

Investigating the Effect of Treated Rice Straw in PLLA/Starch Composite: Mechanical, Thermal, Rheological, and Morphological Study

SEYED MOHAMMAD DAVACHI

School of Chemical Engineering, College of Engineering, University of Tehran, Tehran, Iran

SAEED BAKHTIARI, PEYMAN POURESMAEEL-SELAKJANI,
JAMSHID MOHAMMADI-ROVSHANDEH

Caspian Faculty of Engineering, College of Engineering, University of Tehran, Rezvanshar, Guilan, Iran

BABAK KAFFASHI, SAEED DAVOODI

School of Chemical Engineering, College of Engineering, University of Tehran, Tehran, Iran

ARDAVAN YOUSEFI

Caspian Faculty of Engineering, College of Engineering, University of Tehran, Rezvanshar, Guilan, Iran

Correspondence to: Jamshid Mohammadi-Rovshandeh; e-mail: roshandeh@ut.ac.ir.

Received: May 29, 2015

Accepted: October 21, 2015

ABSTRACT: The aim of this work is to use lignocellulosic wastes as low price additives in biodegradable polymers. The rice straw (RS) was treated by means of different methods, and then it was introduced to the poly(lactic acid)/starch composites. The effects of different treatments on RS properties were investigated using the Fourier transform infrared, tensile, charpy, hardness, differential scanning calorimetry, rheology, contact angle, and scanning electron microscopy. It was found that 5–10% of all the differently treated RS increases the overall properties. Moreover, silica and lignin were mainly affected by such treatments; however, a balance between silica and lignin shows the best results. The modified alkali-treated rice straw (ARS treatment) prevented cellulose from degradation by creating a balance between silica and lignin, which controls the opposing effects of lignin including paste-like and plasticating effects. Finally, the ARS-filled samples show improved overall properties among the other samples. The obtained composites with optimum filler content may be used in the biomembranes and food packaging applications. © 2015 Wiley Periodicals, Inc. *Adv Polym Technol* 2018, 37, 21634; View this article online at wileyonlinelibrary.com. DOI 10.1002/adv.21634

KEY WORDS: Biodegradable, Renewable Resources, Thermal Properties, PLLA/Starch, Rice Straw Treatment

Introduction

Biodegradable polymers are at the center of attention from both researchers and industries' viewpoints since they are trying to improve their quality and production rates.^{1–3} One of the most abundant and useful biodegradable and natural polymers is starch, which is a basic part in plants having an energy saving role in their structure.⁴ Starch contains glucose monomers just like cellulose; however, there exists some differences between the monomer bonds.⁵ It is partially soluble in water and is used extensively in food industries since the human body may employ that as an energy supplier.^{6,7} Starch shows rather weak mechanical properties compared with the other polymers. Therefore, it is required to be blended with other

polymers,⁸ specially poly(lactic acid) (PLA).⁹ PLA is the most famous biodegradable polymer implementing starch as main part of structure. PLA is also a biodegradable polymer with a natural base that is synthesized from lactic acid and widely used in polymer industries for food packaging and medical applications.^{9–13} In our recent study, the effects of lignin removal from filler on mechanical, thermal, and morphological properties of the PLA/starch/rice husk composite were investigated.⁹ The lignocellulosic additives such as rice husk, rice straw (RS), rice bran, wheat straw, saw dust, and bagasse have been shown to be effective on the polymer mechanical and thermal properties.¹⁴ They may improve properties such as tensile strength, hardness, impact strength, and thermal stability.⁹ These materials have been used in both biodegradable and nonbiodegradable polymers and many studies demonstrated their ability to make several polymers stronger.^{15–17} The lignocellulosic biomasses are mainly

RESEARCH ARTICLE

composed of cellulose, hemicellulose, and lignin.¹⁸ The main components of RS are supposed to be 40.09% cellulose, 26.8% hemicellulose, 18.9% lignin, and 10.76% ash (94% silica).¹⁹ The presence of lignin, besides the cellulose strong chains, makes them stiff in terms of the mechanical properties because of the lignin's paste-like effect.²⁰ On the other hand, the existence of cellulose composed of glucose monomers (such as starch as mentioned above) makes good interaction between these two, mainly because of the hydrogen bonding.²¹ Lignin is a phenolic polymer with a complex structure that acts as a paste in lignocellulosic materials and make the material stronger against mechanical strength, while it can act as plasticizer that leads the materials chains to more freedom of motion.^{9,22} In the present study, PLA/starch composite was selected as a base matrix, and RS was added to this composite as filler in different amounts. The RS was treated by different methods such as the hot water treatment (hot water treated rice straw, HWRS), alkali treatment (alkali-treated rice straw, ARS), bleaching (bleached rice straw, BRS), and alkali bleaching treatment (alkali-bleached rice straw, ABRS). The methods were used to treat the RS to either make it lignin free or remove it from the structure. Diphenyl-methane-4,4'-diisocyanate (MDI) and triethyl citrate were used as coupling agent and plasticizer, respectively. The tensile, charpy impact, and shore A hardness were employed to evaluate the mechanical properties. The differential scanning calorimetry (DSC) and thermogravimetric analysis show the thermal properties and crystallization behavior of samples. The rheological properties were investigated for better evaluation of the melt behavior and microstructure of composites. Scanning electron microscopy (SEM) was also used to show the morphology of fractured surfaces for the samples. Finally, the contact angle measurement was employed to show the hydrophobicity of the prepared samples. The main goal of this study is to use a lignocellulosic biomass, as a low price filler, in PLA/starch composites and investigate the effects of different treatment methods of RS on the properties of the prepared composites. The results can be used to produce cost-effective biocomposites with stronger attachment and appropriate dispersion of natural filler in polymer matrix, which can be ultimately used in different applications such as food packaging and membranes.

Materials and Methods

MATERIALS

The technical grade corn starch was used in this study. The moisture content in the starch was ca. 12% by weight. It was measured by drying the starch in an oven heated up to 105°C for 24 h. Poly(L-lactide) was prepared from 90% L-lactic acid solution (Merck, Germany) according to a research by Davachi et al.²³ Monomer (L-lactide) was purified by multiple recrystallizations from ethyl acetate and was dried under vacuum at room temperature for 24 h. The catalyst, stannous octoate ($\text{Sn}(\text{Oct})_2$) (Sigma, St. Louis, MO), was purified by the vacuum distillation. The polymer was synthesized inside a glass ampule²⁴ with the molecular weight (M_w) and polydispersity index (PDI) of 100,000 g/mol and 1.64, respectively. The RS, as an additive, was supplied by a

TABLE I Content Percent of Cellulose, Lignin, and Silica in Untreated and Treated Rice Straw

Sample	Holocellulose	Lignin	Ash and Other Contents	Silica ^a
RS	66.89	18.9	14.21	13.36
HWRS	68.68	19.4	11.92	11.92
BRS	79.17	5.83	15	14.1
ARS	62.13	23.04	14.83	13.94
ABRS	82.43	0.1	17.47	16.42

^a94% of ash and other contents is silica.

local mill (Guilan, Paresar, Iran) and its powder prepared at the mesh size of 70–80. The RS flour was dried at 110°C for 24 h to set the moisture content within 1–2%, and then it was stored over desiccant in some sealed containers. All the other chemical and solvents were reagent grade from Merck (Darmstadt, Germany).

RS HOT WATER TREATMENT

To obtain hot water treated rice straw (HWRS), the RS powder was washed with hot water at 100°C for 2 h using a mechanical mixer at 150 rpm. After washing the supplied material with hot water, it was washed with distilled water at 25°C and finally dried in an oven for 48 h at 110°C.²⁵ The holocellulose and lignin content of all treated RSs including HWRS are obtained according to our previous study⁹ and are reported in Table I.

