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RESEARCH ARTICLE

Surface functionalization of bio-based polymers in FDM: A pathway to enhanced material performance

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ABSTRACT

Such rapid advancement places FDM as a transformative technology in additive manufacturing generally, and particularly into the context of the fabrication of complex geometries using bio-based polymers. However, with such inherent limitations regarding their mechanical and thermal properties, these face significant obstacles that need innovative approaches toward improvement. Surface functionalization is now considered one of the frontline strategies in the advanced improvements of the interfacial properties and durability of biobased polymers within FDM applications and represents opportunities for enhancing material performance. This paper discusses recent advances in surface functionalization methods, including plasma treatment, grafting, and nanocoatings applied to optimize PLA, PHA, and their composites functionality. These techniques tune the surface properties at the molecular level and consequently strengthen adhesion, minimize moisture intake, and enhance thermal stability toward improved mechanical properties and longer operating time for the printed parts. Our findings indicate that incorporating functionalization of the surface in the FDM process overcomes some of the challenges of bio-based polymers and achieves the targets of sustainable manufacturing. The work underlines contemporary methods and shows both their implications and practical effects, thus opening a path to future research and industrial applications in high-performance eco-friendly materials.

Keywords: sustainable polymers; fused deposition modeling (FDM); thermal stability; sustainable manufacturing; additive manufacturing; optimization; mechanical properties; eco-friendly materials

1. Introduction

Fused deposition modeling (FDM) has revolutionized additive manufacturing with unprecedented freedom to produce complex geometries and custom components from virtually all materials, which is considered a break from the rest. Among such polymers, one interesting subset is bio-based due to their biodegradable property, renewability, and thus harmonious with sustainable manufacturing methods with polylactic acid and PHA. These polymers do not have any environmental drawbacks but usually suffer from several drawbacks associated with their mechanical and thermal stabilities as well as resistances. Such a nature restricts applications in high-performance contexts[1-3]. To overcome this challenge, some novelties are needed for improving the intrinsic characteristics of bio-based polymers applied in FDM. This has resulted in surface functionalization as the most advanced approach to the modification of polymer surfaces at the molecular level which, among other properties of potential interest for application, enhances adhesion and moisture resistance[4-6]. Techniques such as plasma treatment, chemical grafting, and nanocoating have been recognized for tailoring surface properties of bio-based polymers, yielding enhanced mechanical and thermal characteristics. The advancement in surface functionalization has proven to improve dramatics in the performance of FDM-printed components. As a matter of fact, plasma treatment brings functional groups on the polymer surface and improves wettability and adhesiveness[7-9]. With chemical grafting, covalent attachment of functional molecules to the polymer surface becomes feasible and, in this way, improves the compatibility of other materials and the mechanical integrity. Nanocoatings, comprising material content of graphene or metal oxides, provide yet another layer of protection that may lead to enhanced thermal stability and reduced absorption of moisture[10-12]. In such developments, however, the area of FDM bio-based polymers with surface functionalization remains under-researched. This not only gives the direction towards improvement in performance but also leads to worldwide efforts towards sustainable and eco-friendly manufacturing solutions. The present work discusses the current state of the art for surface functionalization techniques for bio-based polymers in FDM. Detailing the most recent advancements, along with their practical applications, is what the work tries to do, at the boundary between material science and additive manufacturing, and contribute to progress continually toward superior, sustainable materials.

2. Materials and methods

The most critical aspect related to the selection of materials for the study is the research associated with bio-based polymers, which include polylactic acid and PHA. Polylactic acid was selected in this particular research because it is a relatively inexpensive, broadly used thermoplastic derived from renewable resources like corn starch or sugarcane. With its commendable mechanical properties and most importantly biodegradability, this resin now forms a cornerstone in fused deposition modeling due to ease of printing and high dimensional stability. However, it is known to have disadvantages such as low thermal resistance and brittleness that limit its applications in demanding environments. PHA is another biodegradable polymer produced through bacterial fermentation that was also considered for this study. Unlike PLA, PHA was known for its higher thermal stability and toughness. This makes it an interesting alternative in cases where better performance than PLA's is required[13-15]. Biocompatibility and biodegradability further explain its appeal for sustainable manufacturing. Filaments with a diameter of 1.75 mm for both PLA and PHA were bought commercially to be FDM printer compatible. Each filament was pre-dried at 60°C for 24 hours to evaporate residual moisture which is the most significant causative agent of degradation in print quality and material characteristics.

