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Research article

Lignin and biodegradable polymer blends with chemically treated biofiller for green thermoplastic composites

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Abstract. This study investigated the development of thermoplastic composites by incorporating crude lignin extracted from coir fiber waste, into poly(3-hydroxybutyrate-*co*-3-hydroxyvalerate) (PHBV), a biodegradable polymer. The extracted crude lignin was blended with PHBV as a matrix, and spent coffee grounds (SCG) were used as biofillers. SCG were chemically modified through sodium hydroxide (NaOH) treatment and maleic anhydride (MA) grafting to enhance their compatibility with the PHBV/lignin blend. Raw and modified SCG were characterized for their functional, morphological, and thermal properties before being incorporated. Thermoplastic biocomposites were prepared via melt compounding and compression molding and evaluated for water barrier, morphological, mechanical, and thermal properties. Results showed that MA-grafted SCG significantly enhanced PHBV-lignin properties, increasing tensile strength by 23.7% and thermal stability by 11.9% compared to the control matrix. Optimal performance was observed at 5% MA-grafted SCG filler loading. However, higher SCG concentrations (7%) led to filler agglomeration, negatively affecting the material properties. This research demonstrated the potential of utilizing agricultural and food waste to create high-performance thermoplastic composites for future applications in biodegradable packaging, contributing to the advancement of a circular economy and environmental sustainability.

Keywords: *biopolymer, extracted lignin, polymer blend, biofiller, compatibility*

1. Introduction

The environmental challenges posed by conventional petroleum-based plastics, such as their persistence in ecosystems and contribution to global pollution, have spurred the search for alternative materials with biodegradable and renewable properties [1]. In this context, biopolymers have gained significant attention as eco-friendly substitutes due to their ability to degrade naturally and their potential to reduce reliance on fossil-based feedstocks. Poly(3-hydroxybutyrate-*co*-3-hydroxyvalerate) (PHBV), a type of polyhydroxyalkanoate (PHA), is one of the most promising biodegradable biopolymers. PHBV is produced by microorganisms from renewable resources and exhibits favorable properties such as biodegradability, non-toxicity, and good biocompatibility [2]. These features make PHBV an ideal candidate for applications in packaging, and other industries

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focused on sustainability. However, despite these advantages, PHBV's relatively low mechanical strength, poor thermal stability, and high production cost limit its widespread use in practical applications [3].

To address these limitations, blending PHBV with other materials to form biopolymer-based blend composites has become a prominent strategy. In recent years, blending biodegradable aliphatic polyesters has attracted significant interest as a sustainable alternative to conventional polymers [4]. Among various reinforcing agents, lignin, a complex aromatic polymer abundant in plant cell walls, has attracted considerable interest as a natural filler for thermoplastic composites [5]. Lignin is widely available as a byproduct from the pulp and paper industry, as well as from other agricultural residues, as well as from agricultural residues such as coir fiber and other lignocellulosic wastes, and is relatively inexpensive compared to synthetic polymers. When used as a reinforcement, lignin can boost the mechanical and thermal properties of biopolymer matrices while also contributing to the composite's sustainability profile [6]. Research has demonstrated that lignin, due to its high aromatic content, can improve the stiffness, hardness, and thermal stability of polymer composites, as well as introduce additional benefits such as UV protection and antioxidant activity [7]. Lignin extracted from coir fiber waste has been shown to offer superior reinforcement, as it possesses a high degree of aromaticity and a more accessible structure compared to lignin derived from other sources. Additionally, soda-pulped lignin, which is extracted using an alkaline (soda) pulping process, has demonstrated good dispersibility and compatibility with various polymer matrices, making it an excellent candidate for use in biopolymer blends [8]. Furthermore, to achieve better performance in PHBV-lignin composites, it is necessary to enhance the interfacial compatibility between the biopolymer matrix and the lignin.

However, while lignin has shown potential as a reinforcing agent for PHBV-based composites, the role of other natural fillers, such as spent coffee grounds (SCG), has been relatively underexplored. SCG, a food waste byproduct from the coffee industry, is rich in cellulose, hemicellulose, and lignin, making it a potential candidate for use as an alternative biofiller in biopolymer composites [9]. SCG's natural fiber structure, along with its high lignin content, presents an opportunity to enhance the mechanical and water barrier properties of PHBV-based composites [10]. However, the hydrophilic nature of SCG can limit its compatibility with the hydrophobic PHBV matrix, necessitating surface modification to enhance filler dispersion and interfacial bonding [11]. Methods such as grafting and surface treatments have been explored to enhance the hydrophilicity and reactivity of biofillers, thereby improving their dispersion within the composite and its compatibility with the polymer [12]. Alkali treatment can remove lignin and other non-cellulosic materials from the surface of fibers, improving their interaction with the polymer [13]. Maleic anhydride grafting, on the other hand, introduces functional groups that promote better compatibility and bonding with the polymer chains [14]. These chemical modifications are expected to enhance the dispersion of SCG within the PHBV-lignin matrix, thereby improving the overall performance of the composite material. While SCG has been studied as a filler for various polymer matrices, its potential in PHBV/lignin blend has not been extensively explored, particularly in relation to surface modification techniques.

The incorporation of modified SCG as a biofiller not only adds value to waste materials but also offers a solution to the limitations associated with PHBV, such as mechanical fragility and low thermal resistance. By exploring the synergistic effects of SCG and lignin in PHBV blends, this study presents a novel approach to biopolymer composite development by utilizing a combination of two biomass-derived fillers, lignin and SCG, along with a biodegradable polymer, PHBV. This study not only contributes to the understanding of how chemical treatments and modifications can enhance the properties of PHBV/lignin/SCG composites but also offers a sustainable solution to the increasing problem of biomass waste disposal. By valorizing both agricultural and food waste, this research supports the principles of a circular economy, where waste materials are transformed into valuable products, thus reducing environmental impact.

2. Material and methods

In this study, PHBV powder, Enmat-Y1000, was procured from Tianan Biologic Material Co., Ltd., Zhejiang, China. Black liquor, obtained from the soda pulping process of coir fibers, was sourced from Universiti Sains Malaysia, Penang, Malaysia.

The lignin microparticles (LMPs) used in this study were synthesized via H_2SO_4 acid precipitation from the spent liquor obtained from coir fiber waste. These LMPs were filtered to attain an average particle size range of 25–53 µm, as demonstrated in an earlier study [14]. Spent coffee grounds used in this study were procured from He and She Coffee, a local coffee shop in Penang, Malaysia. The grounds were then filtered and ball-milled to produce fine powder particles, following a similar procedure employed in our previous study [15]. Chemicals used in the study, including maleic anhydride ($C_4H_2O_3 \geq 98.0\%$), *N*,*N*-dimethylformamide ($C_3H_7NO \geq 99.8\%$), sodium hydroxide (NaOH), ethanol ($C_2H_5OH \geq 99.8\%$), acetone ($C_3H_6O \geq 99.5\%$), and sulfuric acid ($H_2SO_4 \geq 98.0\%$), were obtained from Sigma Aldrich, Subang Jaya, Selangor, Malaysia.

2.1. Alkali treatment of SCG

For alkali treatment, 25 g of SCG were immersed in 200 mL of a 2% sodium hydroxide (NaOH) aqueous solution [16]. The mixture was stirred continuously at room temperature for 24 h. After treatment, the SCG was thoroughly rinsed with distilled water until the pH of the rinse solution reached 7, confirming the complete removal of NaOH. The alkali-treated SCG particles were then separated and dried at 65 °C for 24 h to remove any remaining moisture.

2.2. Anhydride grafting of SCG

The SCG was immersed in a thimble solution of maleic anhydride in *N*-dimethylformamide, with an anhydride-to-solvent ratio of 7:3. The grafting was carried out at 120 °C for 3 h. For safety, the process was performed under a fume hood with appropriate protective equipment. Once the reaction was complete, the flasks were taken off the heat, and the hot reagent was carefully poured out. The grafted SCG samples were then rinsed three times with dry ethanol during filtration to remove any residual acids or reactants. The modified SCG was isolated by filtration using a Buchner funnel with filter paper, a filtration flask, and a vacuum pump. Following filtration, the grafted SCG was air-dried for 2 h and then oven-dried at 60 °C overnight before weighing.