RS ALKALI TREATMENT

To obtain ARS, the RS powder was soaked in 4 wt% of sodium hydroxide (NaOH) at 100°C for 1 h using a mechanical mixer at 150 rpm rotor speed. Afterward, the treated RS was washed by distilled water to completely leach out the absorbed NaOH and finally was dried in an oven for 48 h at 110°C.²⁵ Owing to the degradation of cellulose in NaOH, the treatment time is short and the effect of short alkali treatment is investigated in this research. The holocellulose and lignin content of ARS are shown in Table I.

RS BLEACHING TREATMENT

To obtain BRS, the RS powder was bleached by 4–6 wt% of sodium hypochlorite at 25°C for 30 min using a mechanical stirrer at 150 rpm. After washing the supplied material with a 2–4 wt% of 1N sodium hydroxide solution and then distilled water, it was dried in an oven for 48 h at 110°C.⁹ The holocellulose and lignin content of BRS are shown in Table I.

RS ALKALI BLEACHING TREATMENT

To obtain ABRS, the RS powder was soaked in 4 wt% of NaOH at 100°C for 1 h using a mechanical stirrer at 150 rpm. Afterward, the treated RS was washed by distilled water to completely leach out the absorbed NaOH and was dried in an oven for 48 h at 110°C. The ARS was grinded and bleached by 4–6 wt% of sodium hypochlorite at 25°C for 30 min using a

TABLE II
Composition of Samples (%)

Sample	PLLA	Starch	Rice Straw	Treatment Method	MDI	TC
PSRS0	50	50	—	—	1	10
PSRS1	42	42	5	—	1	10
PSRS2	39.5	39.5	10	—	1	10
PSRS3	37	37	15	—	1	10
PSRS4	42	42	5	Hot water	1	10
PSRS5	39.5	39.5	10	Hot water	1	10
PSRS6	37	37	15	Hot water	1	10
PSRS7	42	42	5	Bleaching	1	10
PSRS8	39.5	39.5	10	Bleaching	1	10
PSRS9	37	37	15	Bleaching	1	10
PSRS10	42	42	5	Alkali	1	10
PSRS11	39.5	39.5	10	Alkali	1	10
PSRS12	37	37	15	Alkali	1	10
PSRS13	42	42	5	Alkali bleaching	1	10
PSRS14	39.5	39.5	10	Alkali bleaching	1	10
PSRS15	37	37	15	Alkali bleaching	1	10

MDI, diphenyl-methane-4,4'-diisocyanate; TC, triethyl citrate.

mechanical stirrer at 150 rpm rotor speed. After washing the supplied material with 2–4 wt% of the sodium hydroxide solution (1 N) and then distilled water, it was then dried in an oven for 48 h at 110°C. The holocellulose and lignin content of ABRS are shown in Table 1.

PREPARATION OF PLLA/STARCH AND TREATED RS COMPOSITES

MDI was dissolved in diethyl ether and then was sprayed over starch and PLLA with an equal ratio 1 wt% of total polymer. Then, the materials were dried in a vacuum oven at 50°C to evaporate extra diethyl ether in the mixture. All composites were mixed with 50:50 PLLA/starch content according to the previous studies^{9,26} as shown in Table II. The mixing process was carried out using an internal mixer (Brabender, Duisburg, Germany) at 180°C for 15 min at 60 rpm. The obtained blends were molded in 3–4 mm sheets by a hot press at 180°C applying 14 bar pressure for 5 min.⁹

CHARACTERIZATION

The molecular weight and PDI of PLLA were determined by the gel permeation chromatography (GPC) technique using an Agilent GPC 1100 chromatograph (Palo Alto, CA, USA). Chloroform was used as eluent. The temperature and flow rate in this experiment were fixed at 35°C and 1 mL/min, respectively. Two PL Mixed C columns with a Viscotek 3580 refractive index detector and an injection volume equal to 100 μL were used. The sample molecular weight was calibrated with the standard polystyrene. All the methods mentioned above were performed according to ASTM D 6579. The infrared spectroscopy was performed using a Bruker instrument (Equinox 55LS 101 series; Bruker, Karlsruhe, Germany) with the resolution of 4 cm⁻¹ (averaging 50 scans) for determination of functional groups of polymers. The rheological properties of synthesized PLLA were measured at 180°C using an Anton Paar Physica MCR102 (Graz, Austria) with parallel-plate geometry according to ASTM D4440-07 under air atmosphere. The dynamic experiments were

performed under oscillatory shear mode with the dimensions of 25 mm (diameter) and 0.5 mm (gap). The frequency sweep measurements were carried out for the angular frequencies ranging from 0.05 to 500 rad/s. Prior to the frequency sweep measurement, the strain sweep at various frequencies was carried out to confirm that the applied strain did not exceed the limit of linear viscoelasticity. The DSC was carried out using a Mettler Toledo 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°C/min, under nitrogen atmosphere and at temperatures ranging from -50 to 260°C. The glass transition (T_g), melting temperatures (T_m), crystallization enthalpy (ΔH_c), and relative degree of crystallinity (X_c) were obtained from the DSC. The repeated heating scans were performed to verify the reproducibility of the results. All the adjustments were carried out according to ASTM D3418. The stress-strain measurements were carried out on samples by means of a Gotech Universal AI-7000-LA (Taiwan) according to ASTM D638. The measurements were conducted at room temperature (25°C). The cross-head speed was 5 mm/min. At least three test specimens of every composition were tested. The impact strength of the composites was measured according to ASTM D256 standard. A FRANK Baldwin-Model-BLI pendulum Impact testing machine (Germany) was used to measure the not-notched rectangular specimens (80 × 10 × 3.8 mm³). At least three specimens were tested for each sample. The shore A hardness of each bioblend was measured with a FRANK testing machine (Germany) according to DIN53505. Five measurements were taken into account for each sample. The hydrophilic properties have been measured through contact angle measurement of two times distilled water droplets on the surface of composites using a Kruss G10 by repeating every measurement for three times. The average of measurements data was taken and reported. The SEM micrographs were obtained with KYKY-EM3200 (People's Republic of China) on the fracture surface of samples in liquid N₂.

Results and Discussion

Fourier Transform Infrared ANALYSIS

The Fourier transform infrared (FTIR) analyses of fillers and composites are shown in Fig. 1. Since there is a similar base structure for fillers and composites in different samples, the treatment has affected few peaks, therefore, the composites with higher content of fillers are selected as representatives.

For analysis of fillers, a peak at 3383 cm⁻¹ was related to the free hydroxyl groups, which was decreased by decreasing or removing the lignin from the structure.²⁷ The peaks at 2919, 1641, and 1511 cm⁻¹ represent alkane CH, lignin, and aromatic C=O and C=C, respectively. The peak of aromatic C=O was also decreased since lignin was removed from the fillers. A peak at 1371 cm⁻¹ belongs to aromatic CH and carboxyl carbonate stretching bonds. The peaks at 1031 cm⁻¹ represent SiO₂ component of the samples as well as cellulose and hemicellulose. Rahnama et al. showed that NaOH degraded cellulose or hemicellulose by lowering 1031 cm⁻¹ peak; however, such result was not observed in the current study for the ABRS treated with both alkali and bleaching. Conclusively, we believe that the mentioned peak can

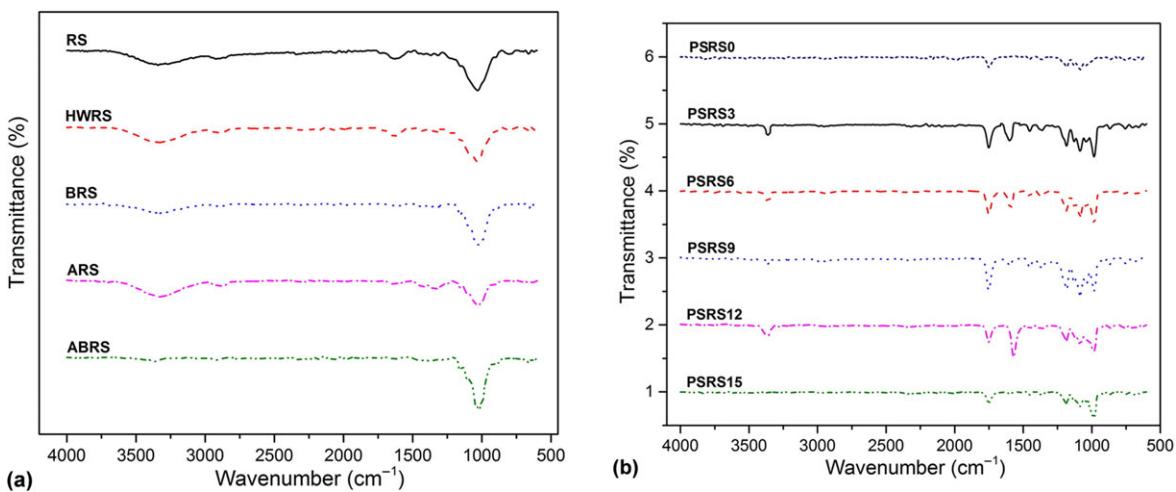


FIGURE 1. FTIR spectra of (a) untreated and differently treated rice straws (b) PLA/starch composites.

