although the DMTA values are larger than those from the DSC, due to the well-known frequency effect, both T_α and T_g follow a common trend.^{30,31}

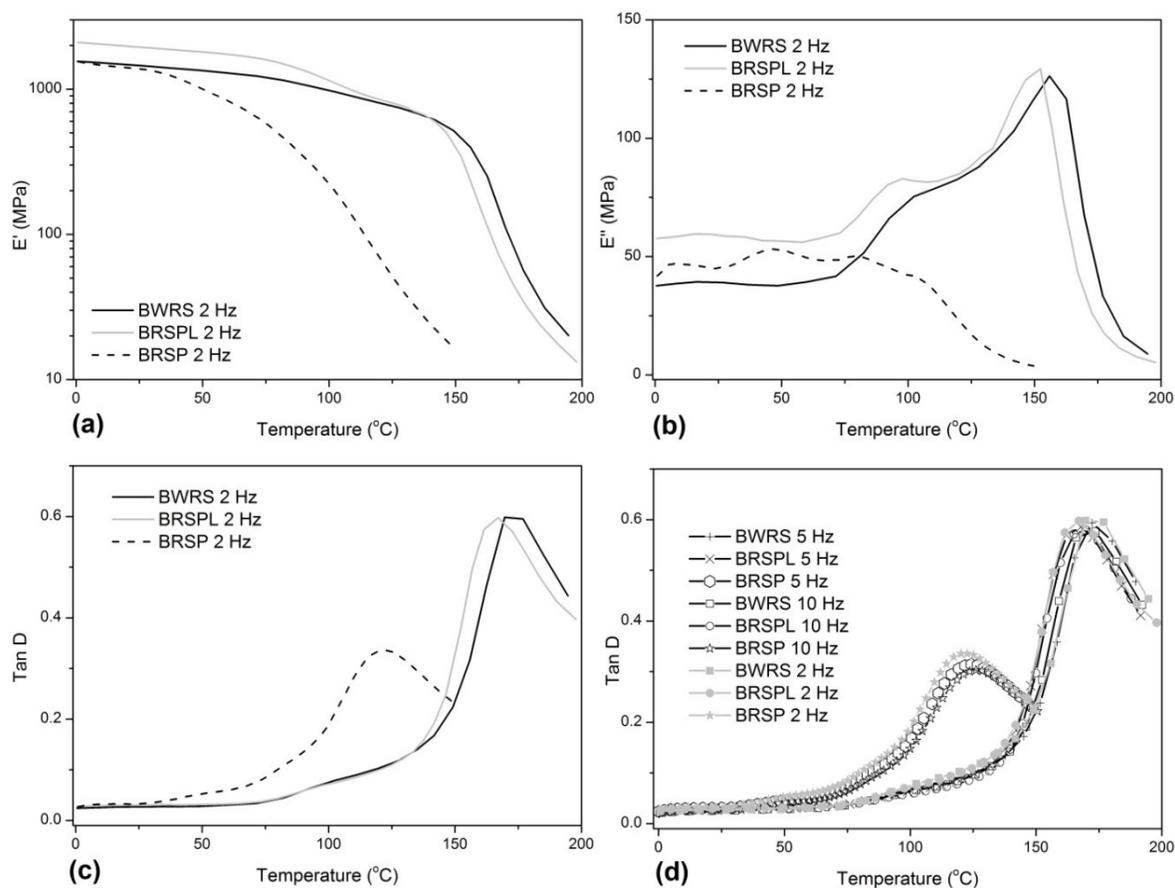


Figure 5: DMTA analysis for BWRS, BRSP and BRSP

Table 4
T_g of samples according to DMTA data

Sample	BWRS			BRSPL			BRSP		
Frequency (Hz)	2	5	10	2	5	10	2	5	10
T _α (°C)	169	172	174	167	168	170	122	124	126