2.3. Preparation of bioblend thermoplastic composites

The thermoplastic composites were produced by varying the loading concentrations of raw, NaOH-treated, and maleic anhydride (MA) grafted SCG microfilters in a PHBV/lignin blend matrix. Initially, a blend of PHBV and lignin (15% lignin based on the blend weight) was prepared and selected according to previous literature studies [17]. Three types of composites were then formulated, incorporating raw SCG, NaOH-treated SCG, and MA-grafted SCG, as microfillers. In each composite, SCG was incorporated at varying loading concentrations of 1, 3, 5, and 7%, relative to the dried weight of the blend. To create these composites, we used a Lab Tech 26 mm co-rotating twin-screw extruder (model LTE20-40) for melt compounding. The extruder's mixing zone was kept at temperatures between 165 and 185 °C, with the screw speed set at 200 rpm. Once extruded, the samples were cooled in a water bath to reduce their temperature and then granulated into small 2–3 mm pellets. These pellets were subsequently dried under vacuum at 70 °C to prepare them for hot compression molding. For molding, the dried pellets were compressed at 180 °C in a metal mold measuring 200×200×3 mm. Afterward, the molded composites were transferred to a cold press to cool down to room temperature. Before any additional characterization or testing, each sample was conditioned for at least 48 h in a desiccator at 50% relative humidity. Table 1 summarizes the different sample formulations, which include untreated, NaOH-treated, and MA-grafted SCG microfillers, each at various percentages within the PHBV/lignin blend matrix.

2.4. Raw material characterization

The particle size distribution (PSA) and zeta potential (ZP) of both raw and modified SCG were determined in a Malvern Zetasizer Nano ZS (Version 7.11) from Malvern Instruments, UK. To study changes in functional groups of SCG surface before and after modification, Fourier-transform infrared

Table 1. Formulation of composites with different concentrations and types of SCG microfiller.

PHBV/Lignin blend matrix [wt%]	SCG as microfiller [wt%]	Alkali treated SCG as microfiller [wt%]	MA-grafted SCG as microfiller [wt%]
100	0	0	0
99	1	1	1
97	3	3	3
95	5	5	5
93	7	7	7

spectroscopy (FT-IR) was performed, employing the KBr pellet method using Perkin-Elmer Model PC1600, USA. The microstructure of both raw and modified SCG was analyzed at magnifications of 3000× and 10 000× using a Field Emission Scanning Electron Microscope (FE-SEM), operated with a model FEI Quanta FEG 650, Thermo Fisher Scientific, Netherlands. The thermal properties were investigated via thermogravimetric analysis (TGA) using a Mettler Toledo analyzer, with sample sizes of 5–10 mg. Samples were heated under nitrogen from 30 to 800 °C at a rate of 10 °C/min.

2.5. Characterization of bioblend thermoplastic composites

The water absorption behavior of of control PHBV/lignin blend matrix and matrix/SCG composite samples 50×50 mm was evaluated in accordance with the BS 317:1993 Standard. The samples were submerged in pure water at a pH of 7 and a temperature of 20 °C. The water absorption test was carried out over a span of up to 15 days, or until the samples maintained consistent weight. Using a contact angle analyzer with an automatic microsyringe, 2 µL of water was carefully placed on the composite surfaces. The contact angle (WCA) was measured at room temperature, with five measurements taken per sample, and the results were averaged.

Tensile tests were performed on specimens of the control PHBV/lignin blend matrix and matrix/SCG composites using an Instron 5567 machine in compliance with ASTM D3039 standards. The specimens, each measuring 165×13×3 mm, were tested while strain was measured with a mechanical extensometer set to a 50 mm gauge length. Flexural testing was conducted according to ASTM D790 using an Instron 5582 machine on samples measuring 127×12.7×3 mm. The Izod notched impact test followed ASTM D256 guidelines and was conducted on a GOTECH GT-7045-MDL machine with a 1 J pendulum energy setting and a speed of 3.46 m/s. Prior to impact testing, specimens were V-notched at a 90° angle with a 2 mm depth using a Go-Tech V-notch machine. The specimens 63.5×12.5×3 mm were cut using a bandsaw, and five samples were prepared for each PHBV/SCG composite test.

The fractography of composites, after tensile fracture, was examined using the same machine mentioned earlier, with magnifications ranging from 1000× to 3000×. To assess the morphological topography and miscibility of the control PHBV/lignin blend matrix and matrix/SCG composites, an Atomic Force Microscope (AFM) from NanoFocus Inc., Guro Gu, Seoul, Korea, was employed. The AFM provided topographical images of the biocomposite surfaces, and the surface roughness was calculated using the WS×M image viewer.

Functional group changes in the control PHBV/lignin blend matrix and matrix/SCG composites were examined using FT-IR spectroscopy. The thermal stability of composites was assessed at the same operating conditions and in the same machine mentioned earlier. The thermogravimetric data was used to determine the weight loss percentage, maximum decomposition temperature ($T_{\max}$), and char residue through the DTG curve. The glass transition and melting temperatures of composites were determined via differential scanning calorimetry (DSC) on a Perkin-Elmer DSC 6. Samples of 5–10 mg were tested in a nitrogen atmosphere with a heating rate of 20 °C/min. Each sample was initially heated to 110 °C to remove moisture, cooled to 25 °C, and then reheated to 200 °C the same rate of 20 °C/min.

3. Results and discussion

3.1. Characterization of SCG

The particle size distribution (PSA) of SCG suspension was determined by using dynamic light scattering. The raw SCG microparticles used in this study were previously utilized and characterized in our earlier studies [10, 15]. Figure 1a displays a particle size distribution, with average diameters between 1.11 and 1.28 µm and intensities from 44.9 to 55.1%, indicating most coffee ground particles are within the microscale range. This scale increases the potential for agglomeration at higher concentrations during composite fabrication. Zeta potential analysis in Figure 1b revealed a negative value of –20 mV for raw coffee grounds, reflecting an almost neutral charge and adequate colloidal stability due to sufficient particle repulsion (above –27.0 mV), which prevents aggregation. This stability is essential for enhancing the mechanical properties of the composites. Ultrasonic treatment further increased the negative zeta potential, enhancing their cadmium ion adsorption capacity.

The FT-IR spectrum of raw, NaOH-treated, and MA-grafted SCG microparticles is presented in Figure 1c, highlighting the effects of chemical treatment on SCG that can be advantageous to maintain better