only be attributed to the Si–O–Si bond and a minimum degradation was detected in the cellulose content of ca. 4% as compared to the results as previously reported in Table I.²⁸ In BRS and ABRS, due to the removal of lignin, the silica content has become more clear and can be detected by the extended peaks, while the C=O and hydroxyl groups have been decreased in a sensible manner. The HWRS exhibited no discernible changes, although the silica peak is slightly decreased probably due to the dust, and silica formed on the surface washed away by hot water.²⁵ ARS has shown an increase in lignin-related peaks since sodium hydroxide makes the RS matrix free of lignin, which may also prevent the silica group to be detected by the IR.²⁹ Figure 1b illustrates the FTIR spectra of the composites produced in this study. The C=O stretching of PLA or ester groups are visible at 1750 cm⁻¹. There was detected a decrease in the intensity of C=O in the alkali-treated samples indicating the fact that NaOH may reduce the activity of C=O after treatment as it may still exist on the surface of treated silica even by a severe washing after the alkali treatment.^{28,30} The C–O of PLA is observable at 1182 cm⁻¹. The methyl groups of PLA and also C–H bending vibration has been shown as peak at 1363 cm⁻¹. The peak appeared at 836 cm⁻¹ belongs to the C–C stretching. The cellulose and starch C–OH and C–O–C bonds have been detected at 1129 and 1182 cm⁻¹, respectively. The absorption of the OH group of lignin has been shown at 3359 cm⁻¹ and aromatic rings stretching bonds of lignin has shown at 1587 cm⁻¹, which both were decreased in the samples lowered in their content of lignin.^{31–33} As can be seen in PSRS9, this peak has a slight decline, while it has been completely disappeared in PSRS15. Similar to ARS, for PSRS12, there is an increase in peaks related to lignin since sodium hydroxide makes the lignin free in the RS matrix. One can postulate that there are some interactions between cellulose and lignin. According to Wu et al.²⁷ and the FTIR peaks of the prepared composites, there exist hydrogen bonds between cellulose, starch, and lignin in the composites. The OH groups of hydrogen bonding are appearing at wavenumber of 3359 cm⁻¹²¹. Quite interestingly, this peak has been weakened by removal of lignin from the structure. A new peak that belongs to the CO stretching vibration in starch has been appeared in 982 cm⁻¹, which attributes to the new interaction between cellulose and starch in composites.²¹

MECHANICAL PROPERTIES

Tensile Properties

The tensile properties of samples are shown in Table III. The addition of differently treated fillers to the PLA–starch blend in all samples decreased the elongation at break and increased elastic modulus compared with the unfilled PLA–starch (PSRS0) due to the hard nature of RS, as this filler prevents the polymer chain movements making them solid. However, no specific trend can be detected to describe the tensile strength changes upon the addition of RS fillers.

Tensile strength of PSRS1 containing 5% of untreated RS has a slightly lower tensile strength compared with PSRS0 containing no filler. However, with an increase in the content of untreated RS, tensile strength is increased and the tensile strength in PSRS3 with 15% RS reaches from 7.93 to 11.30 MPa. By introduction of RS into PSRS0, an initial decrease can be seen in tensile strength comparing to the unfilled PSRS0, since the particulate fillers (silica) resides on the surface of RS generally increase the stiffness and decrease the tensile strength.³⁴ The RS contains silica and lignin that can be more influential upon increasing the filler content leading to higher resistance of samples against stress.^{9,35} Incorporation of filler results in an abrupt drop in elongation at break compared to the PSRS0 matrix, and it was found that by increasing the filler content, the reduction rises. Such behavior is expected since silica and lignin cause less motion in polymers chains in PLA/starch composite.³⁶ Lignin acts as paste and keeps chains together in a strong form.²⁰ This behavior can be observed in the elastic modulus of samples, which were increased in the samples containing RS and also further increased by adding a higher level of filler to the composite. Comparing PLA/starch/RS with PLA/starch/HWRS, larger tensile strength in PSRS4 and PSRS5 comparing with PSRS1 and PSRS2 are seen, however in PSRS6 with 15% of HWRS lower tensile strength was observed as compared to PSRS3. Hot water treatment could remove small amounts of silica and waxes that are present in the RS structure.²⁵ Moreover, in our opinion, it can make the lignocellulosic structure to move more freely. The higher strength in the hot water treated samples is because of more freely lignin in the structure. Higher free lignin in the structure means higher cohesion that leads to higher strength.^{9,22} As is

RESEARCH ARTICLE

TABLE III
Mechanical and Thermal Properties of Composites

Sample	Tensile Strength (MPa) ^a	Elongation at Break (%) ^a	Elastic Modulus (MPa) ^a	Charpy Impact Strength ^b (kJ/m ²)	Hardness ^c (Shore A)	T _g ^d (°C)	T _m ^d (°C)	ΔH _c ^d (J/g)	X _t ^e (%)
PSRS0	7.93	20.33	284.89	36.39	66.66	47	146.40	8.47	9.11
PSRS1	5.61	7.62	577.92	38.08	68.15	3.05	141.73	14.98	16.11
PSRS2	8.03	5.70	1057.60	55.85	71.25	—	—	—	—
PSRS3	11.31	5.12	1903.10	80.12	72.75	4.25	140.38	14.37	15.45
PSRS4	9.41	15.21	1304.90	57.88	74.25	0	141.38	12.96	13.94
PSRS5	10.14	9.83	1228.60	49.62	76.75	—	—	—	—
PSRS6	7.32	4.16	774.14	37.21	77.25	4	140.19	12.91	13.88
PSRS7	8.91	18.33	1031.70	51.65	73.25	15.35	146.14	10.15	10.91
PSRS8	11.31	6.34	1006.20	45.48	74.5	—	—	—	—
PSRS9	9.82	4.27	842.13	29.96	77.75	12.91	146.97	13.32	14.32
PSRS10	8.38	13.28	652.19	51.75	73.00	-9.71	140.82	15.37	16.53
PSRS11	9.31	5.97	812.39	54.23	73.50	—	—	—	—
PSRS12	12.61	4.18	916.92	59.75	74.75	-12.24	139.83	15.51	16.68
PSRS13	5.06	19.26	375.51	37.21	74.75	16.65	147.35	15.74	16.92
PSRS14	11.18	7.14	828.32	43.42	76.75	—	—	—	—
PSRS15	8.42	3.81	875.75	35.15	78.50	18.57	148.98	16.16	17.38