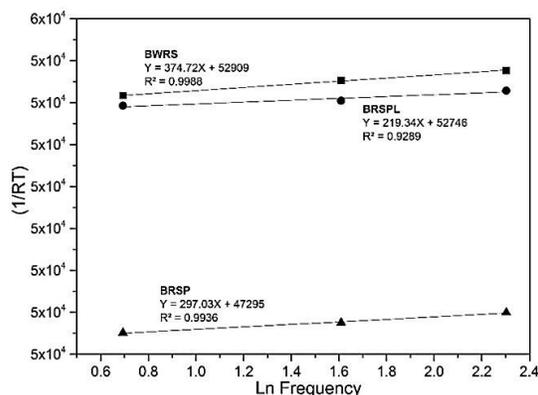


Figure 6: Arrhenius plot for BWRS, BRSP and BRSPL based on DMTA

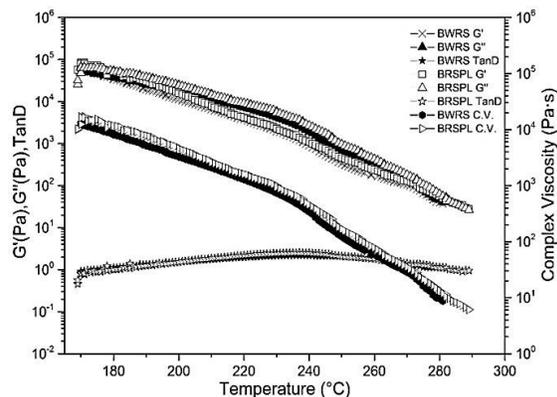


Figure 7: Temperature sweep tests for BWRS and BRSPL

The activation enthalpy for relaxation was calculated using the Arrhenius equation (Eq. 2):

$$\ln f = \ln A + \frac{\Delta H}{RT_{\alpha}} \quad (2)$$

where *f* is the frequency, ΔH is the activation enthalpy of relaxation, *A* is a constant, *R* is the gas constant and *T_α* is the glass transition temperatures reported in Table 4. An Arrhenius plot of *Ln f* against *1/RT* was used (Fig. 6) to determine the activation enthalpy for the relaxation of the samples. This was found to be 374, 297 and 219 KJ/mol for BWRS, BRSP and BRSPL respectively, which is in the range of values for β -relaxation.³²

As can be seen, the activation energy is decreased by the extraction of lignin or cellulose, as lignin could depress the mobility of polymer chains, which increases *T_g*. The rise in *T_g* will reduce the activation energy, however, the complete extraction of lignin will give the thermoplastic sample a thermoset behavior. It can act as an obstacle to the mobility of BRSP, so it shows a small *T_g*, compared with BWRS, which has the advantage of cellulose and lignin altogether.²³

Rheological properties

The temperature sweep test was carried out on the samples to investigate the maximum temperature that may be used without affecting

the physical properties. The strain of 1% and frequency of 1 Hz were selected to carry out the temperature sweep. Temperature was set at 170 °C up to 280 °C. As can be seen in Figure 7, both storage and loss moduli are decreased with increasing temperature, however the slope is significantly increased when the temperature goes above 180 °C. This indicates that the maximum temperature to obtain the optimum result from the new materials should be in the range of 170-180 °C. This is in accordance with the DSC results. BRSP did not show any melting point and acted as a complete thermoset material, so the rheological properties were only studied on BWRS and BRSPL.

BRSPL shows larger storage and loss moduli, compared with BWRS, which is due to the lack of cellulose groups, however, the difference is not great. It can be observed that BRSPL has larger *tanD* which means cellulose groups somehow inhibit the movement of chains. The temperature of 180 °C was selected as the maximum temperature for processing. The strain sweep tests (Fig. 8) at various frequencies were carried out to confirm that the applied strain did not exceed the limit of linear viscoelasticity. This test was carried out at 180 °C in the strain range of 0.01 to 100%. Eventually, the strain of 1% was chosen for the frequency sweep where the modulus is linear. It is obvious that by extracting cellulose, the modulus was increased in BRSPL due to more

benzylation of lignin; however, the ability to resist the strain was decreased compared with BWRS.

The time sweep test was carried out to ensure that there was no change in the overall properties over time. A sensible change for BWRS can be observed at first, due to the presence of cellulose and more non-benzylated groups, which means that this sample requires preheating for 15

minutes. Afterwards, there would be a minimum change during this time, as seen in Figure 9. It should be mentioned that BRSPL shows more stability in modulus from the beginning and has higher values compared with BWRS. It also shows elastic behavior, as storage and loss moduli are apart and the storage modulus is larger than the loss modulus.