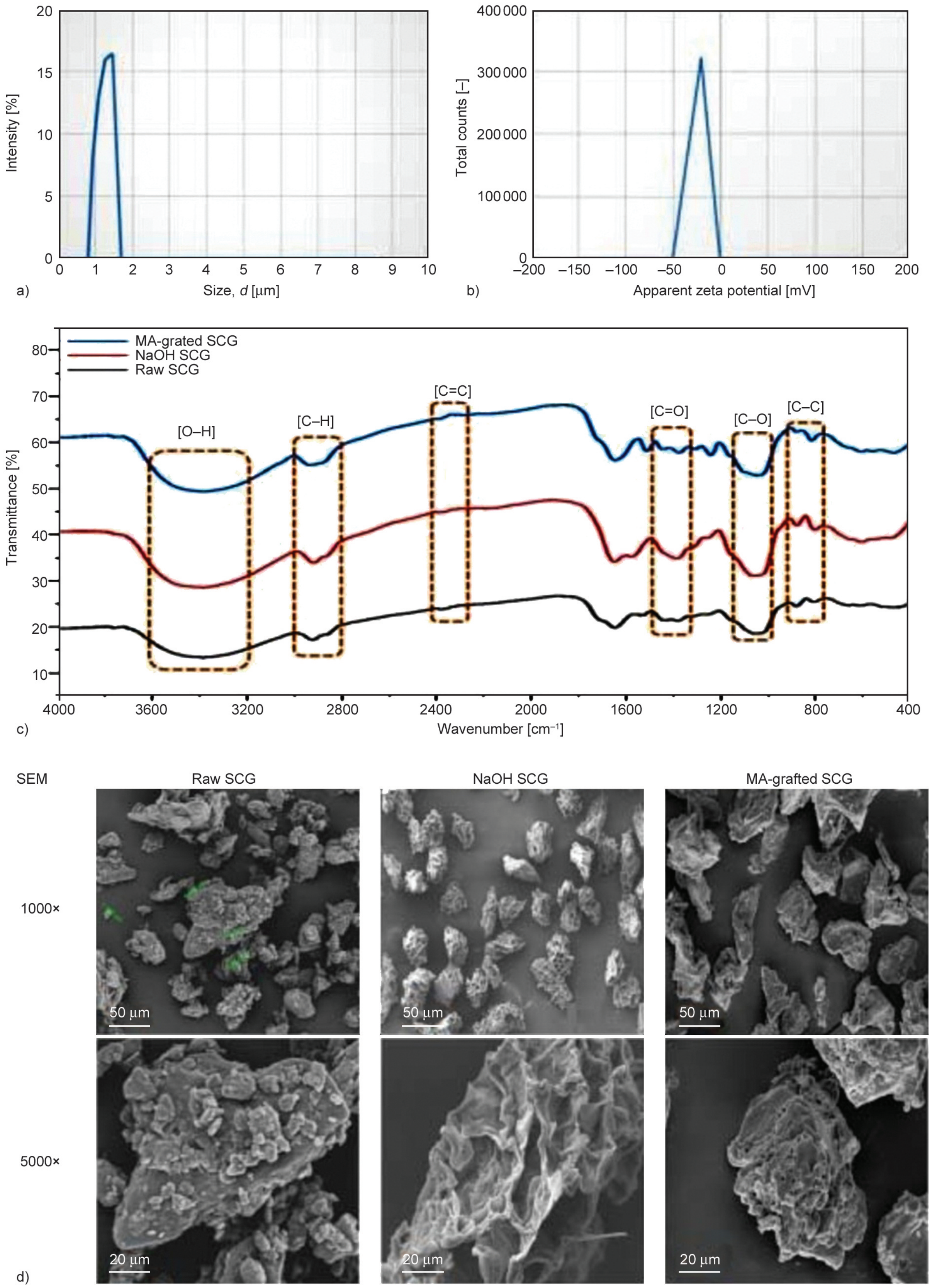

Figure 1. a) Particle size distribution of raw SCG particles, b) Zeta potential of raw SCG particles, c) FT-IR graph of raw, NaOH-treated, and MA-grafted SCG particles. d) SEM images of SCG particles at magnifications of 1000× and 5000×.

interfacial bonding with the PHBV/lignin matrix when incorporated as a microfiller. All SCGs show distinct FT-IR bands characteristic of lignocellulosic material, including a prominent peak in the range of 3200–3550 cm^{-1} associated with cellulose and polyphenols [18]. This broad peak, likely due to the presence of proteins in raw SCG, indicates a high concentration of hydroxyl (–OH) groups. Following NaOH treatment and MA-grafting, the –OH stretching peak in SCG becomes sharper. This change indicates a reduction in hydrogen bonding, as the NaOH treatment partially removes lignin and hemicellulose, while MA-grafting consumes some –OH groups by forming ester bonds, aiming to enhance SCG's compatibility with the matrix, resulting in better dispersion within the composite. Additional peaks are observed at 2924 and 2860 cm^{-1}, corresponding to asymmetric and symmetric C–H stretching, while a strong peak at 1651 cm^{-1} is linked to the C=O stretching of hemicellulose and lignin. In NaOH-treated SCG, the reduced intensity of peaks around 1655 cm^{-1} for C=O and C=C bonds indicate partial removal of lignin and hemicellulose. The absence of a peak near 1528 cm^{-1} further confirms the removal of aromatic rings from lignin [16]. FT-IR confirms the successful grafting of maleic anhydride onto SCG, shown by characteristic peaks within the 1200–1600 cm^{-1} range. Specifically, this region includes peaks associated with the stretching vibrations of carbonyl (C=O) groups around 1700 cm^{-1}, indicative of maleic anhydride's carbonyl structure. Additionally, peaks near 1250–1300 cm^{-1} reflect the formation of C–O–C bonds, signifying ester linkages created during the grafting process when maleic anhydride reacts with hydroxyl (–OH) groups on the SCG surface [19]. These new ester bonds improve the compatibility between SCG and the matrix, enhancing interfacial adhesion and contributing to better dispersion and mechanical properties in the composite.

Surface morphology analysis of both raw and modified SCG was performed using SEM imaging, as depicted in Figure 1d at magnifications of 1000× and 5000×. The SEM images reveal that raw SCG particles exhibit a dense, irregular, and somewhat abrasive structure. Particle size for the SCG microbiofiller was confirmed to range between 1.106 and 1.281 µm, consistent with prior findings from our previous study [15]. The NaOH treatment of SCG resulted in a more porous particle structure, as observed in SEM images, along with a reduction in particle size. This increased porosity significantly enhances the specific surface area of SCG particles, providing more sites for physical interaction with the biopolymer blend matrix. The rough, porous structure allows for better mechanical interlocking with the matrix, creating stronger interfacial bonding and potentially improving load transfer between the filler and polymer phases [16]. Additionally, smaller particle size promotes a more uniform dispersion of SCG within the matrix, reducing the likelihood of aggregation. On the other hand, SEM images of MA-grafted SCG particles would likely show a smoother and more uniform surface compared to untreated or NaOH-treated SCG particles. The grafting process typically reduces the natural porosity by forming a thin layer of maleic anhydride on the particle surface. This results in less surface roughness and better dispersion of the particles, as the MA modification improves the interfacial compatibility between SCG microfillers and the biopolymer blend matrix [20]. These changes promote stronger bonding, which can enhance the mechanical and thermal properties of the resulting composites.

The thermal properties of raw, NaOH treated, and MA-grafted SCG evaluated through TGA/DTG analysis are shown in Figure 2. The TGA curves revealed a two-stage mass loss, corresponding to moisture evaporation and the decomposition of primary constituents. At 100 °C, raw SCG particles experienced a mass reduction of 7.96%, while treated SCG and grafted SCG showed different reductions of 6.75 and 5.5%, respectively, both due to moisture loss. The onset degradation temperature of raw SCG particles was 200 °C, compared to 260 and 271 °C for treated and grafted SCG, respectively, indicating improved thermal stability of the treated and grafted SCG material. Raw SCG exhibited a mass loss of 11% between 160–200 °C, attributed to the thermal decomposition of hemicellulose [21]. This phase was very low, 4% in alkali-treated SCG, as treatment removed the majority of hemicellulose. The reduction in mass loss observed in this range for the MA-grafted SCG was just 2%, which can be attributed to the chemical modification induced by MA-grafting. MA-grafting further enhances thermal stability by forming covalent bonds with the SCG, reducing the number of volatile components that decompose at lower temperatures, suggesting that the hemicellulose content has been significantly altered, and the

