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Chemical and Nanomechanical Analysis of Rice Husk Modified by ATRP-Grafted Oligomer

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Abstract

Rice husk (RH), an abundant agricultural residue, was reacted with 2-bromoisobutryl bromide, to convert it to a heterogeneous polyfunctional macroinitiator for Atom Transfer Radical Polymerization (ATRP). The number of active sites placed on the RH surface was small, but they were ATRP active. Non-polar methyl methacrylate (MMA) and polar acrylonitrile (AN) were polymerized from the RH, and a sequential monomer addition was used to prepare an amphiphilic PMMA-b-PAN copolymer on RH surface. FTIR qualitatively confirmed the grafting. Gravimetric and XPS analysis of the different RH surface compositions indicated thin layers of oligomeric PMMA, PAN, and PMMA-b-PAN. The modified surfaces were mapped by nanomechanical AFM to measure surface roughness, and adhesion and moduli using the Derjaguin-Muller-Toropov model. RH grafted with MMA possessed a roughness value of 7.92, and a hard and weakly adhering surface (13.1 GPa and 16.7 nN respectively) while RH grafted with AN yielded a roughness value of 29 with hardness and adhesion values of 4.0 GPa and 23.5 nN. The PMMA-b-PAN modification afforded a surface with a roughness value of 51.5 nm, with hardness and adhesion values of 3.0 GPa and .75.3 nN.

Keywords

Rice husk; nanomechanical; heterogeneous ATRP; macroinitiator; surface modification; grafting

Introduction

Utilization of biomass is of increasing importance because of the limited quantities of fossil feedstocks ⁽¹⁾. Cellulose rich biomass is increasingly important as a potential alternative fuel feedstock, but also as a chemical feedstock. Cellulose, hemicelluloses and lignins can be broken down into smaller compounds or, given their high functionality, are suitable for chemical derivatization ^(2,3).

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While wood resources are abundant in North America and have a long history of use as reinforcements, more recently it has become of great interest as a source of chemical feedstocks. But, for those regions of the world that do not have abundant forest resources rice husk (RH) is a more convenient biomass resource. RH contains 25–35% cellulose, 8–21% hemicelluloses, 26–31% lignin, 15–17% amorphous silica and waxes, and 2–5% of other soluble substances⁽⁴⁻⁷⁾.

Like wood, RH can be used as a resource for chemical feedstocks or as reinforcement. For example, Silvia et al.⁽⁸⁾ mercerized RH with NaOH and then acetylated the RH surface using acetic acid. This was done to improve the RH compatibility with non-polar polymers for use in composites. Emiliano et al.⁽⁹⁾ modified of RH with NaOH followed by H₂O₂ (bleaching) and found it to be an efficient treatment to partially eliminate hemicelluloses, lignin and silica from the RH. Rozman et al.⁽¹⁰⁾ chemically modified RH with glycidyl methacrylate, maleic anhydride and succinic anhydride, and Wong et al.⁽¹¹⁾ reported the modification of RH using different carboxylic acids (citric, salicylic, tartaric, oxalic, mandelic, maleic and nitrilotriacetic acid).

Grafting studies of oligomers or polymers onto RH surfaces do not appear to have been reported before, though polymers have been grafted to cellulose and even to wood fibers^(12,13). However, RH is a more complex material than wood, and is compositionally ‘assymetric’ having one side that is silica enriched and an inner surface that is waxy. So, grafting to RH may be significantly less efficient than grafting to wood.

Typical grafting strategies can be described as occurring by (1) the ‘grafting through’ process, (2) the ‘grafting onto’ process and (3) the ‘grafting from’ process. Common examples of the ‘grafting through’ technique include copolymerizing pre-made vinyl-functionalized cellulose with comonomers.⁽¹³⁾ The ‘grafting onto’ technique requires the pre-synthesis of endfunctionalized linear chains that are subsequently covalently bonded to the cellulose.⁽¹²⁾ This strategy usually suffers from low grafting density due to steric hindrance. The ‘grafting from’ technique, involves the growth of polymer grafts directly from the substrate surface, and has been extensively investigated by step growth and by chain growth processes.

Radicals can be conveniently generated along cellulosic backbones in the presence of chemical initiators or by applying irradiation. Both methods afford the straightforward preparation of cellulosic-based graft copolymers through ‘grafting from’ free radical polymerization. The irradiation route is simple but characterized by cellulosic backbone degradation. Neither method gives control over the graft molecular weight, molecular weight distribution (PDI), or the control needed to obtain block copolymer grafts. That level of control is possible using controlled radical polymerization techniques (CRP), e.g. nitroxide-mediated polymerization⁽¹⁴⁾ (NMP), atom transfer radical polymerization^(15,16) (ATRP), or reversible addition-fragmentation chain transfer⁽¹⁷⁾ (RAFT). These methods are also tolerant of moisture and compatible with a large range of functional groups.