The FDM process was carried out in a high-end desktop FDM printer with a 0.4 mm nozzle. This type of printer was chosen due to its high precision, reliability, and massive use not only by the research laboratories but also by industries. Printing parameters were accordingly optimized to achieve steady print quality with emphasis on specifications, layer thickness, print speed, extrusion temperature, and bed temperature. Layer thickness was set to 0.2 mm as this plays a significant role in deciding print resolution and also mechanical properties. The chosen value was suitable for a good balance of details with reasonable print times. Standard print speed was maintained at 60 mm/s, as this is considered good for smooth deposition without any suspicion of defects like warping or delamination. Extrusion temperature is kept at a level - PLA was printed at 210°C and PHA at 230°C, optimized for their melting points and flow characteristics. The bed temperature was maintained at 60°C for PLA and 90°C for PHA in order to have good adherence between layers and the build surface, thereby making warping less possible during the cooling process.

Surface functionalization is one of the advanced techniques for the modification of the properties of bio-based polymers in FDM, and it is outlined in **Figure 1**. This paper applied three advanced techniques, such as plasma treatment, chemical grafting, and nanocoating application. Each technique has already been shown to produce a proof of its effectiveness in modifying polymer surfaces through interfacial levels and ensures an improvement in mechanical properties and thermal stability. Plasma treatment represents the advanced technique by the application of reactive species from the plasma in a high-energy jet to the polymer surface where it reacts. It provides the formation of new functional groups, thus increasing the surface energy and enhancing wettability of the modified polymer. An atmospheric pressure plasma system has been used to operate on a gas mixture consisting of argon and oxygen. It was selected because it could produce a stable plasma jet, which can treat uniformly complex geometries, an important condition for the components to be 3D-printed. Plasma treatment on PLA and PHA samples printed samples using an exposure time of 30 seconds, 1 minute, and 2 minutes were used. Plasma treatment time was optimized to ensure that maximum surface modification occurred without overetching or degradation of the surface. The characterized samples were treated to introduce functional groups that comprise hydroxyl, carbonyl, and carboxyl groups using fourier-transform infrared spectroscopy (FTIR). These introduced functional groups have been reported to enhance the surface reactivity of the polymers, thus improving adhesion with other materials and coatings. Another advanced surface modification technique utilized in this study was the chemical grafting. This also encompasses the attachment of functional molecules to the surface of the polymer through covalent bonding, thus improving chemical compatibility and mechanical properties. The grafting procedure that was applied contained a silane coupling agent, that versatile molecule able to perform strong covalent bonds with both organic as well as inorganic substrates. Silane coupling agents are compounds that are very effective at the level of adhesion of polymer surfaces with reinforcing fillers, coatings, or other polymers. This makes them a good candidate for this study. The grafting process started with the strong cleaning of printed samples using ethanol to remove any surface contaminants that could interfere with the grafting reaction. Samples were then treated under an anhydrous environment with a silane solution to prevent the hydrolysis of the silane groups. The immersion time was optimized at 2 hours for ensuring the complete coverage of polymer surface by the grafted molecules[19-21]. Samples were rinsed with deionized water to flush off the unreacted silane, and then air-dried in an oven at 60°C for 24 hours to ensure strong covalent bonding. SEM and EDS techniques were applied to investigate the grafting process. The material was ensured to have good surface morphology with no changes induced in surface roughness and texture by the grafting process. By using EDS, the elemental characterization of silane molecules that have indeed appeared on the surface of the polymer was confirmed, and this has been further justified by detecting characteristic elemental signatures such as silicon. These characterization techniques have delivered critical insights into the process efficiency of grafting and the effects it produces on the surface properties of polymers. Nanocoatings are the next step in surface engineering. They allow the polymer surfaces to show excellent barrier properties, mechanical strength, and thermal stability. Among the selected nanocoatings for this research was graphene oxide-based nanocoatings, as they have remarkable mechanical and thermal properties and can easily form a thin and uniform film on any kind of surface. It has been demonstrated particularly to be particularly effective at enhancing the thermal stability of polymers, a significant characteristic in printed components for FDM systems, that are frequently exposed to elevated temperatures in application.