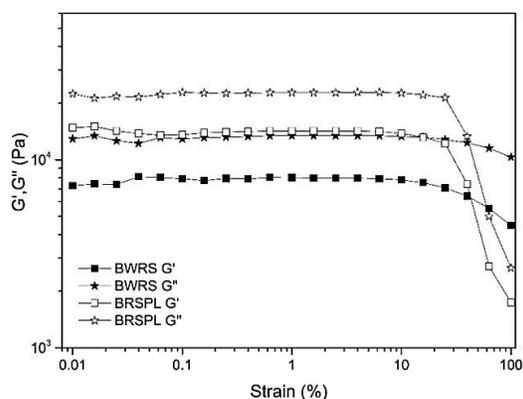


Figure 8: G' and G'' versus strain in an amplitude sweep test for samples at frequency of 1 Hz

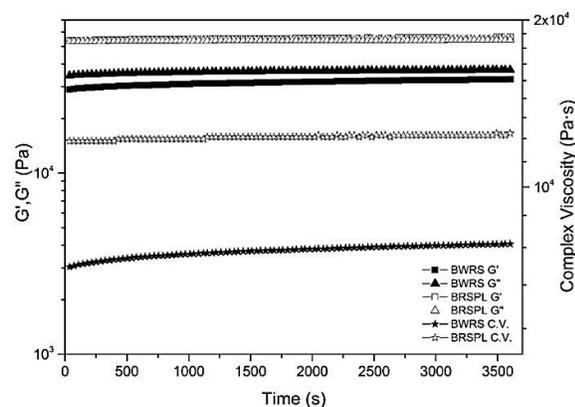


Figure 9: G' and G'' versus time at frequency of 1 Hz and strain of 1%

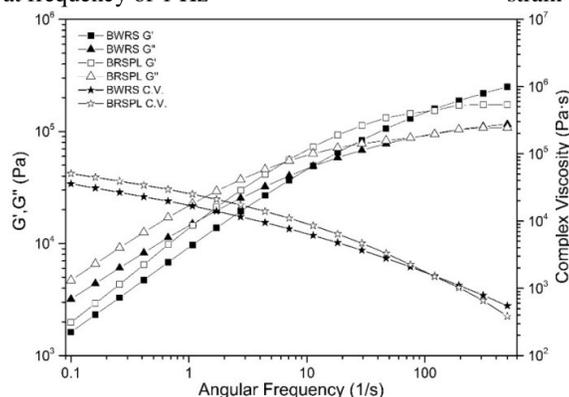


Figure 10: G' , G'' and complex viscosity versus frequency

Table 5
Viscoelastic parameters of BWRS and BRSPL

Sample	BWRS	BRSPL
$\eta_0 \times 10^{-5}$ (Pa.s)	2.42	3.74
$G_N^0 \times 10^{-5}$ (Pa)	5.40	8.22
$\bar{\lambda}$ (s)	2.95	4.26
ν_e (g.mol/cc)	143	204
M_n (g/mol)	116859	158276
M_w (g/mol)	142100	207.500
PDI	1.216	1.311

Table 6
Contact angle of benzylated samples

Material	Theta M (deg)	Area (mm ²)	System
BWRS	74.5	2.86	Twice distilled water
BRSP	65	3.16	Twice distilled water
BRSP	82	2.95	Twice distilled water

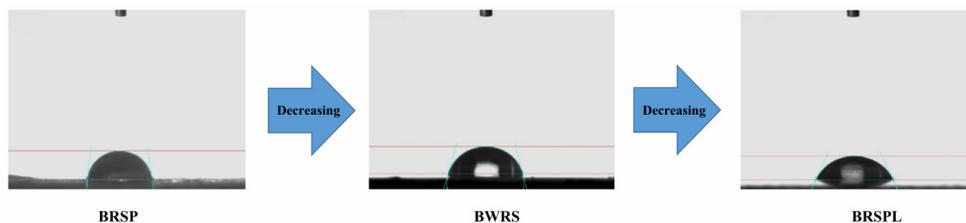


Figure 11: Contact angle of benzylated samples

The dynamic frequency sweep measurements were finally carried out on the samples to investigate the dynamics of the samples. As depicted in Figure 10, the samples show viscoelastic behavior. BWRS shows higher storage modulus at frequencies larger than 11 s⁻¹. At lower frequencies, our samples show viscous behavior. BRSP shows the same trend, however, the intersection point is at the frequency of 7 s⁻¹. As one would expect, BRSP may handle lower frequencies due to the plasticization effect of lignin. The cellulose content of BWRS makes it stiffer against frequency.