ATRP has advantages in “grafting from” reactions because the initiator can be anchored on the surface in advance, and its presence can be confirmed. Also, as with other CRPs, chain termination is reduced. Therefore, using CRP it is possible to tailor the surface properties of cellulosic-based materials by grafting oligomers or polymers with a variety of different monomers, including functionalized monomers, while exercising some control over graft length,. Therefore, through appropriate monomer selection and reaction design, many different surface compositions⁽¹⁸⁾ and architectures^(15,19) can be placed on surfaces. ATRP has already been employed to graft from surfaces such as glass,⁽²⁰⁾ gold,^(21,22)

magnetite⁽²³⁾, silica⁽²⁴⁻²⁶⁾ and from macroscopic cellulose fibers⁽²⁷⁻³²⁾, pulp⁽³³⁾, and powder.⁽³⁴⁾

Although several examples of ATRP polymerization from different forms of cellulose surfaces exist in the literature, no precedent exists for ATRP-grafting from RH. RH is 25-35% cellulose, so in principle the reaction should proceed in the same way as when it is performed on cellulose fiber. However, the surfaces of cellulose pulp or fibers, even in a suspension, are more readily available than the cellulose within the RH due to the asymmetric and compositionally heterogeneous RH anatomy.^[35] The external surface of the RH is a thick 2-5 μm silica layer, covered by a very thin layer of cellulose. The other surface is waxy and shields additional celluloses⁽³⁶⁾. The surfaces are designed to serve as a barrier to gases and moisture to protect the rice kernel inside.

Therefore, the waxy layer needs to be at least partially removed to expose the thicker layer of cellulose below it to expose its hydroxyls for modification, but this is also likely to remove all or part of the thin (~ 50 nm)^[37] cellulose layer on the external surface. Some of these cellulose domains may even be sterically unavailable because of the presence of silica nanodomains dispersed within the RH. The silica domains are also expected to make the RH more dense and less prone to solvent swelling than wood cellulose, though for this work the silica was considered desirable, despite the fact that it is abrasive to some processing equipment, because it may allow composites to maintain some of the barrier properties of RH. For all these reasons, RH cellulose is expected to be less available for modification than wood pulp cellulose.

In this work we describe an ATRP route to give controlled polymerization from RH surfaces. While this route is unlikely to be commercially viable, the ultimate application for the modified RH is for use in fundamental studies of the effect of controlled interface modifications on composite properties. Therefore, the surface compositions must be controlled and thoroughly characterized before it is possible to understand the effect of variables such as interface thickness, composition, rigidity, etc. on selected composite properties, particularly moisture properties (to be described in a paper to follow). The purpose of this paper is to describe the manipulation and surface and nanomechanical characterizations of the RH surface. Gaining an understanding of the effects of these kinds of modifications on the properties of the reinforcement, particularly biobased reinforcement that is prone to moisture uptake and biological attack, may give access to a new range of improved composites.

2. Experimental

2.1. Materials

Rice Husk (RH, 80 mesh) was donated by Rice Hull Specialty Products (Stuttgart, Arizona). 2-bromoisobutryl bromide (BiBB) pyridine (99.5%, extra dry over molecular sieves), and dimethylformamide (DMF, 99.8%, extra dry over molecular sieve) were purchased from Acros Organics (New Jersey), N,N,N',N'',N'-Pentamethyldiethylenetriamine (PMDETA, 99%) ethyl α -bromoisobutyrate (EBiB), and copper (I) bromide (98%,) were from Aldrich Chemicals (Milwaukee, WI) were used as received. Methyl methacrylate (MMA, 99%, Aldrich) and acrylonitrile (AN, 99%, Acros) were distilled under vacuum just before use. Dichloromethane (DCM) and tetrahydrofuran (THF) were from Fisher Scientific (Pittsburgh, PA) and were degassed by bubbling nitrogen for 20 min just before use,

2.2. Instrumentation

2.2.1. Fourier Transform Infra-Red (FTIR)—Fourier transform infra-red (FTIR) spectra were taken on a Perkin-Elmer Spectrum One FTIR Spectrometer from 4,000 to 650

cm⁻¹ (4.0 cm⁻¹ resolution) were used to confirm changes in functional groups on the chemically modified RH.