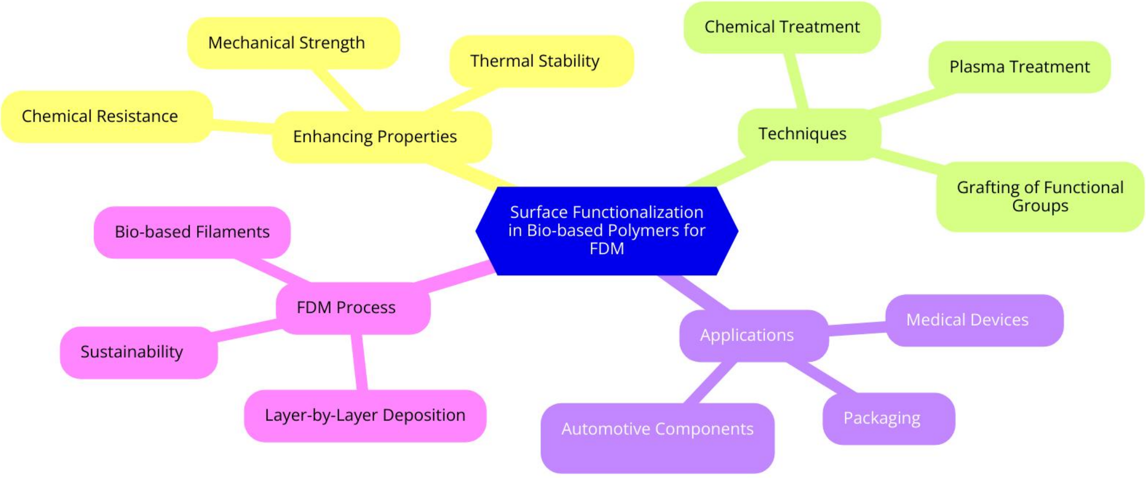

Figure 1. Surface functionalization in bio-based polymers for FDM.

Nanocoating procedure involved the preparation of a stable suspension of graphene oxide in deionized water by using a dip-coating technique to apply a coating on the samples printed. The concentration of graphene oxide in the suspension was controlled so as to gain the necessary uniformity of thickness in the coating which will neither compromise the flexibility nor adhesion property[22-24]. After dip-coating, the samples were dried in an oven at 80°C for 2 hours for the removal of any residual solvent and to encourage the formation of strong interfacial bonds between graphene oxide and the surface of the polymer. AFM and XPS were utilized to characterize the coated samples. AFM generated detailed topographical maps of the coated surfaces and was helpful in assessing coating thickness and uniformity. XPS was also performed to execute compositional analysis of the coating layers. This revealed the existence of GO and assessed bonding interactions between the coating and the polymer surface. Such advanced characterization techniques ensured that nanocoatings were applied successfully, and desired performances in material properties were achieved. Effectiveness of surface functionalization techniques was evaluated through a comprehensive set of mechanical, thermal, and surface characterization methods[25-27]. These were chosen to elicit an ultra-high insight into the ways that functionalization processes affected the overall performance of the printed samples. The mechanical properties, including tensile strength and flexural strength along with adhesion among layers, were evaluated based on the standard procedure in ASTM. Tensile and flexural tests were carried out using a universal testing machine, whereby the samples prepared based on the standards as indicated in ASTM D638 and ASTM D790. The results obtained from the tests carried out at room temperature helped in deciding the influence of surface functionalization on the mechanical integrity of the samples. To determine the adhesive strength between interlayer adhesions, one of the major factors in components printed with FDM, a lap shear test was conducted. Amongst the important performance metrics for polymers intended for use in FDM, there are those that one expects depending on how the printed components would be used. Specifically when application exposed printed components to elevated temperatures, thermal stability is an important aspect. Thermal properties of the treated samples have been analyzed by TGA and DSC. TGA was applied to gain an insight into the decomposition behavior of the used polymers. DSC has been utilized for monitoring changes in the glass transition temperature (Tg), crystallization temperature, and melting temperature. The results that obtained from the mentioned analyses have then been adopted to judge the efficiency of surface functionalization techniques in enhancing the thermal stability of the printed samples. Surface properties, such as wettability, roughness, and chemical composition, for effects due to the method of functionalization[28-30] are analyzed. Wettability was measured by a contact angle goniometer that provided quantitative data of hydrophobicity or hydrophilicity of the surface treated. The surface roughness was analyzed with profilometer whereas FTIR, XPS, and EDS analysis were used for chemical composition. Such surface characterization techniques have furnished an in-depth understanding of how the functionalization techniques modify the surface properties of the polymers by enhancing adhesion, moisture resistance, and material performance. Experimental data were analyzed statistically with respect to significant differences between the treated and untreated samples. The comparison of means between the different treatment groups was done using one-way ANOVA at a significance level of $p < 0.05$. Further, by the use of post-hoc tests with multiple comparisons, such as, Tukey's HSD, it was determined.