^aObtained from tensile test.^bObtained from Charpy test.^cObtained from Hardness test.^dObtained from DSC.^eBy considering the melting enthalpy of 100% crystalline poly(l-lactide) as 93 J/g.^{9,58}

clear from the data, the strength in HWRS samples has increased by increasing the filler content further confirming the above reasoning. This behavior has been described in similar studies^{37,38} and it has been explained by increasing the interfacial area with filler loading and easy agglomeration of HWRS. Since the filler particles are very small, a high interfacial surface exists between the polar filler and nonpolar matrix. As this area is increased, the fillers cannot manage the bonding and due to the inability of the filler to support stresses transferred from the polymer matrix, the worsening bonding between the polymer and matrix decreases the tensile strength in higher contents.³⁹ In case of elongation at break, higher contents are achieved in the samples filled by HWRS. This behavior is because of lignin's nature and its opposing effect.⁹ For this type of treatment, more content of free lignin plays a role as plasticizer in addition of its paste-like effect. It leads to higher strain in the samples.⁴⁰ The elongation at break of samples is decreased by increasing filler. At higher contents, there will be a debonding between filler and matrix. Poor interfacial bonding causes partially separated microspaces between the filler particles and the polymer matrix. The presence of voids obstructs stress propagation when tensile stress is applied inducing some increased brittleness.^{41–43} Elastic modulus shows a descending trend upon addition of fillers, which is due to the plasticizer role of lignin. Owing to the hot water treatment, the free silica particles have been removed, and the effect of lignin may be explored. In HWRS-treated samples, plasticization effect of lignin dominates its paste effect since silica particles facilitate the attachment of lignin molecules together, and with an increase in the amount of lignin,^{44,45} it could fit between the polymer chains and make them less mobile compared with the samples with less amounts of free lignin.⁴⁶ This is exactly what happened in untreated RS samples for which the modulus is increased by increasing the filler content. To study the effect of

lignin removal, the bleached samples of RS is investigated. The tensile strength increased in the all bleached samples compared to PSRS0; however, with increasing the filler content, the tensile strength is increased up to 10% which is decreased for 15% of BRS. In the bleached samples, lignin is removed partially from the filler. The lignin removal makes cellulose and hemicellulose chains more free. So, they can have better interaction with starch in the structure of composite because their (starch and cellulose) monomers are isomers of glucose and they have the same nature.⁵ This could be the main reason of the increase in the tensile strength; however, in higher content of rigid filler, debonding between filler and matrix could happen, and this poor interfacial attachment may cause microspaces between filler and the polymer. Elongation at break of BRS-filled samples shows a descending trend; however, this increase will get a considerable drop in contents more than 5% showing a change from 18 to 6%. Owing to the lower content of lignin, silica particles control the mechanical properties and with an increase in the content of BRS, the samples become more brittle. On the other hand, a trace of lignin remains in the structure of BRS that could make samples more plastic. This lignin has a plasticization effect because it has small content in the sample and do not disturb the chains movement.⁴⁷ The elastic modulus in BRS-filled samples is decreased with increase in the filler content. With a look to elastic modulus of samples, we can find out that there is a little increase in the 5% sample (PSRS7) compared to the 5% RS-filled sample. But in PSRS8 and PSRS9 the elastic modulus is lower than RS-filled samples under the same filler content, which could be due to the lignin removal from the RS. The lignin's paste-like effect makes the RS-filled samples tougher than the BRS samples. But for the lower contents of filler (5%), its plasticizing effect is more dominative making samples more elastic. The treatment by NaOH does not remove lignin from lignocellulosic materials

RESEARCH ARTICLE

structure. It makes lignin to move freely in the structure, and thus can localize anywhere in the composite of PLA/starch/ARS. The attained results further confirm this claim according to the overall higher tensile strength, higher elongation at break and lower elastic modulus in the samples that is treated by sodium hydroxide compared to the untreated samples. The last series of samples that are almost lignin free based on the two methods of treatment (alkali treatment and bleaching) are the ABRS-filled samples. The tensile strength of this series is lower than the untreated samples at 5% content of filler (PSRS13), but by increasing filler content, it was increased and became higher than the untreated sample at 10% of filler. Since there is no lignin in this filler, which has been confirmed by FTIR previously, there can be seen no paste effect, and similar to the BRS samples tensile strength shows an increase upon addition of 10% filler and then shows a decrease. Owing to the removal of lignin from RS, starch and cellulose could make a better interaction, although at lower filler content a lower interaction between cellulose and starch occurred. By increasing of filler content to 10% and normal increasing of cellulose, the interaction will rise. However, by increasing filler to 15% in a solid manner (without any lubricant), it could make the polymer chains more brittle and sample shows lower tensile strength.⁴⁸ As in the BRS samples, a small amount of lignin still exist, and debonding filler and matrix is lower than the ABRS samples and the tensile strength in ABRS samples is smaller for all filler contents. The opposing effect of lignin removal and the starch–cellulose interaction and the filler–matrix debonding can be seen in the elongation at break data as addition of filler without its natural plasticizer (lignin) shows extremely high reduction in elongation at break at higher ABRS content. In PSRS13, due to the fine interaction between cellulose and starch,⁴⁹ the sample shows a high elongation at break close to the PSRS0 sample. However, with an increase in the filler content from 5 to 10%, due to the nonexistence of lignin, the elongation at break drops from 19 to 7%. The same behavior was seen for the BRS-filled samples; however, the elongation at break of the BRS-filled samples were larger at higher contents due to the existence of small amount of lignin compared with the lower content samples. The elastic modulus clearly supports the mentioned behaviors, as it is lower than the untreated samples and shows that the stiffness of the composites is contributed predominantly by inherent stiffness of rice husks and the PLA/starch matrix; in the other words, the ABRS-filled samples show higher elastic behavior, but this behavior is decreased by increasing amount of filler.

Charpy Impact Test

The results of not-notched charpy impact strength of the composite samples are shown in Table II. The charpy impact strengths of samples are increased by adding treated or untreated RS to PLA/starch compared with the filler free sample (PSRS0). Owing to the existence of silica and paste effect of lignin, by increasing RS filler, the impact strength is increased. The hot water treatment made the composite impact resistant at low filler content, but more filler amount makes it brittle. As discussed before, hot water treatment expands the structure and makes lignin partially free, in addition of removing some parts (waxes and silica). In lower contents of filler, the paste effect of lignin could dominate; however, with an increase in filler content and reduc-

tion of silica particles, due to the hot water treatment, the lignin might act as a plasticizer, and by diffusing between starch and PLA, makes the composites structure weaker. In the bleached fillers, a small amount of lignin still exists, and therefore, impact strength increased at PSRS7 in comparison with PSRS1 because of better interaction of cellulose chains with starch in the absence of lignin. However, increasing of filler content decreased the impact strength and it also has lower value than untreated samples with the same concentration of filler. This phenomenon can be explained due to the poor interfacial bonding caused by microspaces between the filler particles and the polymer matrix. These microspaces prevent stress growth once the impact is applied, and due to inability of filler to support stress, transferred from the polymer matrix, the composites become weaker due to mechanical impacts.³⁹ According to the results from ARS-filled samples measurements, due to the paste effect of lignin and the better cellulose–starch interaction, the charpy impact results show an ascending trend. For ABRS-filled samples, where lignin has been completely extracted by bleaching and sodium hydroxide treatment, similar to the tensile strength, impact strength is low at first upon increasing filler, and a higher level of interaction between cellulose and starch increases the strength; however, at the higher amounts of filler without any plasticizer and poor interfacial bonding caused by the microspaces, the structure becomes brittle and weaker once subjected to impact.

Hardness

The shore A hardness data for all the produced composites are available in Table II. As it is obvious, the hardness values of PLA/starch composites have been increased by adding different types of RS to the structure. By increasing the content of RS in PLA/starch blend, the hardness is expectedly increased. The HWRS-filled samples exhibit the same behavior as the RS-filled samples; however, they show higher hardness compared to the RS-filled samples, which is because of free lignin in the structure of HWRS that can move in the composite and paste between the chains and make the sample harder. Bleaching of lignocellulosic filler removes the lignin partially from the sample, so it removes plasticizer from fillers making the samples harder, which is totally demonstrated in the chart. The hardness was increased by increasing the filler content, which is because of higher filler with lower lignin (plasticizer). Alkali treatment of RS also makes the lignin free to move. So, the free lignin leads the composite to higher hardness because of its paste-like effect compared with the untreated samples. As expected, similar to the tensile strength, the elastic modulus and charpy impact of the hardness would be increased with an increase in the filler content. With complete removal of lignin in ABRS-filled samples, they have the higher hardness in relation with all other samples and with an increase in the filler content these values were increased, as adding cellulose-based filler without plasticizer (lignin) creates larger hardness.