2.2.2. X-ray Photon Spectroscopy (XPS)—X-ray photon spectroscopy (XPS) were performed in a Surface Science Instruments S-probe spectrometer that uses monochromatized Al K α X-ray and a low energy electron flood gun for charge neutralization of non-conducting samples. Samples were prepared by lightly pressing samples of the material to be analyzed onto double-sided tape that had first been affixed to a silicon wafer. The silicon wafers were fixed to the sample stage by double-sided tape. The samples were run as insulators and the X-ray spot size for each acquisition was approximately 800 μ m. Pressure in the analytical chamber was maintained below 5×10^{-9} Torr. The pass energy for survey and detail spectra (to calculate composition) was 150 eV. Pass energy for high resolution spectra was 50 eV. The take-off angle (the angle between the sample normal and the input axis of the energy analyzer) was $\sim 55^\circ$ (55° take-off angle at ~ 50 Å sampling depth). Then Service Physics ESCA2000A Analysis Software was used to determine peak areas above a linear background in order to calculate the elemental compositions using elemental sensitivity factors, and to perform peak fitting on the high-resolution spectra. The binding energy scale of the spectra was calibrated by assigning the hydrocarbon C1s peak to a binding energy of 285.0 eV.

2.2.3. Atomic Force Microscopy (AFM)—Peak force tapping mode was used in Dimension C° Icon C° AFM, to generate nanomechanical maps of sample surfaces. In this mode, at each pixel, the AFM probe generates a small indentation on the sample surface and a force-separation curve is collected (Figure 1)⁽³⁸⁾. In this technique, by using the maximum indentation force (peak force) as the feedback signal, a smaller deformation can be generated on the sample surface, which increases the imaging resolution to a great extent.

On each curve, peak force and adhesion force are the maximum and minimum force values respectively. Deformation is the difference of separation at zero force and peak force. The Derjaguin-Muller-Toropov (DMT) modulus is calculated by fitting the DMT model⁽³⁹⁾ to the initial part of the retrace curve:

$$F = \frac{4}{3} E^* \sqrt{Rd^3} + F_{adh} \quad \text{Eq 1}$$

where F is the force, R is the tip radius, d is the separation, F_{adh} is the adhesion force, and E^* is the reduced elastic modulus. By assuming infinite elastic modulus for the tip (E_{tip}) and knowing the Poisson's ratio of the sample ν_s , the young's modulus for the sample (E_s) can be calculated:

$$E^* = \left(\frac{1 - \nu_s^2}{E_s} + \frac{1 - \nu_{tip}^2}{E_{tip}} \right)^{-1} \quad \text{Eq 2}$$

The generated force-separation curves are used to create quantitative nanomechanical maps (DMT modulus, adhesion and deformation) simultaneously with a topography map. For this purpose, several calibration steps are completed before imaging the sample. First, the deflection sensitivity of the cantilever was measured by indenting a hard sapphire surface (56.67 nm/V). Then, the cantilever spring constant was measured using thermal tuning method ($K = 38.9$ N/m). And finally, the tip radius was measured by changing the tip radius in the AFM software, while imaging a standard polymer sample with known mechanical properties, until the desired value for the DMT modulus was obtained ($R = 4.5$ nm).

All AFM images were collected in air under ambient condition and consisted of 512×512 pixels with scanning rates <1 Hz. The peak force was set such that the resultant average deformation in each scan line was not more than 3 nm. Other scanning parameters include integral and proportional gains, and are automatically set by the AFM software. Although one set of AFM images from each sample is presented here, the same trend was observed during scanning other regions of the samples.

2.3. Alkali treatment of RH

The RH was soaked in 18 wt.% solution of NaOH. The volume of the solution was equivalent to 1.5 times the volume of the filler. Immersion time was 0.5 h × 2. Once this time was over, the fillers were separated from the solution and washed with water to remove the NaOH. The RH was dried at 75 °C for 48 h.

2.4. Immobilization of the ATRP initiator on the RH surface (RH-Br)

An ATRP-initiating bromine (BiBB) was grafted to the surface of RH by mixing RH (5.0 g), DMF (50 mL), and pyridine (10.0 mL, 124 mmol) in a round-bottom flask. The mixture was magnetically stirred at room temperature under nitrogen gas. Then BiBB was added dropwise (10.0 mL, 80.9 mmol) over a period of 25 min. After the addition was completed the reaction mixture was stirred an additional 24 h at 80 °C. The surface-initiated RH (RH-Br) was removed from the reaction mixture, washed thoroughly with acetone and deionized water several times and dried at 50 °C for 48 h. By gravimetric analysis the moles of ATRP-active Br groups introduced to the RH was found to be ~0.2 mmol/5 g RH (0.04 mmol/1 g RH), or a 0.02 % yield overall based on moles of starting BiBB.