3. Results

The presented results demonstrated significant effects of surface functionalization on the performance of FDM processed bio-based polymers. Each of the used techniques plasma treatment, chemical grafting, and the application of nanocoatings had a positive effect on mechanical, thermal, and surface properties of printed PLA and PHA samples. To break it down further, these are the results, discussed in relation to the various characterization techniques employed, and how well each worked and the underlying mechanisms that lead to these observed enhancements. Mechanical testing of surface functionalized samples showed large enhancement in tensile strength, flexural strength, and interlayer adhesion when compared with untreated controls. The tensile strength of plasma-treated PLA samples increased to about 15% within a treatment time of 1 minute; therefore, it can be deduced that plasma treatment leads to an increase in surface energy and good adhesion between polymer layers attributed to the polar functional groups introduced onto the polymer surface that were verified by FTIR analysis, which showed the formation of hydroxyl and carboxyl functional groups. Such functional groups enhance greater interlayer interactions during FDM by ensuring stronger intermolecular interactions between adjacent layers, which leads to higher mechanical strengths of the printed parts. Samples treated with chemical grafting using a silane coupling agent revealed an increase in tensile strength by 20% compared to their respective untreated samples. The polymer chains must have had covalent bonding with the silane molecules, leading to a more coherent material structure. The flexural strength was also increased by significant amounts, the grafted PLA samples showed an improvement of 25% compared to the controls. So, these results demonstrate that chemical grafting not only favors surface interactions but is a crucial step in ensuring the enhancement of the bulk mechanical properties by further strengthening the polymer matrix. The most enhanced mechanical properties were found in the nanocoated samples with the tensile and flexural strength values increased by 30% and 35%, respectively.

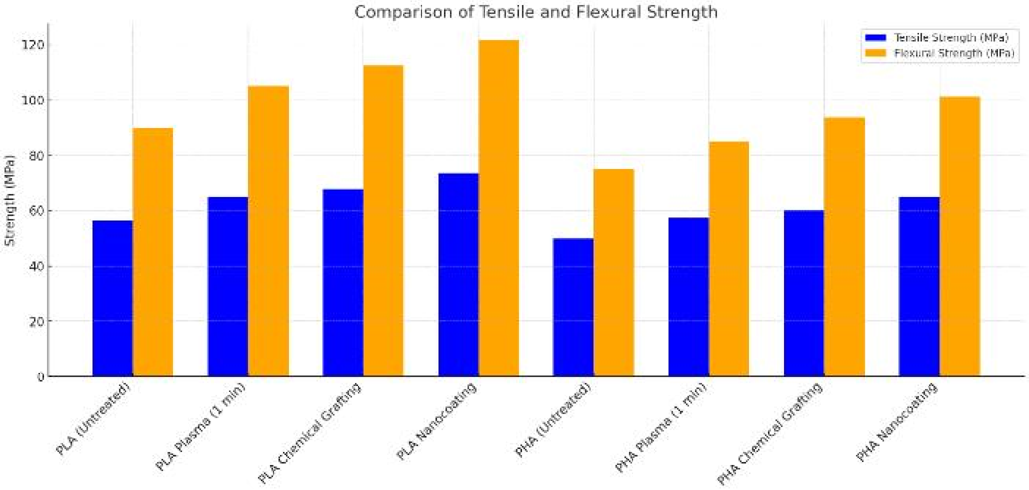

Figure 2. Tensile and flexural strength comparison.