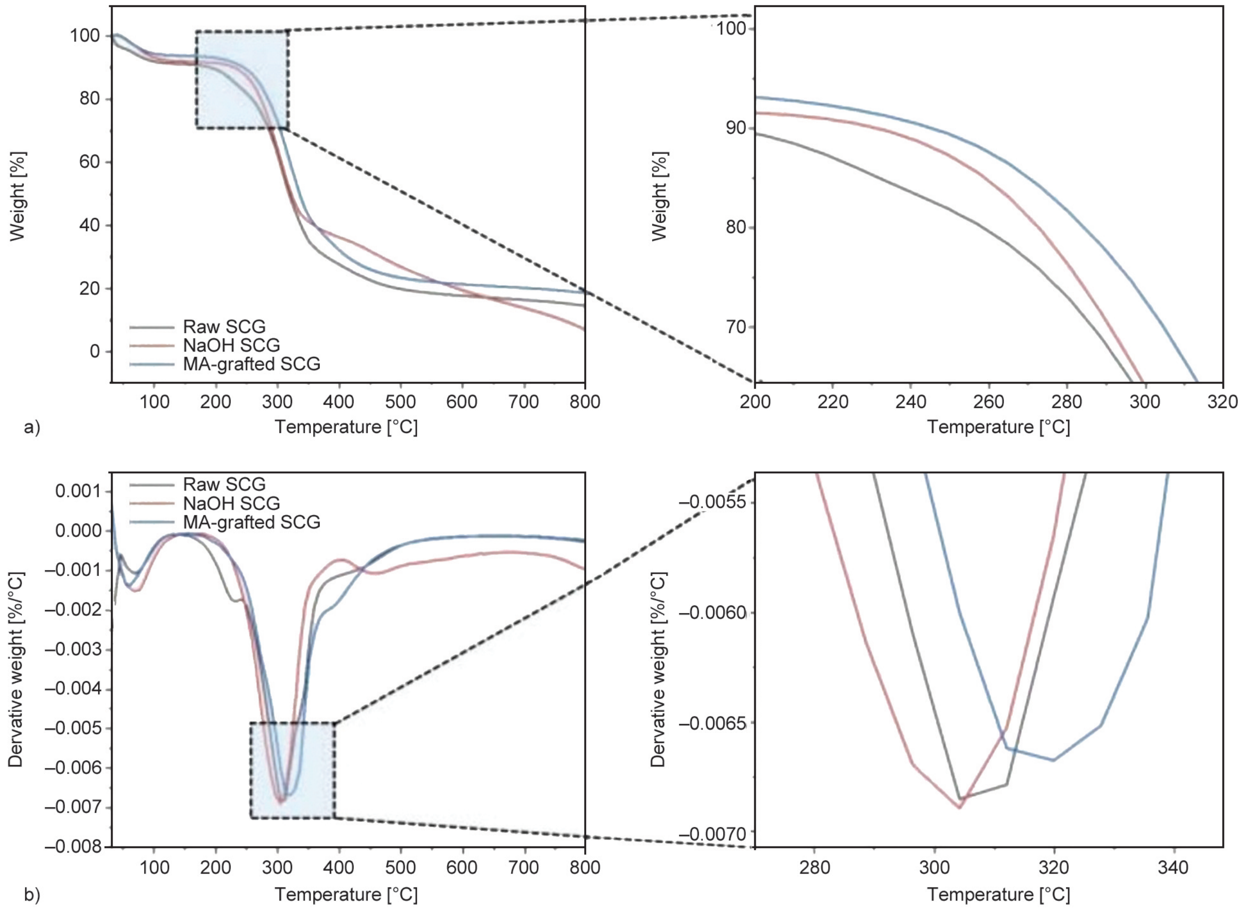

Figure 2. a) Thermogravimetric analysis (TGA) curves, and b) derivative thermogravimetry (DTG) curves of raw, NaOH-treated, and MA-grafted SCG microparticles.

remaining structure is more thermally stable. The most significant weight loss for SCG occurred around 312 °C due to cellulose degradation, similar to our previous study [16]. The final degradation stage, starting at 370 °C, was linked to lignin decomposition in raw SCG. The DTG curves showed that raw SCG reached its peak degradation temperature at 304 °C, while for NaOH and MA-grafted treated SCG, they were observed at 312 and 327 °C, respectively. These findings suggest that the NaOH treatment improved the thermal stability of the SCG, which likely resulted from the removal of non-cellulosic materials. MA-grafting further contributes to stability by forming stronger bonds within the SCG structure, making it more resistant to thermal degradation. The lower residual weight for NaOH-treated SCG indicates that alkali treatment removed significant amounts of hemicellulose and lignin, leaving less material behind. On the other hand, the higher residual weight of MA-grafted SCG suggests that the grafting process improved the thermal stability of the SCG, leading to a greater retention of material during degradation.

3.2. Characterization of bioblend thermoplastic composites

The thermoplastic composites were developed using a PHBV/lignin blend matrix, with modified SCG incorporated as an enhancement microfiller to improve the overall properties of the resulting sustainable composite materials. As shown in Figure 3a, the schematic possible interaction highlights the interaction between PHBV and Lignin in the blend, while Figure 3b depicts the chemical interaction between the PHBV/lignin blend and SCG. Incorporating modified SCG into the composite matrix could enhance certain mechanical properties compared to the standard composites. The fibrous structure of spent coffee grounds helps reinforce the material, improving the transfer of stress and minimizing crack growth. As a result, the overall mechanical performance of the composite can be significantly improved [11].

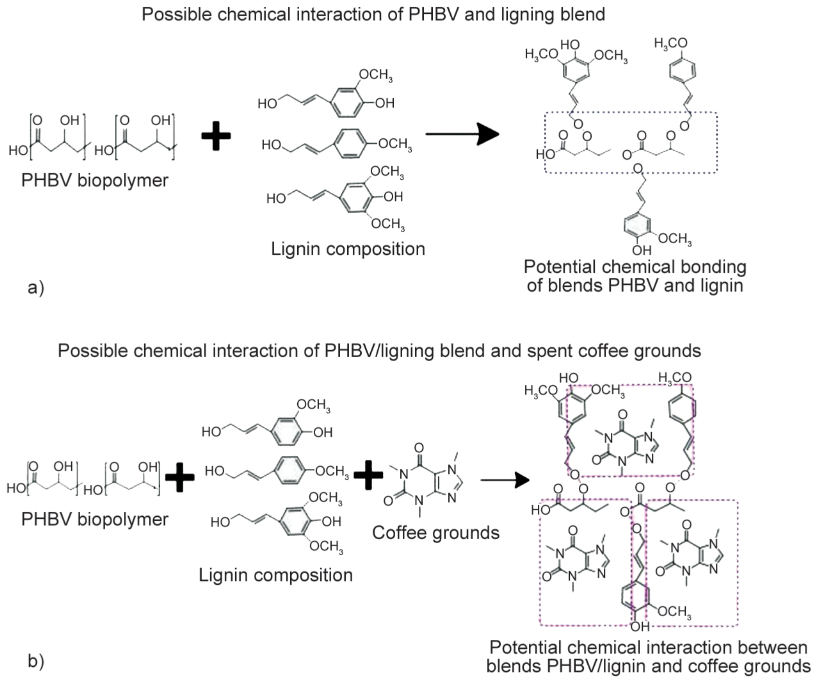

Figure 3. a) Possible interaction of PHBV and lignin as a blend, b) possible interaction of blend matrix and SCG.

The study explored the water barrier properties of bioblend thermoplastic composites, focusing on the effects of incorporating spent coffee grounds (SCG) microfillers in varying loadings (0, 1, 3, 5, and 7%) within a PHBV/lignin blend matrix. Figure 4 illustrates findings on water absorption and contact angle measurements for composites containing raw SCG, NaOH-treated SCG, and MA-grafted SCG microfillers. Among these, composites with MA-grafted SCG showed the lowest water absorption rates due to the enhanced hydrophobicity and compatibility between the SCG microfillers and the PHBV/lignin matrix, attributed to the SCG surface modification which reduces the number of available hydroxyl groups that would otherwise attract water. In comparison, NaOH-treated SCG composites exhibited moderate water absorption, which can be attributed to the treatment process that removes non-cellulosic components and disrupts hydrogen bonds, thus reducing available hydroxyl groups for water interaction [22]. In contrast, composites with raw SCG fillers had the highest water absorption. This is probably due to the natural hydrophilic nature of SCG, which encourages hydrogen bonding between hydroxyl groups and water molecules [23]. Additionally, in all composite types, water absorption consistently increased with higher SCG filler content.