2.5. Grafting of AN from RH-Br (RH-g-PAN)

To a round bottom flask were added RH-Br (1.0 g, ~0.04 mmol active Br sites), CuBr (118.8 mg, 0.828 mmol), PMDETA (0.35 mL, 1.67 mmol) and DMF (50 mL). The mixture was magnetically stirred for 30 min at room temperature and under nitrogen to allow copper-ligand complex formation. AN (26.4 mL, 403 mmol) and EBiB initiator (0.132 mL, 0.899 mmol) were then added. The temperature of the reaction mixture was raised to 80 °C and maintained at that temperature for 24 h. The RH with surface grafted PAN (RH-g-PAN) was removed from the solution, washed thoroughly with deionized water and acetone and dried at 50 °C for 48 h. Yield: 1.16 g. Theoretical X_n if all Br sites initiated at the time and reacted for the same length of time is 10, 075. Calculated X_n (gravimetrically) assuming all Br sites reacted equally is $X_n \approx 76$.

2.6. Grafting of MMA from RH-Br (RH-g-PMMA)

To a round bottom flask were added RH-Br (2.5 g, ~0.1 mmol active Br sites), CuBr (300 mg, 2.1 mmol) and PMDETA (0.9 mL, 4.31 mmol) containing a 4:1 mixture solution of DMF (100 mL) and DCM (25 mL). The mixture was magnetically stirred for 0.5 h at room temperature and under nitrogen gas. MMA (45.0 mL, 422.5 mmol) and the initiator, EBiB (0.3 mL, 2.044 mmol), were then added. The temperature of the reaction mixture was raised to 80 °C and kept for 24 h. The RH with surface grafted PMMA (RH-g-PMMA) was removed from the solution, washed thoroughly with deionized water, acetone and THF several times and dried at 50 °C for 48 h. Yield: 2.675 g. Theoretical X_n assuming all Br sites initiated and reacted at the time for the same length of time is 4,224. Calculated X_n (gravimetrically) assuming all Br sites reacted equally is $X_n \approx 18$.

2.7. Grafting of MMA and PAN from RH-Br (RH-g-PMMA-b-PAN)

To a round bottom flask was added RH-g-PMMA (1.0 g, ~0.04 mmol active Br sites), CuBr (118.8 mg, 0.828 mmol), PMDETA (0.35 mL, 1.67 mmol) and DMF (50 mL). The mixture

was magnetically stirred for 30 min at room temperature and under nitrogen gas. AN (26.4 mL, 403 mmol) and EBiB initiator (0.132 mL, 0.899 mmol) were then added. The temperature of the reaction mixture was raised to 80 °C and kept at that temperature for 24 h. The product, RH-g-PMMA-b-PAN was removed by filtration, washed thoroughly with deionized water and acetone and dried at 50 °C for 48 h. Yield: 1.22 g. The overall reaction steps of ATRP initiator immobilization and grafting of RH are shown in Fig. 2. For all grafted samples, the increase in the mass of the extracted samples from that of the original RH yielded the grafting percentage. Calculated (gravimetrically, assuming all initial RH-Br sites remained active) X_n AN segment ≈ 103 .

3. Results and Discussion

ATRP is a useful technique for grafting from a complex cellulosic material like RH because once the waxy inner layer is removed the primary hydroxyl groups on the cellulose surface can be converted to α -bromoesters, which are excellent initiators for ATRP polymerization. Fig. 2 outlines the synthetic route used to produce the surface-grafted α -bromoester, RH-Br. The RH-Br functioned successfully as a heterogenous ATRP macroinitiator, being insoluble in the solvent. Despite possessing a relatively low number of active Br sites was then used to initiate three grafting-from polymerizations to give a hydrophobic RH-g-PMMA material, a hydrophilic RH-PAN material, and an amphiphilic RH-g-PMMA-b-PAN material. These modifications were made for use in studies of the effects of surface-modified RH on the stability of composite interfaces when this reinforcement is used instead of unmodified RH. Before these studies can be done however, the surfaces of unmodified and modified RH must be thoroughly characterized, which is the purpose of this work.