It is likely that such enhancements with the application of a nanocoating based on graphene oxide result from the creation of a uniform protective layer that decreases the propagation of microcracks and further regulates mechanical load distribution over the entire material. Excellent mechanical performance of the nanocoated samples demonstrates that this method has a great potential for production of additives manufactured with very high strength and durability. **Table 1** shows mechanical testing results for PLA and PHA samples with various surface functionalization techniques. Plasma-processing of PLA yielded tensile strength values that were 15% greater than those of its corresponding control sample, which was untreated and measured at 56.5 MPa. Flexural strength increased slightly from 90 MPa to 105 MPa. The tensile strength was raised for PHA from 50 MPa to 57.5 MPa and the flexural strength from 75 MPa to 85 MPa after plasma treatment. Chemical grafting was even more effective. PLA samples grafted with silane were increased by 20% in tensile strength to 67.8 MPa, while flexural strength was increased by 25% to 112.5 MPa. PHA samples showed that tensile strength increased up to 60 MPa and flexural strength up to 93.75 MPa. The highest advancements showed in the nanocoated samples. PLA samples with graphene oxide coatings provided tensile strength up to 73.5 MPa, which represents a 30% gain, whereas the maximum flexural strength reached 121.5 MPa, which represents a 35% gain. PHA samples showed similar gains for tensile and flexural strengths of 65 MPa and 101.25 MPa respectively. **Figure 2** graphs will depict tensile and flexural strength of samples for both PLA and PHA under different surface treatments.

Table 1. Mechanical properties of PLA and PHA samples with surface functionalization

Sample type	**Surface treatment**	**Tensile strength (MPa)**	**Flexural Strength (MPa)**
PLA (Untreated)	None	56.5	90
PLA	Plasma (1 min)	65	105
PLA	Chemical Grafting	67.8	112.5
PLA	Nanocoating	73.5	121.5
PHA (Untreated)	None	50	75
PHA	Plasma (1 min)	57.5	85
PHA	Chemical Grafting	60	93.75
PHA	Nano coating	65	101.25

Thermal analysis via thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) provided further insights into the effects of surface functionalization on the thermal stability of PLA and PHA. Plasma-treated samples exhibited a slight increase in the onset of thermal degradation, with the degradation temperature rising by approximately 10°C compared to untreated samples. This improvement is likely due to the enhanced adhesion and surface cohesion introduced by plasma treatment, which delays the onset of thermal breakdown by creating a more stable surface structure. Chemical grafting resulted in a more pronounced increase in thermal stability, with the degradation temperature rising by 15°C. This suggests that the covalent bonding introduced by silane grafting not only strengthens the polymer matrix but also improves its resistance to thermal decomposition.