The relaxation spectra of BWRS and BRSP were obtained using the plots of G' and G'' data versus angular frequency at some reference temperature. From the relaxation spectra, the zero shear viscosity (η_0), plateau modulus (G_N^0), mean relaxation time ($\bar{\lambda}$) and entanglement density (ν_e) of the benzylated materials were calculated.³³ Table 5 shows the obtained parameters from the relaxation spectrum.

$$\eta_0 = \sum \lambda_i G_i \quad (3)$$

$$G_N^0 = \sum G_i \quad (4)$$

$$\bar{\lambda} = \frac{\sum \lambda_i^2 G_i}{\sum \lambda_i G_i} \quad (5)$$

$$\nu_e = \rho_a / M_e, \quad M_e = \rho RT / G_N^0 \quad (6)$$

where ν_e , the entanglement density, is defined as the number of entanglement junctions per unit volume; R denotes the ideal gas constant; T represents the temperature; ρ is the melt density and ρ_a is the amorphous density.

Although there is no data available for amorphous density of rice straw, as it mainly consists cellulose and lignin, according to the

mixture law, they can be calculated based on cellulose and lignin contents. BWRS contains 80% cellulose and lignocellulosic material and 20% lignin, while BRSP consists mainly of lignin. The amorphous density of cellulose and lignin are 1.376 and 1.4 g/cm⁻³, respectively. It has been reported that the densities of cellulose and lignin are 1.5 and 1.4 g/cm⁻³.^{34,35} The zero shear viscosity shows a higher value for BRSP and the entanglement density calculation shows that BRSP has a higher level of entanglement compared with BWRS. The mean relaxation time is the ratio of the elastic and viscous response. BRSP shows a somewhat higher value compared with BWRS, which may be due to the difference in the nature of cellulose and lignin. BWRS contains both cellulose and lignin, while BRSP has only lignin. Finally, M_n , M_w , and PDI were calculated by the rheometer US200 software.³⁰ As can be seen, the sample with the higher level of entanglement presents larger molecular weight than that of the other sample, as expected.

Surface behavior and morphological studies

The surface behavior of benzylated samples was determined by measuring the contact angle (Theta M), and the results are presented in Table 6. As may be seen, all the benzylated samples are completely hydrophilic, and the hydrophobicity of BRSP is higher than that of the other samples, which could be due to the high content of silica in this sample. The lowest angle is reported for BRSP. Figure 11 shows that by increasing the lignin content, the contact angle is decreased.

The contact angle results prove the completely hydrophilic nature of the benzylated samples. Their hydrophilicity is much greater than that of the pure rice straw, as it keeps distilled water on the surface. As has been previously reported, neat

rice straw has only kept water on the surface for 900 seconds and then it was completely absorbed.³⁶ The contact angle clearly shows the effect of the benzylation process on the data.