FTIR spectra (Fig. 3) qualitatively support the modification sequence outlined in Fig. 2 to produce the RH-Br macroinitiator, and then give the RH-g-PAN, RH-g-PMMA, and RH-g-PMMA-b-PAN respectively through ATRP. The key features in the FTIR supporting the modification sequences are: a new band at 1730 cm^{-1} in the RH-Br spectrum, which is attributed to the carbonyl vibration of the ester group in RH-Br (sequence 2a); an increase in the intensity of the carbonyl band in the spectrum of RH-g-PMMA compared to the RH-Br attributed to the grafting of MMA (sequence 2b); the appearance of a new absorption band at 2242.8 cm^{-1} in the RH-g-PAN spectrum, attributed to the nitrile group of AN (sequence 2c); and the presence of both the increased carbonyl band from the PMMA as well as the nitrile band of the AN in the spectrum of RH-g-PMMA-b-PAN (sequence 2d).

The FTIR data qualitatively support the successful modifications proceeded as proposed, but do not quantify the modifications or the distribution of the modifications. Therefore, AFM and XPS were also used to characterize the different RH surfaces to understand how well the RH surfaces are covered with grafted polymer, and if the RH-g-PMMA-b-PAN is appropriately layered to give a hydrophobic PMMA layer at the RH and a PAN layer on the surface.

AFM gave both qualitative and quantitative information on the surfaces of modified and unmodified RH. Fig. 4 and 5 show representative adhesion and DMT modulus maps of the samples. Fig. 4a shows the complex features and anatomy of unmodified RH. The basic anatomy is obscured in the images of the different grafted RH (Fig 4b-d). The roughness of the samples was also measured from the topography images (given in Supplemental Information, Fig. 1S). Average roughness (R_a) was equal to 7.92, 29.8 and 51.5 nm on RH-PMMA, RH-PAN and RH-g-PMMA-b-PAN surfaces respectively. This trend also correlates with the extent of grafting from the surface, indicating that the surfaces may not be uniformly covered with grafted polymer. For example, the surface of unmodified RH is initially relatively rough (Fig. 4a), and grafting with MMA yielded oligomers with $X_n \approx 18$

(based on reacted mass and number of active grafting sites). This low molecular weight would not have had a significant effect on the surface roughness. By contrast, the AN modification yielded an $X_n \approx 76$, and the PMMA-b-AN copolymer $X_n \approx 103$. The increase in oligomer chain may have increased roughness without being sufficiently long to afford a uniform coating of the RH.

The adhesion test (Fig. 4a-d) shows that tip adhesion to the RH-PMMA surface (mean value 16.7 nN) is much less than to the surfaces of RH-g-PAN or RH-g-PMMA-b-PAN (mean value 23.5 and 75.3 nN respectively). This is because the PMMA surface is less polar and harder than the other surfaces and so adheres less to the AFM tip.

The DMT modulus values (Fig 5a-d) show that RH-g-PMMA has the highest modulus (mean 13.1 GPa) so it is the hardest surface. The RH-g-PAN surface is much softer than the RH-PMMA surface (mean value of only 4.0 GPa). These data correlate well with observations on the adhesion maps, since it is easier for the AFM tip to separate from a harder surface (lower adhesion force) than a softer one. Interestingly, the modulus of the RH-g-PMMA-b-PAN surface is the softest, at a mean value of 3.0 GPa. The RH-g-PMMA-b-PAN surface also has the thickest oligomer-modified layer. It is possible that the thin modulus of the RH-g-PMMA layer was influenced by silica, which exerts less influence as the thickness of the oligomer layer increases.

These data also supported the successful grafting reactions and non-uniform coverage of the RH surface. However, the sample surfaces in general are quite rough for AFM analysis, which makes imaging larger scan areas and the “transition region” between phases troublesome. Addressing these kinds of issues and improving quantitative analysis is the subject of ongoing research in the Yassar lab.

XPS provided detailed quantitative information about the changes in surface composition following grafting reactions. Fig. 6 shows representative XPS spectra of alkali-treated RH and RH-Br. The alkali-treated RH (Fig. 6a) exhibits 4 distinct lines: C 1s (285 eV), O 1s (533 eV), N 1s (402 eV) and Si 2p (103 eV) lines. Both O 1s and C 1s arise from carbohydrate components (e.g. celluloses and lignin) while Si 2p arises from the silica in the outer surface of RH, and the N 1s may be a contaminant. The RH-Br (Fig. 6b) spectrum shows the Br 3d (70 eV) line verifying the RH-Br is available for use as a heterogeneous ATRP macroinitiator.