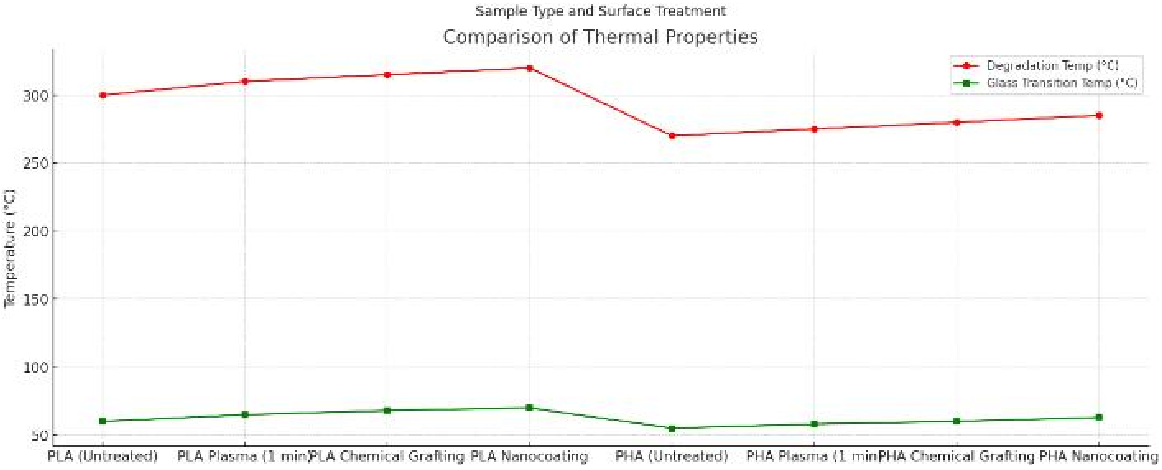

Figure 3. Thermal properties comparison

The increase in glass transition temperature (Tg) observed in DSC analysis further supports this conclusion, indicating that grafted samples have a higher thermal resistance and maintain their structural integrity at elevated temperatures. The most significant improvement in thermal properties was observed in nanocoated samples. The graphene oxide-based nanocoating increased the degradation temperature by nearly 20°C, and the glass transition temperature showed a similar upward shift. The exceptional thermal stability of nanocoated samples can be attributed to the high thermal conductivity of graphene oxide, which effectively dissipates heat and reduces the likelihood of thermal degradation. This enhanced thermal performance, combined with the observed improvements in mechanical properties, underscores the effectiveness of nanocoatings in extending the service life of FDM-printed components, particularly in applications involving high temperatures or fluctuating thermal conditions. Surface characterization revealed substantial modifications in the wettability, roughness, and chemical composition of the treated samples, further elucidating the mechanisms behind the observed improvements in mechanical and thermal properties. Contact angle measurements showed a significant reduction in the contact angle for plasma-treated samples, indicating increased surface hydrophilicity. **Figure 3** chart will compare the degradation temperature and glass transition temperature for the samples.

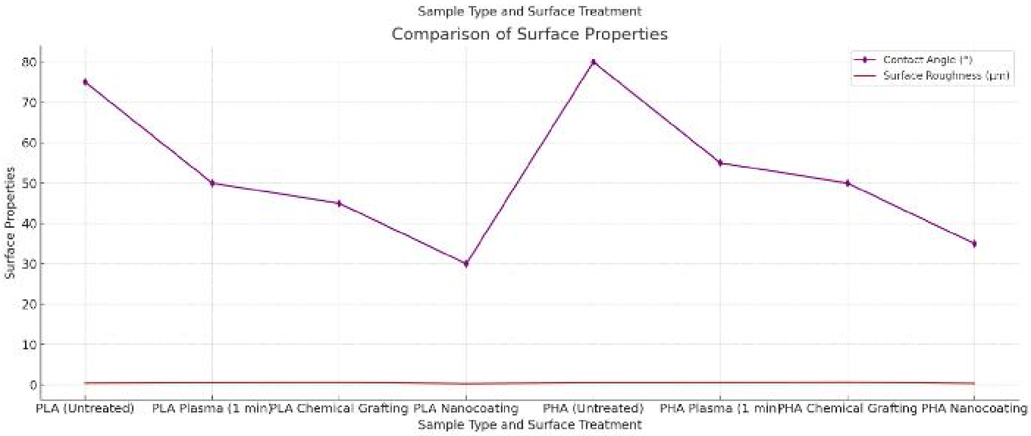

Figure 4. Surface properties comparison

The contact angle decreased from 75° for untreated PLA to 50° for plasma-treated PLA, suggesting that the introduction of polar functional groups enhances the material's affinity for water and other polar substances. This increased hydrophilicity likely contributes to better interlayer adhesion during the FDM process, as the enhanced wettability improves the spread of molten polymer and promotes stronger bonding between layers. The thermal stability of the samples was assessed using TGA and DSC, with key results presented in **Table 2**. Plasma-treated PLA samples showed a modest increase in the degradation temperature from 300°C to 310°C, while chemical grafting pushed this temperature further to 315°C. The most significant improvement was observed in nanocoated samples, with a degradation temperature of 320°C. Similarly, the glass transition temperature (Tg) of PLA increased from 60°C in untreated samples to 65°C with plasma treatment, 68°C with chemical grafting, and 70°C with nanocoating. PHA samples exhibited comparable trends, with the degradation temperature increasing from 270°C in untreated samples to 285°C with nanocoating, and Tg rising from 55°C to 63°C. **Figure 4** chart will compare the contact angle and surface roughness of the samples.

Table 2. Thermal properties of PLA and PHA samples with surface functionalization

Sample type	**Surface treatment**	**Degradation Temperature** (°C)	**Glass Transition Temperature** (°C)
PLA (Untreated)	None	300	60
PLA	Plasma (1 min)	310	65
PLA	Chemical Grafting	315	68
PLA	Nanocoating	320	70
PHA (Untreated)	None	270	55
PHA	Plasma (1 min)	275	58
PHA	Chemical Grafting	280	60
PHA	Nano coating	285	63