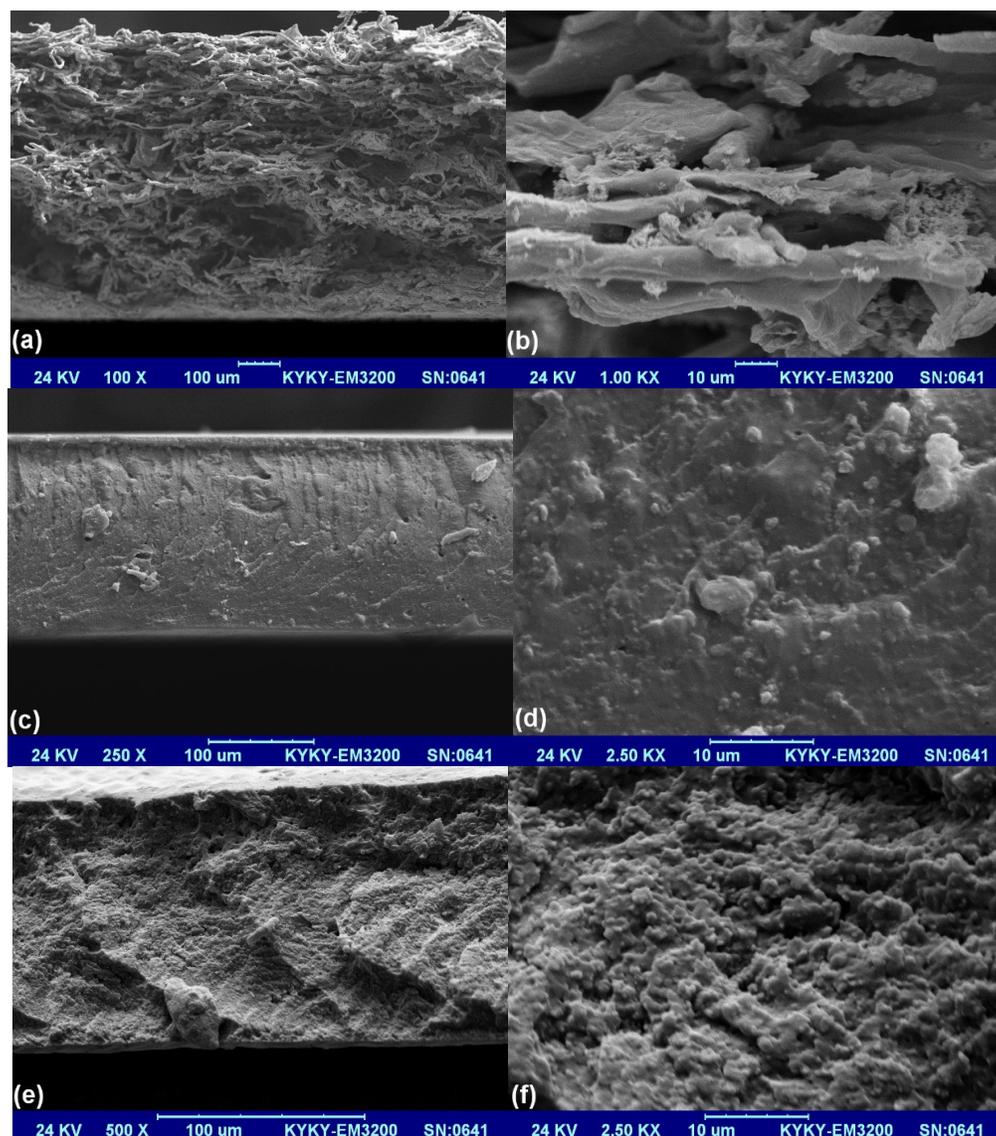


Figure 12: SEM micrographs of chemically modified samples (a,b) BRSP, (c,d) BRSPL, (e,f) BWRs

For further investigations on the samples, the fracture of the surface was investigated in liquid nitrogen using the SEM technique. Figure 12 shows the SEM micrograph of the flexural surface of the chemically modified samples.

According to Figure 12a and b, the BRSP illustrates separated polymeric fibers showing

weak mechanical properties. The lack of lignin influences the structure of the material and dramatically decreases the mechanical strength, strain, elastic modulus and thermal stability of the samples. However, the observed surface behavior is due to the lack of lignin and the structures would not let distilled water to be absorbed. In

Figure 12c and d, BRSPL shows a very smooth flexural surface and large conflict between the chains in its structure. It confirms the plasticization of lignin and also a paste-like effect, which has been previously observed by the small contact angle value. According to Figure 12e and f, the BWRS structure is smoother than the structure of BRSP, but it has some voids that make it more brittle compared with BRSPL and BRSP. The observed voids and the amount of lignin may be the reason for the observed surface behavior, which is larger than that of BRSPL and smaller than that of BRSP.

CONCLUSION

Rice straw was separated into pulp and pulping liquor and the separated products were chemically modified by the benzylation process. The FTIR clearly depicted the reduction of OH group bonds, an increase in aromatic bonds, by reducing the relative cellulose crystallinity, and increasing benzyl groups. The mechanical tests confirmed that BRSPL shows a more plastic behavior than BWRS and BRSP. The removal of lignin increased modulus; however, the elongation at break and strength decreased. The thermal properties show a decrease upon the removal of lignin, which could be due to the plasticizing effect of lignin. BRSPL has the highest properties among the samples. According to the rheology results, the samples were stable over time and their modulus was quite linear up to 10% strain. Moreover, BRSPL can manage lower frequencies due to the plasticization effect of lignin. The cellulose content of BWRS makes it stiffer, as reported by the frequency sweep tests. The DMTA data showed a larger modulus for BRSPL and higher activation energy for BWRS, due to the opposing effect of lignin and cellulose together, compared with BRSP containing cellulose. The surface behavior clearly depicted a hydrophilic behavior, although BRSPL manifested the lowest angle due to the plasticizer effect of lignin. Finally, SEM images confirm more cohesion in the structure of BRSPL, a high number of voids in BWRS, due to the existence of silica and other extractives, and the resistant structure of BRSPL, leading to high thermal stability. The benzylated products can all be used as a new set of fillers, as recycling the materials would lead to cost-effective final products.

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