Water contact angle analysis further indicated that, compared to composites with raw SCG, those with NaOH-treated and MA-grafted SCG microfillers demonstrated enhanced water resistance. This improvement is attributed to better compatibility between the matrix and filler, leading to a denser structure with fewer voids and less water absorption. It was also noted that as the SCG content increased up to 5%, the water contact angle increased as well, indicating the added SCG microfillers enhance surface hydrophobicity and improve matrix-filler bonding, creating a compact structure that resists water. However, when SCG content goes beyond 5%, the water contact angle decreases, thereby reducing the composite's water resistance, attributed to the [24]. Composites with MA-grafted SCG showed the greatest increase in contact angle, followed by those with NaOH-treated SCG, indicating an improved hydrophobic surface. Introducing hydrophobic SCG microparticles alters the composite surface, enhancing resistance to water uptake. These modified surfaces act as barriers that significantly hinder moisture absorption over time, effectively minimizing water absorption, as observed in both the contact angle and water absorption analyses.

A tensile test was performed to assess the mechanical properties of the composites, specifically focusing on tensile strength, tensile modulus, and elongation at break, as shown in Figure 5. The results revealed that increasing SCG microfiller content up to 5% in all composite types led to improvements in both tensile strength and modulus. This improvement is attributed to the reinforcing effect of SCG at

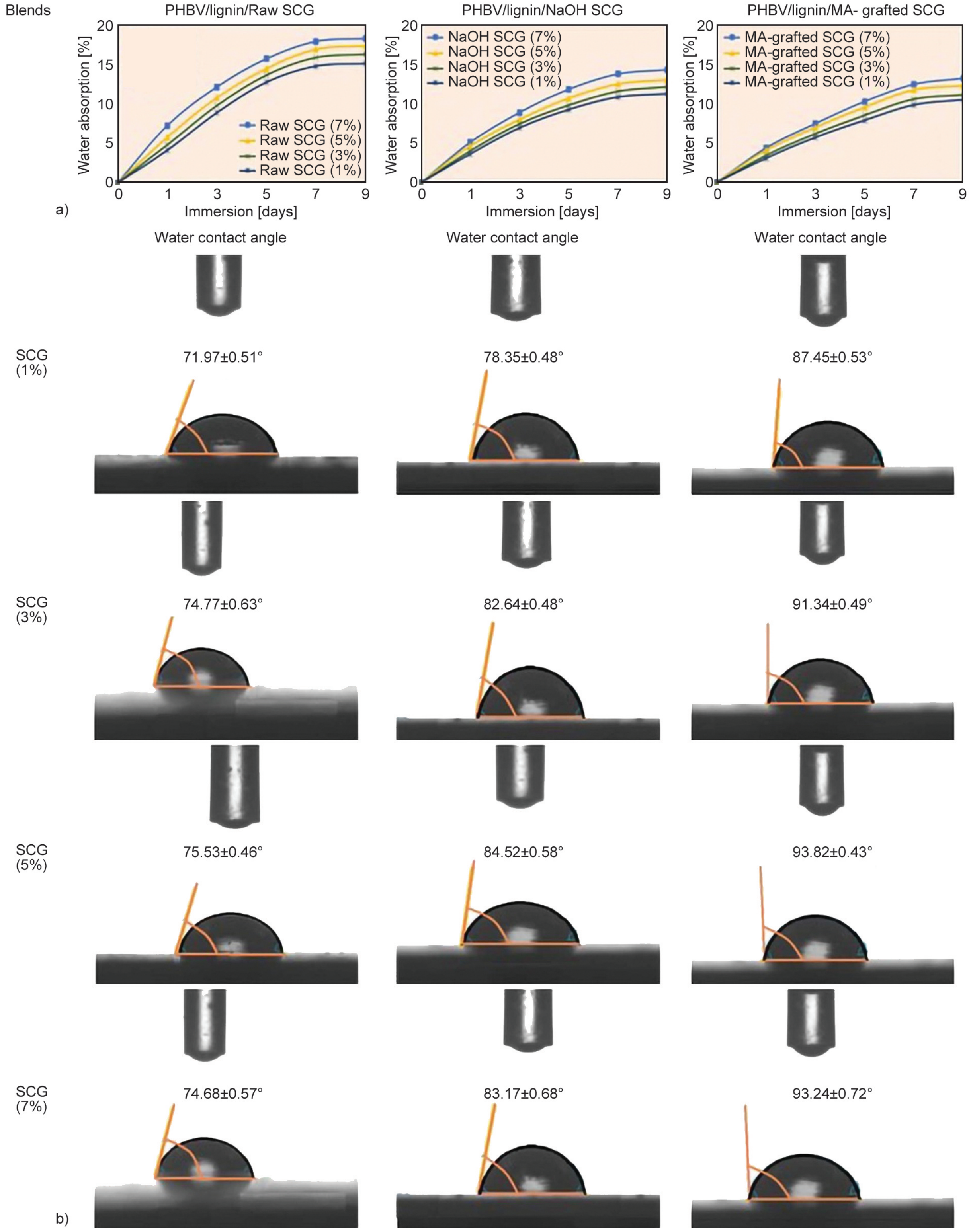

Figure 4. a) Water absorption and b) water contact angle values for raw SCG, NaOH treated SGC, and MA-grafted SCG-based PHBV/lignin blend composites materials.

lower concentrations, where the particles effectively strengthen the composite and increase stiffness. However, at 7% SCG filler loading, a gradual reduction in these properties was observed, likely due to the agglomeration of SCG particles. This agglomeration could create clusters that form localized stress points, weakening the bond between the matrix and the filler and reducing the overall reinforcing effect of SCG [25]. Notably, composites containing MA-grafted SCG particles consistently achieved the

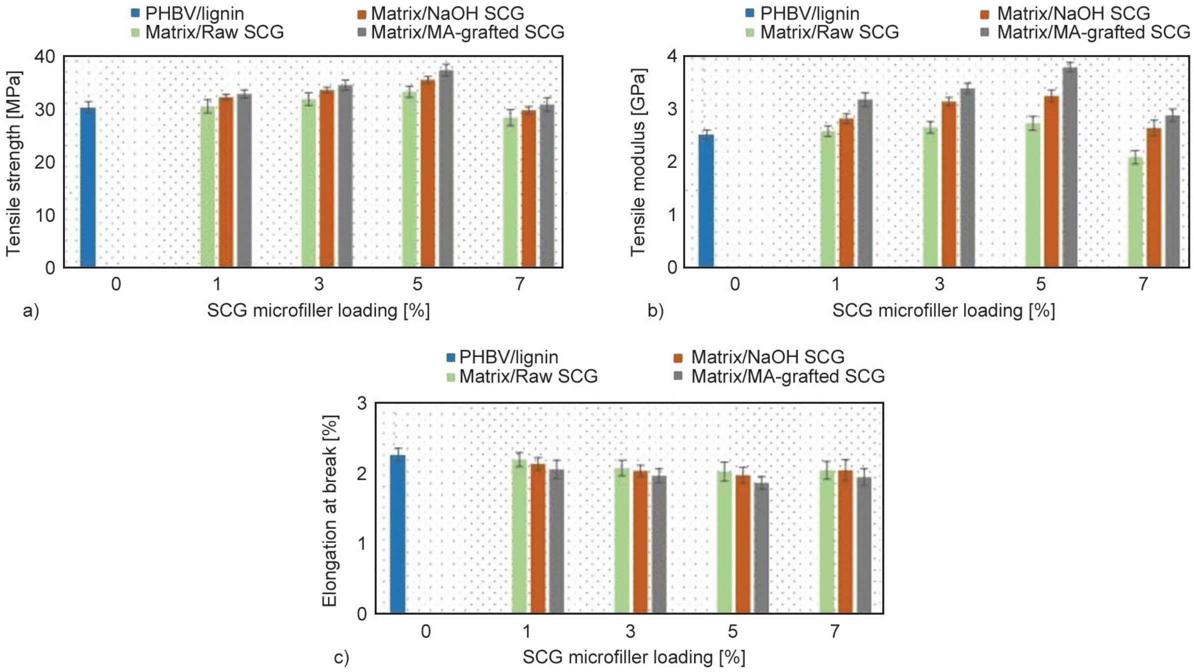

Figure 5. a) Tensile strength, b) tensile modulus, and c) elongation at break of control PHBV/lignin blend and raw SCG, NaOH SCG, and MA-grafted SCG-based PHBV/lignin blend composites with varying SCG microfilter loadings.