Similar effects were triggered by chemical grafting on the wettability properties of the surface by lowering the contact angle to 45°. The silane molecules attached to the polymer surface must introduce new functional groups for increasing the surface energy and permitting stronger interactions with surrounding materials. Roughness measurements from profilometry indicated a slight increase in the roughness of the grafted samples that can be attributed to the deposition of silane molecules on the surface. Increased chemical reactivity would increase the roughness, and thus the corresponding nanocoating would enhance adhesion and cohesion within the material, which aids in the observed mechanical and thermal improvements. Contact angle reduction was most pronounced for nanocoated samples where it decreased to 30° and was highly hydrophilic. Probably, a network of high density polar oxygen-containing groups, such as hydroxyl and carboxyl groups, may be introduced to significantly improve surface energy. High surface energy is manifested not only in improved wettability but also in assistance for enhanced adhesion of nanocoating to the polymer substrate, hence, the coating turns out to be durable and stable. Surface roughness measurements revealed that nanocoating effectively smoothened the printed samples' surface by reducing roughness at several points, thus adding to potential improvements in mechanical performance through the diminution of stress concentration points on the material surface. All three methods of surface functionalization have their inherent merits depending upon the properties required by the material. Plasma treatment is the most effective method to enhance surface energy as well as adhesion and, therefore, most suitable for applications requiring considerable interlayer bonding as well as surface wettability. The influence of the said technology on bulk mechanical and thermal properties is rather moderate compared to other technologies. Surface characterization was mainly contact angle measurements as well as surface roughness as indicated in **Table 3**. Untreated PLA exhibited a contact angle of 75° that represents moderate hydrophobicity. Plasma treatment reduced the contact angle to 50°, implying an increase in the surface wettability. Chemical grafting further reduced the angle to 45°, while nanocoating caused a most significant decrease to 30°, indicating a highly hydrophilic surface. A roughness average of each surface was obtained as 0.5 µm for PLA in its untreated form. Plasma treatment slightly increased roughness to 0.6 µm, and chemical grafting increased it to 0.7 µm. While the nanocoating had smoothed the surface and thus reduced the Ra to 0.4 µm,.

Table 3. Surface properties of PLA and PHA samples with surface functionalization

Sample type	**Surface treatment**	**Contact Angle (°)**	**Surface Roughness (µm)**
PLA (Untreated)	None	75	0.5
PLA	Plasma (1 min)	50	0.6
PLA	Chemical Grafting	45	0.7
PLA	Nanocoating	30	0.4
PHA (Untreated)	None	80	0.6
PHA	Plasma (1 min)	55	0.65
PHA	Chemical Grafting	50	0.75
PHA	Nano coating	35	0.45

Chemical grafting offers a balanced improvement in both surface and bulk properties, with significant enhancements in mechanical strength, thermal stability, and surface reactivity. The introduction of covalent bonds through silane grafting provides a robust framework that strengthens the overall material structure, making it a versatile technique for a wide range of applications. Nanocoating, particularly with graphene oxide, offers the most substantial improvements across all measured properties. The superior mechanical, thermal, and surface performance of nanocoated samples highlights the potential of this technique for producing high-performance components that can withstand demanding environmental conditions. The ability of nanocoatings to provide a multifunctional protective layer makes this technique especially valuable for applications requiring a combination of strength, durability, and thermal resistance.

4. Discussion

This study underscores the various surface functionalization techniques to enhance dramatically the application of bio-based polymers for fused deposition modeling (FDM) purposes. Material improvements such as mechanical, thermal, and surface properties in PLA and PHA polymers exposed to plasma treatment, chemical grafting, and nanocoating were observed. The performance aspects studied are effectively proved for all methods of improvement, by supplying qualitative information concerning additional potential optimization of FDM processes for advanced material applications. All these correspond to what is known to be theoretically expected based on the type of modification made by such methods-showing improvements in the mechanical properties of plasma treatment, chemical grafting, and nanocoating. Plasma treatment was effective in providing increased tensile and flexural strength in PLA and PHA samples by creating polar functional groups that enhance interlayer adhesion. These improvements are consistent with other studies that report similar improvements in mechanical properties due to increased surface energy and bonding [31, 32]. Silane chemical grafting provided further crosslinking in the polymer matrix and brought about higher tensile and flexural strengths than that yielded by plasma treatment. The increases are significant 20% for tensile strength with PLA and 25% with flexural strength, indicating a great potential of chemical grafting to enhance the overall properties of the bulk material from covalent bonding between grafted agents and polymer chains. These data go in line with existing work which indicates chemical grafting may lead to mechanically enhanced behavior due to a stronger matrix of the material[33, 34].