The quantitative results from these XPS measurements are summarized in Table 1. The Br 3d signal, representing the surface active sites for ATRP, rises from 0 to 2.8 %. When the RH is converted to RH-Br the C 1s electron signal increases and the O 1s signal decreases, accounting for the increased C/O and C/Si ratios. The data verify the successful introduction of the ATRP initiator on the surface and its attachment through an ester bond from exposed RH hydroxyl groups. The reduction in Si 2p on the surface with the increase in C 1s shows the modified surface of the RH-Br is considerably more organic than the RH, even though the yield of active bromine sites introduced onto the surface is relatively small. The low yield of bromine sites is attributed to the non-uniform nature of the RH substrate. That is, the outside surface of RH possesses some thin cellulose layer on the surface that is likely to be at least partially degraded by the base washing. The inside layer is also thought to be mixed silica and cellulose, so the availability of primary hydroxyl units to be brominated on the RH is unlikely to be high. Bromination efficiency might be increased by improvements in conditions, but do not appear to be necessary to accomplish controlled modifications of the interface region between RH and a polymer matrix.

Fig. 1S (shown in Supplemental documents) shows a typical high-resolution C 1s spectra of alkali-treated RH and RH-Br. Analysis of the different carbon types (three for RH at 250.0,

286.4 and 288.7 eV, arising from (C-C, C-H), (C-O, C-OH) and (C=O), respectively and four from RH-Br at 285.0, 286.6, 288 and 289.4 eV, that are attributed to (C-C, C-H), (C-Br, C-O, C-OH), (C=O) and (O-C=O) respectively). These data with their relative percentages and binding energies are summarized in Table 2. The data show that approximately 9.5% of the surface carbons are in the α -bromoester groups that provide the ATRP active bromine sites. The linking to the cellulose is through its primary hydroxyl groups, and the number of C-C and C-H groups on the surface decreased (from 50.6 to 39.0%), while surface contributions from different C-O bonds increased.

The XPS survey spectra of RH-g-PMMA, RH-g-PAN and RH-g-PMMA-b-PAN are shown in Fig. 7. RH-g-PMMA shows strong C 1s and O 1s peaks at 285 eV and 534 eV respectively that are attributed to carbon and oxygen atoms of the grafted PMMA with possible contribution from carbohydrate components that are very near the surface or are not coated by PMMA. Weak lines are also found from Si 2p (100 eV) and Br 3d (69 eV). These peaks demonstrate incomplete surface coverage of the original silica surfaces of the RH. This indicates a low PMMA grafting percentage or a very thin PMMA layer, or the Si 2p regions would have been coated. Other minor lines (Cu 2p, N 1s and Cl 2p) are likely to be residual contaminants.

The RH-g-PAN and RH-g-PMMA-b-PAN spectra show a strong N 1s line at 399 eV that is contributed by the AN nitrogen. The intensity of O 1s, Si 2p and Br 3d lines are less than in RH-PMMA. This suggests the PAN chains are higher molecular weight and cover the RH surface more effectively than did the PMMA chains. Minor peaks for Cu 2p and F 1s are contaminants. The quantitative surface composition results are summarized in Table 3, along with percentages of the different monomers grafted to RH-Br, that were calculated as:

$$G\% = (W_g - W_o/W_o) \times 100 \quad \text{Eq 3}$$

Where W_g is the RH weight after grafting and W_o is the original RH weight.

Table 3 shows that the polymer-grafted samples possess a higher percentage of the C 1s electron than either the alkali-washed RH or RH-Br (Table 1). For RH-g-PMMA, the measured C/O ratio (2.78) is close to the theoretical ratio (2.5). This suggests that the uppermost layer of this structure is mostly PMMA, despite a low grafting efficiency (7%). The low MMA grafting efficiency may be due to its lower reactivity compared to acrylonitrile. At 60 °C the $k_p \times 10^{-3}$ of MMA is reported as 0.515 compared to 1.96 $\text{Lmol}^{-1}\text{s}^{-1}$, for AN.^[40] This lower reactivity is in part due to the large steric bulk of MMA (the Arrhenius factor in propagation, $A_p \times 10^{-7}$, is given as 0.087)^[40], reducing its ability to react with the ATRP active Br sites on the solid RH substrate. The XPS data, including the C/O ratio and the presence of the Si 2p (2%), along with the low G% confirm that the surface of the RH-g-PMMA is either incompletely covered by the polymer or in some locations on the RH-g-PMMA there is a carbon contribution from components in the RH underlayer.