highest tensile properties among the samples. The strength increased from 30.12 MPa (control blend matrix) to 37.25 MPa at 5% MA-grafted SCG filler loading, which corresponds to an approximate percent increase of 23.69%. This enhancement is likely due to improved interfacial adhesion and compatibility between the microfillers and the PHBV/lignin matrix; a similar increase in tensile strength was observed when MA was used as a coupling agent [26]. The progression from raw SCG to NaOH-treated SCG and finally to MA-grafted SCG composites led to a continuous improvement in both tensile strength and modulus, probably due to better fiber-matrix bonding. Maleic anhydride likely plays a key role in promoting mechanical interlocking between the components. However, at 7% SCG content, both tensile strength and modulus decreased, likely due to increased SCG particle agglomeration. Elongation at break showed an opposite trend with SCG content, being highest for composites with raw SCG, followed by NaOH-treated SCG, and lowest for MA-grafted SCG. This pattern indicates stronger fiber-matrix bonding, especially in MA-grafted composites, which enhances stiffness and delays plastic deformation, similar to previous studies [27]. As SCG content increases, elongation at break decreases, attributed to the inherent stiffness of SCG particles, which restricts polymer chain mobility within the matrix, making the composites more brittle [28].

The evaluation of composites with SCG microfillers focused on their flexural strength and flexural modulus, as illustrated in Figure 6a and Figure 6b. Across all composite types, increasing the SCG microfiller content resulted in an upward trend in flexural strength and modulus, peaking at 5% filler loading. This increase is attributed to the reinforcing effect of the SCG microfiller, consistent with findings in other polymer composite studies [29]. However, when the SCG content exceeded 5%, there was a noticeable decrease in these properties, especially at 7% filler content. This decline is likely due to an overload of microfiller that caused poor dispersion and agglomeration within the polymer matrix, weakening the bond between SCG and the PHBV/lignin blend. Among modified SCG composites, those with MA-grafted SCG exhibited the highest flexural strength and modulus values. There was a clear progression in strength from raw SCG to NaOH-treated SCG to MA-grafted SCG composites, achieving peak levels at 5% SCG content. Flexural modulus values remained relatively stable across the composites, with 5% SCG fillers achieving flexural modulus values of 2.56, 3.28, and 3.42 GPa in the respective composite groups.

Impact properties followed a similar trend with increasing SCG content, as shown in Figure 6c and Figure 6d. From 0 to 5% filler, there was a steady increase in impact resistance, likely due to effective

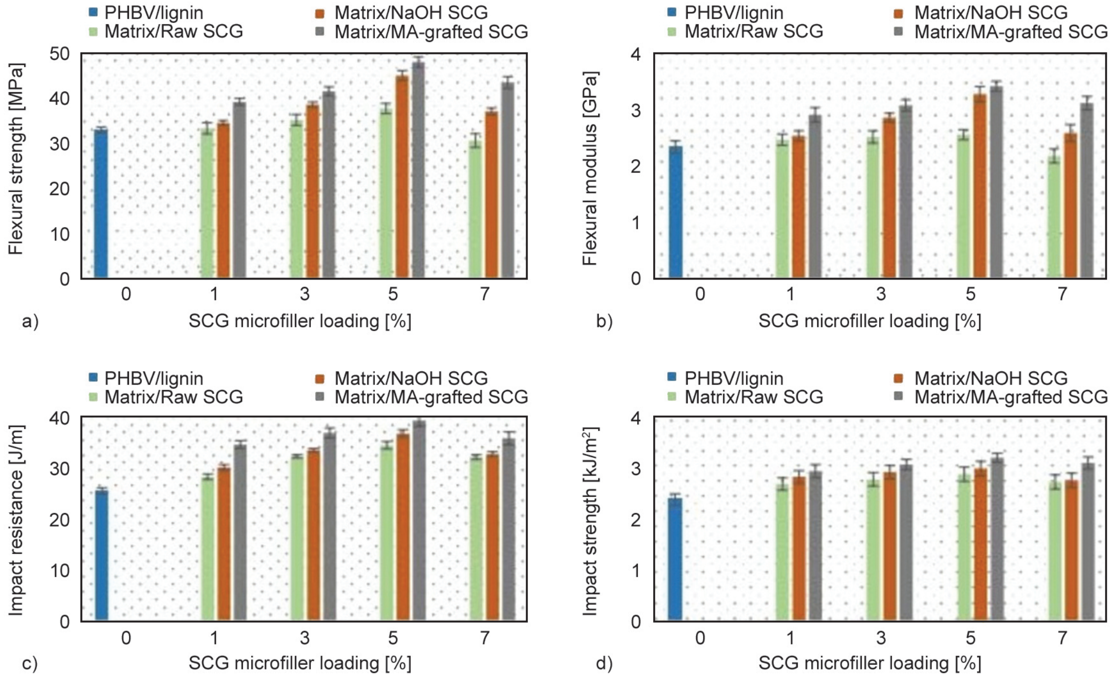

Figure 6. a) Flexural strength, b) flexural modulus, and c) impact resistance, d) impact strength of the control PHBV/lignin blend and raw SCG, NaOH SCG, and MA-grafted SCG-based PHBV/lignin blend composites with varying SCG microfiller loadings.

reinforcement enhancing the material's ability to absorb energy and resist cracking during impact. The addition of SCG enhances the composite's toughness, enabling it to withstand higher impact forces before breaking. However, when the filler content exceeded 5%, the impact resistance began to drop, possibly because the fillers started to clump together, reducing the effective interaction between the filler and the matrix. Too much filler may prevent the matrix from absorbing impact energy efficiently, lowering the composite's overall impact resistance. Among modified SCG composites, those with MA-grafted SCG consistently showed the highest impact strength, mirroring the improvements seen in tensile and flexural properties. MA enhances the bonding between the matrix and the natural filler by reacting with the hydroxyl (OH) groups in the natural filler and the carbon-carbon (C–C) bonds of maleic anhydride. This creates ester bonds, improving the interface adhesion and strengthening connections between the matrix and reinforcement [30, 31]. This suggests that MA-grafting enhances SCG toughness and adhesion to the polymer matrix, optimizing the composite's energy absorption and impact resistance. Combining MA-grafting with optimal SCG loading thus synergistically improves the composite's overall mechanical performance.

The investigation analyzed the surface structure of fractured samples from tensile testing of PHBV/lignin blend composites, including samples with varying concentrations of raw, NaOH-treated, and MA-grafted SCG microfillers. Surface morphologies at 5% SCG loading were observed at 1000× and 3000× magnifications, as shown in Figure 7, to assess the impact of SCG modifications and their dispersion within the composites. SEM imaging revealed that compatibility between the PHBV/lignin matrix and SCG microfillers improved significantly with surface modifications, a finding that aligns with mechanical property results. Notably, composites containing MA-grafted SCG demonstrated less crack propagation than those with NaOH-treated and raw SCG fillers. The SEM images also showed enhanced distribution of SCG particles within the matrix for modified composites, with the control samples (without SCG) displaying a relatively smooth surface. At 5% SCG filler content, particles appeared well-dispersed and bonded to the matrix, suggesting strong adhesion. However, at higher filler concentrations, the presence of void pull-outs was observed, where achieving uniform dispersion became challenging, potentially weakening the matrix-filler bond [32]. The addition of SCG particles directly affects the composite's mechanical properties, with lower filler