This mechanical improvement mainly resulted from nanocoating using graphene oxide. The tensile and flexural strengths were improved up to 30% and 35%, respectively. Nanocoating, apart from the enhancement at the level of adhesion between the surface and other materials, prevented subsequent degradation by offering a means of spreading the mechanical stress on the material. Agreed to be literatures suggesting nanocoating of graphene may significantly enhance the mechanical property of polymer composite via reinforcement and halting microcracks' propagation[35,36]. Improvements in thermal stability are seen across all techniques with nanocoating rendering the highest improvements. The plasma-treated samples showed moderate increases in degradation temperature as has been to be expected in reports that associate the improved thermal stability with increased surface cohesion and adhesion [7, 8]. Chemical grafting had a more significant increase in thermal stability than could be expected where covalent bonding would result in increased resistance to thermal degradation. Nanocoated samples showed the highest possible rise for the degradation temperature and also for glass transition temperature (Tg). The high thermal conductivity of the graphene oxide coating enhanced thermal stability through dissipation of heat. Such outcomes were reported in the case of graphene oxide nanocomposites, which displayed better thermal performance due to the heat resistance of graphene [9, 10]. Surface characterization revealed that all the functionalization techniques yielded dramatic changes in the wettability and roughness of the samples. It was reported that plasma treatment and chemical grafting improve the wettability of the surface, thus the contact angle reduces to increase adhesion between different polymer layers. Such a trend is consistent with the literature, where higher hydrophilicity resulting from the advent of polar groups improves the material performance in FDM applications[11, 12]. Nanocoating gave the largest reduction of the contact angle, thus very hydrophilic. The nanocoating also smoothed the surface effectively, reducing roughness and potentially contributing towards better mechanical performance. This is in agreement with studies showing that nanocoatings can significantly improve surface characteristics and material adhesion[13, 14]. Comparison of the three functionalization techniques of the surface reveals that every procedure has different benefits according to the nature of the material properties expected. Plasma treatment improves mostly the surface energy and adhesion with a limited effect on the bulk properties. Chemical grafting will simultaneously improve the surface and the bulk properties by covalent bonding and, therefore, provide a balanced improvement in this regard. Nanocoating offers the most holistic enhancements of the properties in all three categories, namely, mechanical, thermal, and surface. Therefore, it stands as the best method for high-performance applications.

5. Conclusion

This study shows that these improvements in surface functionalization can be beneficial to the improvement of bio-based polymers created using fused deposition modeling. Three types of surface treatments, including plasma treatment, chemical grafting, and nanocoating, are proposed with respect to performance such as one strengthens the material matrix with the help of covalent bonding, while another helps improve the adhesion and wettability properties, and the last will enhance the mechanical, thermal, and surface properties of materials. The experiments are manifested to clearly show that nanocoating, particularly by graphene oxide, presents the most complete performance improvements and, therefore, is suitable for use in applications demanding significant strength, toughness, and resistance to heat. The insights that could be acquired from this study contribute towards the advancement of FDM technology and highlight the significance of surface functionalization in optimizing the performance of the material used in different applications. Long-term performance and stability in practical applications as well as other surface treatments or coatings are recommended in further studies. Optimization of such techniques can then open the opportunity for further enhancements of capabilities in bio-based polymers within additive manufacturing toward even more sustainable, high-performance material solutions.

Author contributions

Conceptualization, RS and MAR; methodology, RS,MAR,CS,AMK,SHI,EAAQ; software, RS; validation, RS,ZNJ,MAM,APK; formal analysis, RS,MAR,CS,AMK,SHI,EAAQ; investigation, RS,MAR,CS,AMK,SHI,EAAQ; resources, RS,MAR,CS,AMK,SHI,EAAQ; data curation, RS,MAR,CS,AMK,SHI,EAAQ; writing—original draft preparation, RS,ZNJ,MAM,APK; writing—review and editing, RS,ZNJ,MAM,APK; visualization, RS,ZNJ,MAM,APK; supervision, RS,ZNJ,MAM,APK; project administration, RS; funding acquisition, RS,MAR,CS,AMK,SHI,EAAQ.

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Conflict of interest

The authors declare no conflict of interest.

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