As expected, a comparison of the surface composition of RH-g-PAN and RH-g-PMMA (Table 3) shows a significant decrease in the number of surface oxygen atoms, along with the corresponding increase in the number of observed nitrogen atoms. However, the lower Si 2p content (1.2, compared to 2.0 for RH-g-PMMA) supports the evidence of higher molecular weight chains and higher G% (16%) leading to a more efficient coverage of the RH surface. The higher grafting of AN may be due to its lower steric bulk compared to MMA, which may have facilitated a more efficient initiation of active Br sites, and a faster propagation rate. Interestingly, the observed C/N ratio in the surface of the RH-g-PAN (4) is greater than the theoretical value (3). The reason is unknown, but suggests that the PAN

chains have a conformation that gives an enriched nitrogen composition near the surface. This will be beneficial for interfaces with some composite matrices.

The RH-g-PMMA-b-PAN possessed the highest G% of measured (22%) and, the lowest quantity of Si 2p detected on the surface (Table 3) indicating the most complete coverage of the husk. The copolymerization succeeded in covering both the MMA chain segments and the silica domains that had remained uncovered in the RH-g-PMMA and the RH-g-PAN. The data in Table 3 also show that while some Br 3d initiating sites remained in the RH-g-PAN, no initiating Br 3d sites were detected in the RH-g-PMMA-b-PAN, so either these sites reacted or also were coated by copolymer.

Because the surface composition of the RH-g-PMMA-b-PAN is nearly identical to that of RH-g-PAN, this confirms that the amphiphilic block copolymer afforded a layered surface. The primary significance of this is that it proves that an amphiphilic copolymer can be produced on the RH surface by ATRP, despite the heterogeneous RH anatomy and composition. This too is a significant benefit for the intended application (biobased reinforcements in composites) because it demonstrates that the surface properties of modified RH can be modulated to impart a needed property or protection at the surface of the biological component while the surface exposed to the matrix can be designed for a different purpose, to interact effectively with a matrix material.

High-resolution C 1s XPS spectra for the RH-g-PMMA, RH-g-PAN, and RH-g-PMMA-b-PAN are given in the Supplemental Information (Fig. 2S). The data from those spectra are summarized in Table 4 (RH-g-PMMA) and Table 5 (RH-g-PAN and RH-g-PMMA-b-PAN). The four C 1s peaks centered at 285.0, 286.3, 287.1 and 289.0 eV, correspond to the different bonding situations of the carbon atoms in the PMMA repeat unit. The RH-g-PAN spectrum shows a small third peak at 288.4 eV, which is consistent with a $>\text{C}=\text{O}$ band seen in the underlying RH that is not seen in RH-g-PMMA-b-PAN. These data further confirms the coverage of the PMMA chain segments and proves both a thicker polymeric layer almost completely coating both the substrate in RH-g-PMMA-b-PAN unlike the case with the RH-g-PAN, thus confirming layering of the amphiphilic copolymer.

Conclusion

Commercial RH was reacted with BiBB to place ATRP active polymerization sites on the RH surface. Despite a relatively low yield of initiating groups on the RH surface, these groups were active, and able to polymerize MMA and AN. MMA gives a low grafting efficiency giving a low molecular weight graft oligomer. FTIR, XPS, and AFM all indicated successful modification of the surface, but AFM results suggest non-uniform coverage of the RH, particularly in the case of RH-g-PMMA. Nevertheless, XPS confirmed the surface was enriched in carbon with decreased O and Si, confirming a low-polarity surface was produced. Nanomechanical testing found the new surface to be rough and hard. AN was found to be more reactive in grafting from the RH surface, and gave a softer and highly nitrogen-enriched surface. Using sequential monomer addition it was possible to polymerize AN directly from the surface of the RH-g-PMMA, yielding an amphiphilic block copolymer grafted to the RH surface. This surface was compositionally very similar to that of the RH-g-PAN, and based on XPS analysis nearly completely covered the original RH surface as well as the PMMA chain segments. Composites prepared using RH bearing amphiphilic copolymers are expected to be able to blend well into polar materials and possess good interfacial adhesion with such materials while the inner non-polar PMMA component may help stabilize the RH against biological decay or debonding from moisture cycling.