THERMAL ANALYSIS

DSC was utilized to study the thermal and crystallization behaviors of composites and the results were depicted in Fig. 2 and Table I. The T_m , ΔH_c , and accordingly X_t are decreased by the addition of untreated RS to the PLA/starch matrix. The RS has enough lignin in its structure to reduce the melting point

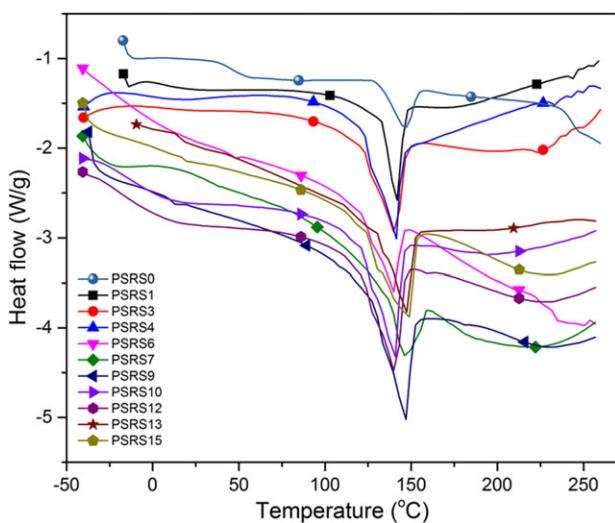


FIGURE 2. DSC thermograms of PLLA/starch/rice straw composites.

due to its plasticization effect and also reduce the crystallinity by its amorphous structure.^{9,50,51} With an increase in the content of RS, all the mentioned parameters are decreased.

The glass transition temperatures of samples filled by RS were also decreased compared to PSRS0, although with an increase in the RS content a slight increase in T_g can be observed, as lignin leads to more mobility in the chains by its plasticization effect at lower contents and in the higher contents its paste effect will dominate.^{40,50} In the HWRS-filled samples, a decrease in T_m , ΔH_c , and X_t may be observed, although due to the removal of silica and wax and the expansion of structure in the HWRS, the lignin is a little free, so the plastication of lignin can be observed in the reduction of crystallinity, T_m and T_g . Upon an increase in the content of HWRS, similar to the RS-filled samples, T_g is increased, while a decrease in T_m is also observed and the effect of silica removal is diminished with the increase in the filler content. Bleaching removes a large amount of lignin (an amorphous structure) from the RS.⁵² Therefore, the samples are expected to show higher crystallinity and T_m as compared to the previous samples. Based on the mechanical properties, a high content of lignin and silica together activates the paste effect and for the lower amounts, lignin may act as a plasticizer, as a result, for lower filler content, both T_m and ΔH_c show a sensible drop in their values compared with the PSRS0 and RS or HWRS-filled samples, although by increasing the filler content silica would actively act as a nucleating agent⁵³ and somehow reciprocate the lignin plastication effect. The effect of silica is obvious in X_t , as the value is increased from 10.91 to 14.32%. The plasticizer removal could make the matrix more glassy leading to higher value of glass transition temperatures.⁵⁴ In ARS-filled samples, an increase in T_m , ΔH_c , and X_t with an increase in filler content and a decrease in T_g was observed. The melting temperature are rather similar to the HWRS-filled samples, as in the HWRS-filled samples wax and silica were removed, lignin was more active and in this study alkali treatment has made the lignin more free and the activity of silica particles have been reduced. Interestingly, glass transition temperatures of these samples have shown negative values indicating that the treatment lowered the glass

transition temperature significantly because of plasticization effect of lignin that gave more freedom to the chains mobility. We postulate that there could be an opposing effect of lignin in different temperatures. On the one hand, at higher temperatures, due to the free activity of lignin and silica particles that act as a nucleating agent outside of the ARS and between PLA and starch, the paste effect of lignin will dominate and lignin can paste anywhere; moreover, there will be a better cellulose-starch interaction. Therefore, an increment in crystallinity and ΔH_c is observed. On the other hand, at lower temperatures, since silica cannot actively join lignin in the PLA/starch matrix and due to the amorphous structure of lignin, it will act as a plasticizer and will reduce the T_g . In conclusion, these two effects are the main dominating factors affecting the transition process and as could be seen they act independently at high and low temperatures. About the samples treated by both bleaching and sodium hydroxide, the highest ΔH_c , X_t , and T_m are observed. Lignin was completely removed from the structure of filler. The cellulose and starch have a better interaction and removal of an amorphous structure leads to a more crystalline structure in ABRS-filled composites.²⁹ Overall, chemical treatments of RS in most of the cases bring the natural fiber to a better situation to interact with the base matrix of PLA/starch.

RHEOLOGICAL INVESTIGATION

The rheological properties of PLA/starch-treated RS composites are shown in Fig. 3. The strain sweep (Figs. 3a and 3b) 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 0.01–100% based on our previous study.⁹ Eventually, the strain of 0.05% was opted for the frequency sweep where the modulus is linear. Except PSRS11 and PSRS12, all the samples show viscous behavior, as storage and loss moduli are apart and the loss modulus is larger than the storage modulus. The main reason for this exception is the domination of the lignin's paste effect at higher temperatures and higher contents of filler. The modulus of samples against strain changes are in the following order: PSRS12 > 11 > 15 > 14 > 9 > 8 > 13 > 7 > 6 > 10 > 5 > 3 > 2 > 1 > 4. It can be seen that the ARS-filled samples with 15 and 10% of filler have higher modulus, then with the same trend are ABRS- and BRS-filled samples. Owing to the complete removal of lignin, PSRS13 with 5% ABRS filler shows higher modulus and elastic behavior compared with PSRS7, HWRS-filled, and the RS-filled samples. The RS- and HWRS-filled samples show the modulus after PSRS7. Finally, the samples with 5% filler have shown the lowest modulus; however, the lignin content is very effective in the modulus trend as in the lower contents of filler lignin acts as plasticizer, alongside its paste effect.

In PSRS10, lignin has utterly acted as a plasticizer and the modulus is lower than PSRS6. As can be seen, the treatments have improved the storage and loss moduli. The dynamic frequency sweep measurements were finally carried out on the samples to investigate the dynamics of samples as shown in Figs. 3c and 3d and the composites with intersection points are shown in Fig. 3e. The modulus and complex viscosity of the samples against frequency changes show the same trend against strain. In the RS- and HWRS-filled samples, the loss moduli are