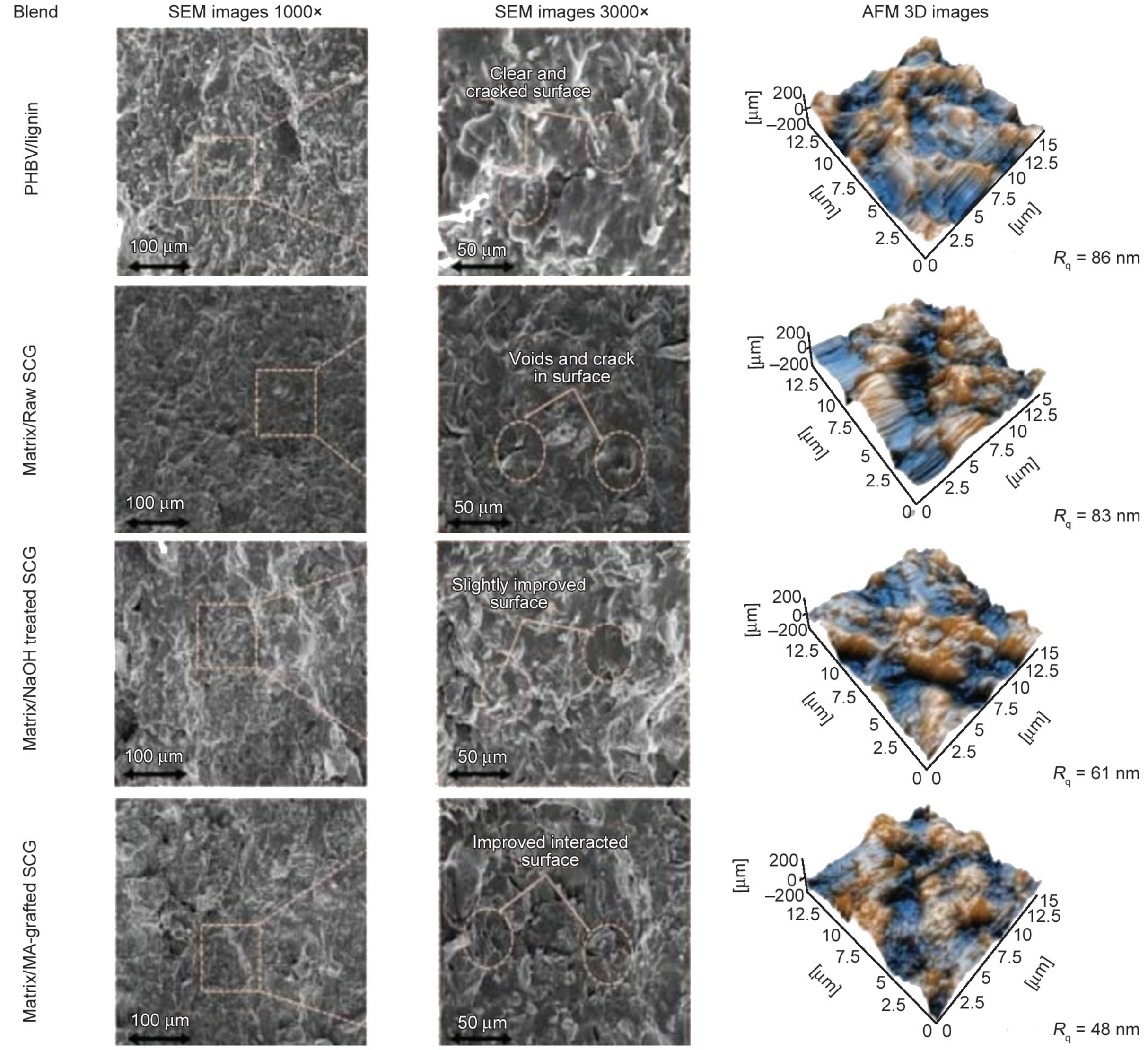

Figure 7. SEM fractographic morphologies and AFM topographical images with surface roughness values of control PHBV/lignin blend matrix and (Raw SCG, NaOH treated SCG, and MA-grafted SCG) based PHBV/lignin blends at 5 wt% microfiller loadings.

levels minimizing the risk of particle agglomeration [33]. Comparing tensile fracture micrographs, composites with MA-grafted SCG exhibited superior surface smoothness and filler dispersion compared to those with NaOH-treated or raw SCG, consistent with their improved mechanical performance. MA-grafted SCG effectively minimizes surface irregularities, promoting fiber dispersion and interfacial adhesion, which in turn enhances fracture resistance and overall composite performance [11]. Additionally, the 3D topography images show enhanced interfacial bonding between the matrix and MA-grafted SCG. Figure 8 illustrates the fracture mechanism of composites with SCG microfillers, highlighting distinctions between composites with modified *versus* unmodified SCG. In MA-grafted SCG composites, crack propagation is significantly reduced compared to unmodified counterparts, likely due to improved

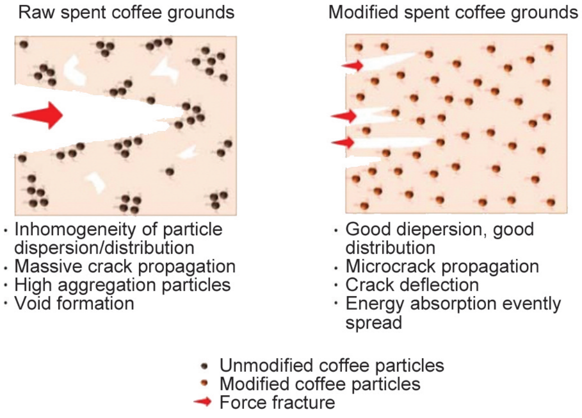

Figure 8. Schematic representation of fracture mechanism of composites with and without modified SCG.

interfacial bonding that limits crack initiation and growth. SCG particles act as agents that help bridge cracks, boosting the toughness and resistance to fractures of the composite.

FT-IR analysis was conducted to investigate structural changes and potential interactions in PHBV/lignin blend composites incorporating 5 wt% SCG microparticles. The FT-IR spectra of both the control (PHBV/lignin composite) and the SCG-incorporated composites are presented in Figure 9, highlighting the effects of raw, NaOH-treated, and maleic anhydride-modified SCG. A significant peak around 3447 cm^{-1}, common to all composites, corresponds to O–H vibrations from hydroxyl groups in cellulose, hemicellulose, and lignin in the SCG, as well as water molecules [34]. The spectra reveal that composites with modified SCG show a narrower and less intense O–H band, indicating that SCG modification has reduced hydrophilicity, contributing to improved hydrophobicity. This change leads to better bonding between the filler and the matrix. Additionally, a stronger peak around 2935 cm^{-1}, linked to C–H stretching in methylene groups, indicates the formation of ester groups and alkyl chains during the modification process [35]. The peak around 1752 cm^{-1}, corresponding to C=O stretching in carbonyl groups, becomes more prominent in all modified composites, confirming the successful NaOH treatment and maleic anhydride modification of SCG [11]. Additional peaks between 1458 and 1053 cm^{-1}, associated with various chemical bonds (C–H, C=O, C–C), are related to lignin and further verify the chemical changes in the SCG. Moreover, composites containing SCG showed enhanced mechanical strength with increased filler content, further supporting the positive impact of SCG modification. The FT-IR results confirm that the SCG modifications successfully integrate into the PHBV/lignin blend matrix, enhancing the composite's structure and performance.

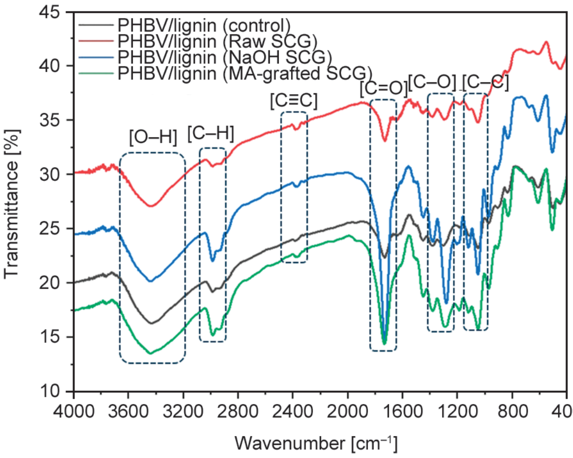

Figure 9. FT-IR graphs of PHBV/lignin blend composites at 5 wt% SCG microfiller loading with raw SCG, NaOH-treated SCG, and MA-grafted SCG.