Given the increasing demands for the use of biomass in place of petroleum-derived materials, and given the relative worldwide abundance of RH compared to forest resources, there may be many as-yet untapped applications for the use of RH biomass. Here for the first time the RH has been shown to be able to be converted into a heterogeneous and multifunctional ATRP initiator that can undergo controlled and sequential surface polymerizations. Also, the natural architecture of RH is intended to allow one surface to function as a barrier material to protect the rice kernel inside. Therefore, it may be possible to take advantage of the natural barrier properties of one side of the RH and the ability to induce controlled organic modification of the surfaces for many different applications.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

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Fig. 1. Analytical values obtained from a peak force-tapping mode in AFM. At each pixel, the AFM tip generates a small indentation on the sample surface, force-separation curves are made, and quantitative nanomechanical properties of the surface are measured.

Fig. 2. The synthetic strategy used in the surface modification of RH (a) conversion of hydroxyl groups to α -bromoesters, giving RH-Br (b) grafting of MMA on the surface, giving RH-g-PMMA (c) Grafting of AN on RH-Br giving RH-g-PAN ; and (d) grafting AN onto RH-g-PMMA , giving RH-g-PMMA-b-PAN .

Figure 3.
FTIR spectra of RH and the different modified RH species.

Fig. 4. AFM adhesion maps of: 500×500 nm² ungrafted RH (a) and 1×1 µm² RH-PMMA (b), RH PAN (c), and RH-g-PMMA-b-PAN (d).

Fig. 5. AFM DMT modulus maps of: 500×500 nm² ungrafted RH (a) and 1×1 μm² RH-PMMA (b), RH-PAN (c), and RH-g-PMMA-b-PAN (d)

Fig. 6. XPS survey spectra of alkali-treated RH (a, top) and RH-Br (b, bottom). (Axes numbers redrawn in Photoshop® for greater visibility.)

Figure 7.
XPS survey spectra of RH-g-PMMA, RH-g-PAN and RH-g-PMMA-b-PAN.

Table 1

Percentages of different elements, C/O and C/Si ratios of alkali-treated RH and RH-Br.

Rice Husk	Element surface composition (%)					Element ratio	
	C 1s	N 1s	O 1s	Si 2p	Br 3d	C/O	C/Si
Alkali-treated RH	55.5	2.0	37.0	5.5	-	1.50	10.09
RH-Br	63.7	3.1	28.2	2.2	2.8	2.26	28.95

Table 2

Identity, quantity, and binding energy of RH and RH-Br surface carbons.

Alkali-treated RH			RH-Br		
Binding energy eV	Bond	Carbon %	Binding energy eV	Bond	Carbon %
250.0	C-C, C-H	50.6	285.0	C-C, C-H	39.0
286.4	C-O, C-OH	29.9	286.6	C-Br, C-O, C-OH	37.9
288.7	C=O	19.6	288.0	C=O	13.6
			289.4	O-C=O	9.5

Table 3

Composition, grafting %, and C/O and C/N ratios of polymer-grafted RH surfaces

Rice Husk	Elemental surface composition % and Grafting %									Elemental ratio	
	C 1s	N 1s	O 1s	F 1s	Si 2p	Cl 2p	Cu 2p	Br 3d	G%	Observed	Theoretical
RH-g-PMMA	65.9	4.9	23.7	-	2.0	1.9	0.1	1.5	7	2.78	2.5
RH-g-PAN	72.9	18.2	7.0	0.8	1.2	-	-	0.2	16	4	3
RH-g-PMMA-b-PAN	74.3	19.5	4.8	0.7	0.5	-	0.3	-	22	3.8	3

Table 4

Binding energy, experimental percentage and theoretical value for the four carbon components of RH-g-PMMA

Different carbons	Binding energy (eV)	Carbon Bond	Experimental %	Theoretical %
C1	285.0	$-\underline{\text{C}}\text{H}_2\text{-C}\equiv$	37.1	40
C2	286.3	$-\text{CH}_2\text{-}\underline{\text{C}}\equiv$	30.8	20
C3	287.1	$-\text{O}\underline{\text{C}}\text{H}_3$	20.0	20
C4	289.0	$>\underline{\text{C}}=\text{O}$	12.2	20

Table 5

Binding energy, experimental percentage and theoretical value for different carbon components of PAN and PMMA-b-PAN grafted from the surface of RH

Carbon	Binding energy eV	Experimental %		Theoretical %
		Carbon Bond	RH-g-PAN RH-g-PMMA-b-PAN	
C1	285.0	<u>—</u> CH ₂ -CH(CN)-	22.6 28.1	33.33
C2	286.2-286.3	-CH ₂ - <u>CH</u> (CN)-	74.7 71.9	66.66
C=O	288.4	> <u>C</u> =O	2.7 -	-