RESEARCH ARTICLE

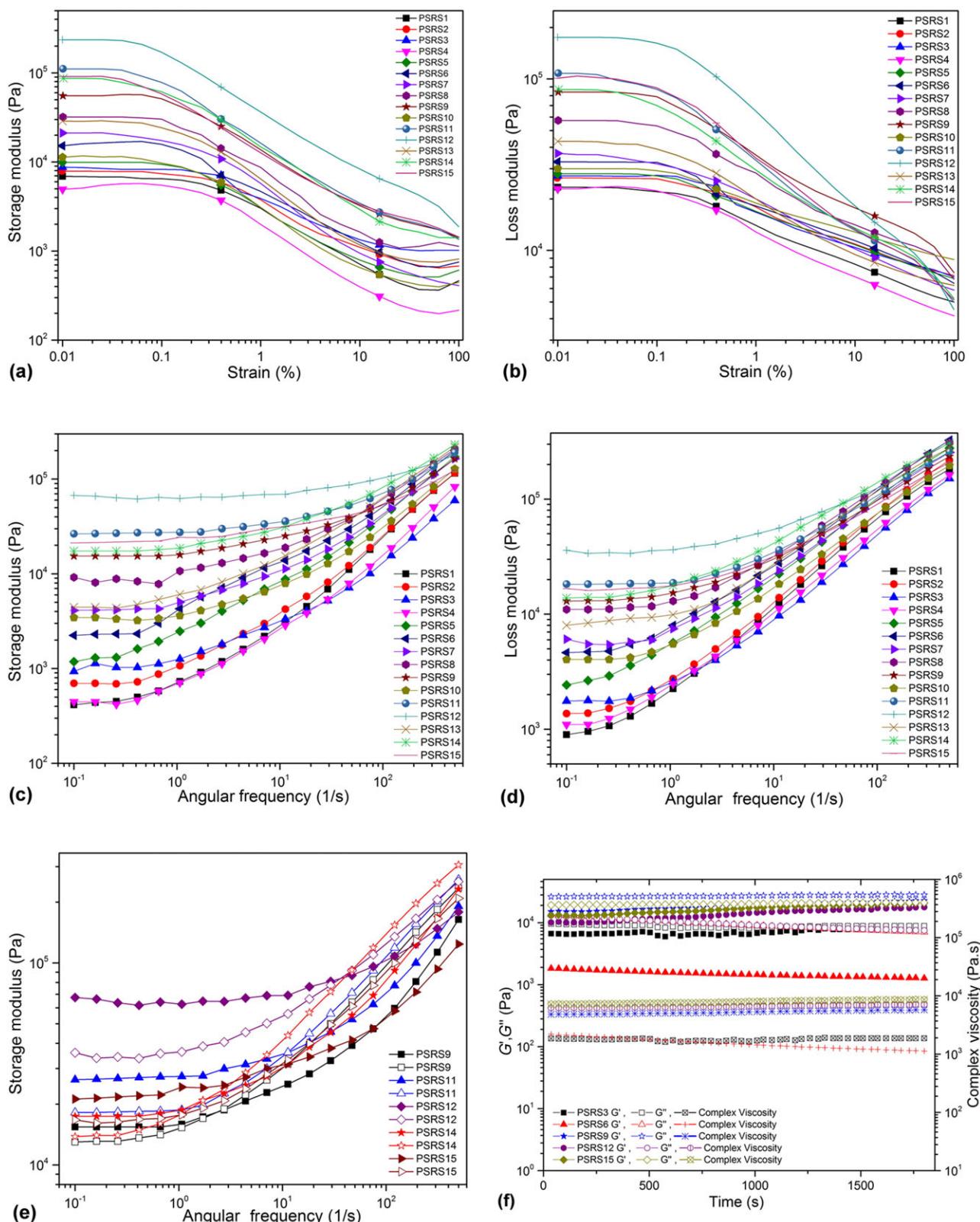


FIGURE 3. Rheological properties of PLA/starch and different treated rice straw: (a) G' versus strain, (b) G' versus strain, (c) G' versus frequency, (d) G'' versus frequency, (e) frequency sweep intersections, and (f) time sweep.

higher than the storage moduli at all frequencies. The BRS-filled samples showed the same trend up to 10%; however, for samples containing 15% filler at low frequencies, the storage modulus becomes higher than loss modulus from the intersection point at frequency of 2.5 s^{-1} ; the main reason for this behavior may be due to the increase in content of silica that acts as a nucleating agent and makes the composite tougher at low frequencies. The ARS-filled samples show a viscoelastic behavior at the filler content of 10% and higher, as the loss modulus is above the storage modulus at higher frequencies and they cross that may be related to the paste-like effect of lignin. The intersection point is shifted to the higher frequencies with an increase in the filler content from the frequency of $11\text{--}36\text{ s}^{-1}$. The ABRS-filled samples show the viscoelastic behavior at the filler contents larger than 10% and the intersection point shifts from 2 to 9.5 s^{-1} . They have the similar behavior compared with the BRS-filled samples; although due to the complete removal of lignin, the effect of silica particles shows its effects on the lower filler contents. The ARS-filled samples show higher intersection points due to the paste-like effect of lignin, which has been described earlier. The time sweep test was carried out (Fig. 3f) to ensure that there is no change in overall properties with time. All the composites with the treated RS show stability during the period of 30 min. The relaxation spectra of composites were obtained using the plots of G' and G'' data versus the 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 (v_e) of the composites were calculated.⁵⁵ Table III shows the obtained parameters from the relaxation spectrum.

$$\eta_0 = \sum \lambda_i G_i \quad (1)$$

$$G_N^0 = \sum G_i \quad (2)$$

$$\bar{\lambda} = \frac{\sum \lambda_i^2 G_i}{\sum \lambda_i G_i} \quad (3)$$

$$v_e = \rho_a/M_e, \quad M_e = \rho RT/G_N^0 \quad (4)$$

where v_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. ρ and ρ_a for PLLA are 1.248 and 1.290 g/cm^3 ⁵⁶ and for starch are 1.5 and 1.498 g/cm^3 , respectively.⁵⁷ For the composites with 50:50 PLLA/starch, ρ and ρ_a need to be calculated based on mixture laws, which are 1.374 and 1.394, respectively.

The zero shear viscosity shows larger value for ARS-filled samples and the entanglement density calculation shows that the ARS-filled samples exhibit the highest level of entanglement among the samples indicating that ARS acts as a physical cross-linker and with the increase in the filler content, both η_0 and v_e are increased in all the composites except the untreated RS samples. However, the rate of increase is higher in the ARS-filled samples, which is a rheological proof for the mechanical and thermal results.

TABLE IV
Viscoelastic Parameters and Contact Angles of PLLA/Starch/RS-Based Composites

Sample	η_0^a (Pa·s) $\times 10^{-5}$	G_N^0 (Pa) $\times 10^{-4}$	$\bar{\lambda}^a$ (s)	v_e^a (g·mol/cc)	Theta M ^b (Deg)
PSRS0	—	—	—	—	71.3
PSRS1	0.4	6.40	8.21	17.2	87.2
PSRS2	0.5	8.20	8.15	22.11	87.0
PSRS3	0.7	7.04	8.59	18.96	86.9
PSRS4	0.34	6.29	8.01	16.95	87.6
PSRS5	1.1	16.2	8.03	43.59	85.4
PSRS6	1.9	24.4	8.03	65.73	83.1
PSRS7	3.2	26.5	8.64	71.37	89.7
PSRS8	5.3	36.8	8.74	99.19	91.6
PSRS9	8.9	49.3	8.88	132.76	94.3
PSRS10	2.9	23.1	8.76	62.19	90.3
PSRS11	12.6	61.7	8.80	166.05	95.2
PSRS12	30.4	117.1	8.81	314.34	97.3
PSRS13	2.1	16.8	8.77	45.37	91.4
PSRS14	7.1	45.8	8.83	123.61	93.4
PSRS15	12.6	55.6	8.91	149.84	95.8

^aObtained from rheology.

^bObtained from contact angle.

The effect of treatment can be seen in the rheological data, as the untreated RS entanglement with matrix is increased up to 10% of filler content and then is decreased, but in all the treated samples this entanglement would be increased with increase in the filler content and nearly all the entanglement densities are higher than the RS-filled samples, which is a proof of physical cross-linking between matrix and filler. The mean relaxation time is the ratio of the elastic and viscous response and is quite similar in all the samples, although it shows a small increase upon addition of filler.