The thermal properties of PHBV/lignin blend composite materials containing 5% SCG microfiller (by dry weight) were evaluated using TGA/DTG analysis, as shown in Figure 10. All composites, including the control blend matrix, exhibited a two-stage degradation process, with the onset of degradation observed at 228.6 °C for the control blend PHBV/lignin matrix. All composites containing raw and modified SCG microfillers demonstrated enhanced thermal stability compared to the control composite. Despite the inherent hydrophilic nature of SCG, the composites showed minimal weight loss (less than 1%) below 100 °C, likely due to the hydrophobic properties of the blend matrix and low concentrations of SCG [36]. Here, the matrix serves as a protective layer for the SCG particles within the composite, slowing down their breakdown due to its low thermal conductivity and allowing them to interact with surrounding gases [33]. The SCG modifications increased hydrophobicity, further enhancing the natural hydrophobicity of lignin in the matrix. The onset degradation temperature (T_{onset}) for composites containing modified SCG was slightly higher than that of the composite with raw SCG, and similar results were observed [37]. Specifically, at 5% SCG microfiller loading, the Tonset values were 250.4 °C for raw SCG, 254.8 °C for NaOH-treated SCG, and 255.9 °C MA-grafted SCG, the most stable composite, showing an an increase of 11.9%, in comparison to control blend matrix. Between 250 and 350 °C, degradation of cellulose, hemicellulose, pectin, and lignin occurs gradually across all composites, following a two-step degradation process involving dehydration followed by the breakdown of volatile components. The MA-grafted SCG composites exhibited the highest thermal stability, improved the chemical structure of the fibers, enhancing bonding and reducing their tendency to degrade under heat. Increasing SCG filler content from 1 to 7% slightly improved the thermal stability of all composite types. However, composites with modified SCG consistently outperformed those with raw SCG and the control regarding maximum decomposition temperatures. In the DTG curves, a clear shift in maximum degradation temperatures was observed, moving

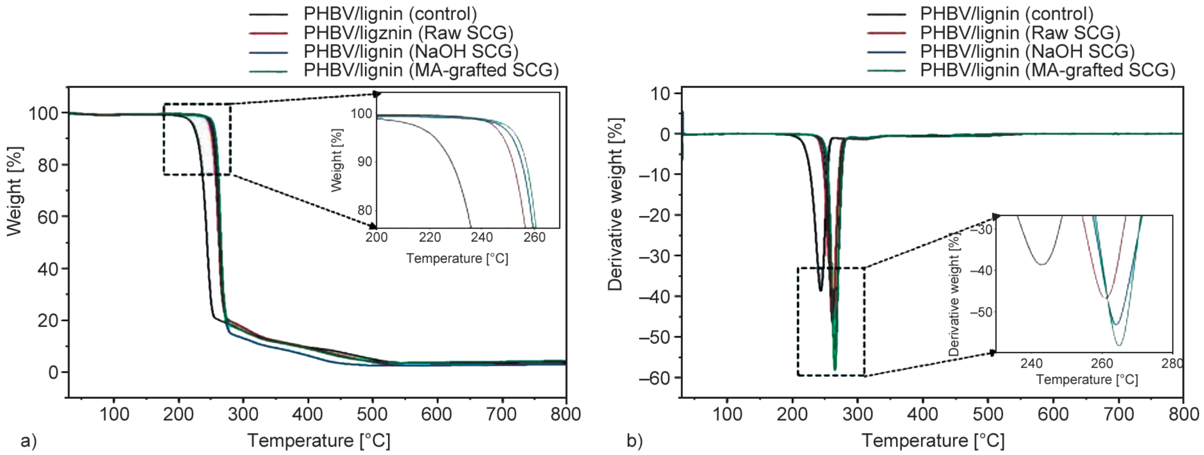

Figure 10. a) TGA thermographs of PHBV/lignin blend composites at 5 wt% SCG microfiller loading, b) DTG thermograph of composites.

from 241 °C in control to 260 °C for raw SCG, 264 °C for NaOH-treated SCG, and 267 °C for MA-grafted SCG composites, confirming the increased thermal stability conferred by SCG modification. The presence of SCG microfiller also shifted the main DTG peaks toward higher temperatures, indicating an improvement in composite thermal stability. However, the char residue across all composites was below 4%. These results underscore the positive impact of SCG modifications and microfiller addition on the thermal performance of PHBV/lignin blend composites with bast fibers.

DSC curves of PHBV/lignin blend composites are presented in Figure 11, with only the second heating and cooling cycles considered to remove any thermal history effects. The curves show endothermic peaks (T_m), corresponding to the melting temperature of PHBV, observed at approximately 171 °C. The addition of SCG microfillers slightly lowered T_m, with raw SCG causing about a 2% decrease, NaOH-treated SCG around a 6% decrease, and a similar reduction for MA-grafted SCG composites, a similar study reported [26]. Despite these variations, the melting temperatures remain close to the neat PHBV/lignin melting range of 171 °C, as reported in the literature. The NaOH-treated SCG led to a small reduction in T_m, while no significant change was observed for the MA-grafted SCG composites.

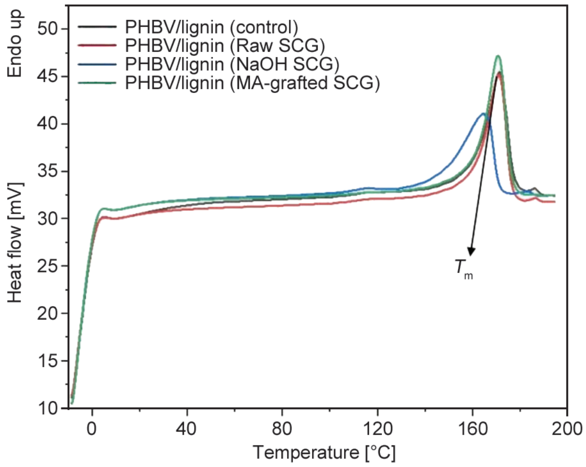

Figure 11. DSC curves of PHBV/lignin blend composites at 5 wt% SCG microfiller loading.

4. Conclusions

Bioblend thermoplastic composites with impressive multifunctional properties were developed by incorporating chemically modified spent coffee grounds (SCG) microparticles into PHBV/lignin blend matrices, with lignin consistently added at a 15% loading in the PHBV matrix. The functionality of SCG was enhanced through chemical modification, introducing alkali-treated and maleic anhydride (MA) grafted SCG as microfillers. The modifications significantly improved the compatibility of SCG with the blend matrix, optimizing the performance of the composites. MA-grafted SCG demonstrated superior improvements compared to alkali-treated SCG, attributed to the enhanced interaction between the hydrophobic grafted particles and the PHBV matrix. Conversely, raw SCG composites exhibited the least improvement in properties. The modified composites displayed improved water barrier, increased stiffness, enhanced structural integrity, better thermal stability, and superior overall functionality, with the optimal performance observed at a 5% SCG content. However, at a 7% filler loading, particle agglomeration negatively impacted the dispersion of SCG, reducing the composite properties. These findings highlight the success of modifying SCG particles and emphasize the potential of hydrophobic, modified SCG as effective reinforcements for sustainable thermoplastic composites. However, advanced dispersion techniques or the use of surfactants must be explored to prevent filler agglomeration at higher loadings. Future studies should focus on optimizing the modification processes to achieve cost-effectiveness and scalability while exploring alternative grafting agents to further enhance compatibility and functionality. These efforts will broaden the application scope of such bio-based materials derived from agricultural waste in diverse fields requiring improved mechanical and barrier properties.

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