CONTACT ANGLE

The surface behavior of benzylated samples were measured through contact angle (theta M) and the results are presented in Table IV. As can be seen, with the addition of filler, the contact angle is increased for all the samples; however, as can be seen, the larger contact angles belongs to the ARS-filled samples as expected, and with an increase in the filler content, the paste effect of lignin has made the structure resistant against the water absorbance. Moreover, the crystallinity of these samples was increased as previously described in the thermal studies. The RS-filled samples showed a descending trend with increasing the filler content. However, there can be suggested an opposing effect for lignin and silica, so the contact angle shows lower values. The contact angle of HWRS-filled samples was also decreased upon an increase in filler content, and based on the mechanical and thermal properties, since this treatment has removed waxes and a part of silica particles, with an increase in the content the reduction in contact angle would be more comparable with the RS-filled samples. The BRS-filled samples show an increase in the contact angle with rise in the filler content and the same trend is seen for the ABRS-filled samples; however, the contact angles in the ABRS-filled samples are higher than the BRS-filled

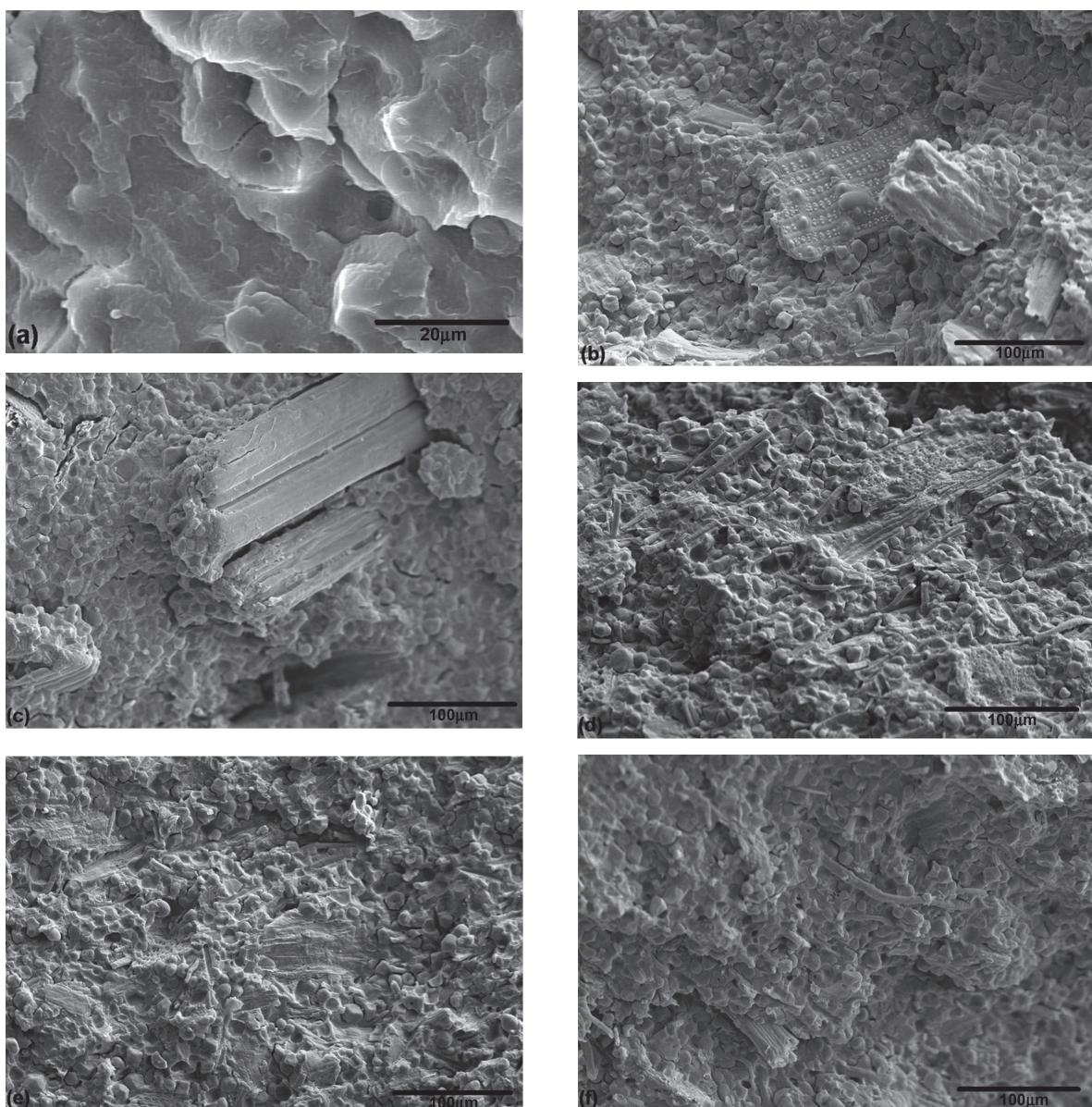


FIGURE 4. SEM micrographs of prepared composites: (a) PSRS0, (b) PSRS3, (c) PSRS6, (d) PSRS9, (e) PSRS12, and (f) PSRS15.

samples, due to the complete removal of lignin and higher crystallinity of ABRS-filled samples.

MORPHOLOGICAL PROPERTIES

Figure 4 shows the SEM micrographs of samples filled with different types of fillers treated by different methods. The PLA/starch composite without any filler has a uniform fractured surface. The interaction between PLA and starch phases is observable in Fig. 4a. On the other hand, Fig. 4b shows the sample filled with 15% RS (PSRS3) without any treatment. The PLA/starch composite and the filler phases are completely separated and a good interaction between PLA and starch was established. Moreover, the silica particles on the surface of filler can be evidently observed. In Fig. 4c, the microstructure of PSRS6

is shown. The filler is treated by hot water and more uniform filler surface in this case shows the removal of silica from the filler and the expanded structure allows lignin to be released out of the structure of RS. Figure 4d shows the SEM micrograph of PSRS9 that contains BRS as a filler. It is clear that bleaching has destroyed the filler structure and has removed lignin. Some voids in the filler structure are because of the delignification process. Figure 4e shows ARS-filled sample PSRS12. As can be seen, the structure of filler is changed in compared with the RS- and HWRS-filled samples, although a strong filler and matrix interaction due to the lignin's paste effect can be observed. Finally, the ABRS-filled sample PSRS15, which is almost lignin free, is depicted in Fig. 4f. The alkali treatment and bleaching could separate the fibers of the filler leading to a better interaction between cellulose chains and starch structure. The more interacted surface is obvious, as shown in Fig. 4f.

Conclusions

RS was treated using different environments including, hot water, alkali, bleaching, and alkali bleaching treatment. The results reveal that increasing the filler content and the different treatments can improve the mechanical, thermal, and rheological properties, as well as surface behavior compared with the unfilled PLA/starch. The mechanical properties reveal that 5–10% of different treated RS may be used in composite that may result in improvement of the tensile properties, charpy impact, elastic modulus, as well as hardness. Generally, due to the effect of silica and lignin in the RS, the properties were improved. It was found that T_g was decreased and crystallinity was increased with the addition of fillers, although ARS-filled samples show a negative T_g and high crystallinity related to the opposing effect of lignin. Based on the rheological studies, entanglement densities of samples were increased upon addition of the filler, and the highest values were seen for the ARS-filled samples among the other composites. Finally, surface behavior of the composites showed an increase in the hydrophobicity of all the composites, although ARS-, BRS-, and ABRS-filled samples showed an ascending trend, while RS- and HWRS-filled samples showed a descending trend. The treated RSs can be used as cost-effective fillers while the obtained composites with opted properties, especially ARS, can be used in the food packaging and biomembranes.

Acknowledgments

The authors would like to extend their gratitude to the Iran National Science Foundation for their valuable support and funding of this project.

References

- Müller, C.; Townsend, K.; Matschullat, J. *Sci Total Environ* 2012, 416, 464–467.
- Imre, B.; Pukánszky, B. *Eur Polym J* 2013, 49(6), 1215–1233.
- Agrawal, A. D. *Indira Mana. Rev* 2013, 7(1), 17–31.
- Cheung, Y. W.; Dobreski, D. V.; Turner, R.; Wheeler, M.; Handa, Y. P. Google Patent, US7872056 B2, 2011.
- Williams, P. T.; Onwudili, J. *Energy Fuels* 2006, 20(3), 1259–1265.
- Eastman, J. E.; Moore, C. O. Google Patent, US4465702 A, 1984.
- van Milgen, J.; Noblet, J.; Dubois, S. *J Nutr* 2001, 131(4), 1309–1318.
- Ghanbarzadeh, B.; Almasi, H.; Entezami, A. A. *Ind Crops Prod* 2011, 33(1), 229–235.
- Mohammadi-Rovshandeh, J.; Pouresmael-Selakjani, P.; Davachi, S. M.; Kaffashi, B.; Hassani, A.; Bahmeyi, A. *J Appl Polym Sci* 2014, 131(22), 41095.
- Shirai, M. A.; Grossmann, M. V. E.; Mali, S.; Yamashita, F.; Garcia, P. S.; Müller, C. M. O. *Carbohydr Polym* 2013, 92(1), 19–22.
- Davachi, S. M.; Kaffashi, B. *Polym-Plast Technol Eng* 2015, 54(9), 944–967.
- Torabinejad, B.; Mohammadi-Rovshandeh, J.; Davachi, S. M.; Zamanian, A. *Mater Sci Eng C* 2014, 42, 199–210.
- Davachi, S. M.; Kaffashi, B.; Zamanian, A.; Torabinejad, B.; Ziaeirad, Z. *Mater Sci Eng C* 2016, 58, 294–309.
- de Carvalho, F. P.; Isabel Felisberti, M.; Oviedo, S.; Alfredo, M.; Davila Vargas, M.; Farah, M.; Fortes Ferreira, M. P. *J Appl Polym Sci* 2012, 123(6), 3337–3344.
- Tong, J. Y.; Royan, N. R. R.; Ng, Y. C.; Ab Ghani, M. H.; Ahmad, S. *Adv Mater Sci Eng* 2014, 2014, Article ID 938961.
- Qin, L.; Qiu, J.; Liu, M.; Ding, S.; Shao, L.; Lü, S.; Zhang, G.; Zhao, Y.; Fu, X. *Chem Eng J* 2011, 166(2), 772–778.
- Chun, K. S.; Husseinsyah, S.; Osman, H. *J Polym Res* 2012, 19(5), 1–8.
- Lin, L.; Yan, R.; Jiang, W.; Shen, F.; Zhang, X.; Zhang, Y.; Deng, S.; Li, Z. *Appl Biochem Biotechnol* 2014, 173(2), 409–420.
- Sarkar, N.; Aikat, K. *J Microbiol Biotechnol Res* 2012, 2(5), 717–726.
- Ghaffar, S. H.; Fan, M. *Int J Adhes Adhes* 2014, 48, 92–101.
- Cao, X.; Chen, Y.; Chang, P. R.; Muir, A. D.; Falk, G. *Express Polym Lett* 2008, 2(7), 502–510.
- Kamoun, A.; Jelidi, A.; Chaabouni, M. *Cem Concr Res* 2003, 33(7), 995–1003.
- Davachi, S. M.; Kaffashi, B.; Roushandeh, J. M. *Polym Adv Technol* 2012, 23(3), 565–573.
- Davachi, S. M.; Kaffashi, B.; Roushandeh, J. M.; Torabinejad, B. *Mater Sci Eng C* 2012, 32(2), 98–104.
- Liu, J.; Jia, C.; He, C. *AASRI Procedia* 2012, 3, 89–94.
- Hwang, S. W.; Shim, J. K.; Selke, S.; Soto-Valdez, H.; Rubino, M.; Auras, R. *Macromol Mater Eng* 2013, 298(6), 624–633.
- Wu, R.-L.; Wang, X.-L.; Li, F.; Li, H.-Z.; Wang, Y.-Z. *Bioresour Technol* 2009, 100(9), 2569–2574.
- Rahnama, N.; Mamat, S.; Shah, U. K. M.; Ling, F. H.; Rahman, N. A. A.; Ariff, A. B. *BioResources* 2013, 8(2), 2881–2896.
- Binod, P.; Satyanagalakshmi, K.; Sindhu, R.; Janu, K. U.; Sukumaran, R. K.; Pandey, A. *Renew Energy* 2012, 37(1), 109–116.
- Kamel, S. *Polym Adv Technol* 2004, 15(10), 612–616.
- García, N. L.; Lamanna, M.; D'Accorso, N.; Dufresne, A.; Aranguren, M.; Goyanes, S. *Polym Degrad Stab* 2012, 97(10), 2021–2026.
- Chen, L.; Qiu, X.; Xie, Z.; Hong, Z.; Sun, J.; Chen, X.; Jing, X. *Carbohydr Polym* 2006, 65(1), 75–80.
- Lisperguer, J.; Perez, P.; Urizar, S. *J Chil Chem Soc* 2009, 54(4), 460–463.
- Anjum, N.; Ajit Prasad, S. L.; Suresha, B. *Adv Tribol* 2013, 2013.
- Wen, X.; Lin, Y.; Han, C.; Zhang, K.; Ran, X.; Li, Y.; Dong, L. *J Appl Polym Sci* 2009, 114(6), 3379–3388.
- Yang, J.; Zhao, J.-J.; Han, C.-R.; Duan, J.-F. *Compos Sci Technol* 2014, 95, 1–7.
- Rosa, S. M. L.; Santos, E. F.; Ferreira, C. A.; Nachtigall, S. M. B. *Mater Res* 2009, 12(3), 333–338.
- Lee, S.-Y.; Yang, H.-S.; Kim, H.-J.; Jeong, C.-S.; Lim, B.-S.; Lee, J.-N. *Compos Struct* 2004, 65(3), 459–469.
- Ismail, H.; Edyham, M. R.; Wirjosentono, B. *Polym Test* 2002, 21(2), 139–144.
- Mohammadi Rovshandeh, J.; Ekhlaei Kazaj, K.; Hosseini, A.; Pouresmael Selakjani, P. *Iran J Chem Chem Eng* 2014, 33(4), 107–116.
- Yang, H.-S.; Kim, H.-J.; Son, J.; Park, H.-J.; Lee, B.-J.; Hwang, T.-S. *Compos Struct* 2004, 63(3), 305–312.
- Hejazi, I.; Seyfi, J.; Sadeghi, G. M. M.; Davachi, S. M. *Mater. Des.* 2011, 32(2), 649–655.
- Seyfi, J.; Hejazi, I.; Sadeghi, G. M. M.; Davachi, S. M.; Ghanbar, S. *J Appl Polym Sci* 2012, 123(4), 2492–2499.
- Fang, J.; Ma, X. *J Zhejiang Univ Sci B* 2006, 7(4), 267–271.
- Patra, A.; Bisoyi, D. K. *J Mater Sci* 2011, 46(22), 7206–7213.
- Sahoo, S.; Misra, M.; Mohanty, A. K. *Composites, Part A* 2011, 42(11), 1710–1718.
- Li, J.; He, Y.; Inoue, Y. *Polym Int* 2003, 52(6), 949–955.
- Siti Rabiatull Aisha, I. *J Mech Eng Sci* 2012, 2, 181–186.
- Prakobna, K.; Galland, S.; Berglund, L. A. *Biomacromolecules* 2015, 16(3), 904–912.
- Zhang, M.; Jin, J.; Ogale, A. A. *Chm Biomolecular Graduate Research Symposium*, 2014.
- Ghatak, H. R. *Ind Crops Prod* 2013, 43, 738–744.

RESEARCH ARTICLE

52. Rencoret, J.; Marques, G.; Gutiérrez Suárez, A.; Jiménez-Barbero, J.; Martínez Ferrer, Á. T.; del Río Andrade, J. C., 17th International Symposium on Wood, Fibre and Pulping Chemistry; Vancouver (Canada), 2013.
53. Azarmgin, S.; Kaffashi, B.; Davachi, S. M. *Int Polym Process* 2015, 30(1), 29–37.
54. Pacetti, S. D.; Stewart, G. S.; Gong, V. M.; Bellam, C.; Weldon, L. M. Google Patent, US8562669 B2, 2013.
55. Ramkumar, D. H. S.; Bhattacharya, M. *Polym Eng Sci* 1998, 38(9), 1426–1435.
56. Ma, P. X.; Zhang, R. *J Biomed Mater Res* 2001, 56(4), 469–477.
57. Benczedi, D.; Tomka, I.; Escher, F. *Macromolecules* 1998, 31(9), 3055–3061.
58. Davachi, S. M.; Kaffashi, B. *Int J Polym Mater Polym Biomater* 2015, 64(10), 497–508.