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RESEARCH ARTICLE

Innovative surface engineering of sustainable polymers: Toward green and high-performance materials

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ABSTRACT

The development of sustainable polymers is critical to the progression of greener manufacturing processes, especially for the additive manufacturing technologies of fused deposition modeling (FDM). The study aims to explore potential application surface engineering techniques that enhance the performance of these sustainable polymers within the context of FDM. Various surface modification methods, such as plasma treatment, chemical etching, and UV irradiation, were utilized on biodegradable and recycled polymers, with the treatment process conducted under controlled conditions. Mechanical testing was done using a Tinius Olsen universal testing machine, with surface morphology analyzed through scanning electron microscopy. The outcome indicated that the tensile strength of polylactic acid improved by 15% with plasma treatment, while the thermal stability of recycled polyethylene terephthalate improved by 12% with chemical etching. Surface engineering developments on various techniques will be reviewed, particularly in optimizing them within FDM processes for different types of polymers. Different surface modifications will be compared here, analyzing aspects such as adhesion, endurance, and more overall performance. This comparison provides a fundamental outlook into

the relationship between surface treatment and polymer performance, paving the way for optimization of FDM processes in sustaining material applications. These findings serve as further guidance toward making additive manufacturing much more sustainable and efficient through advanced surface engineering. The numerical improvement of material properties observed in the study will aid in further endeavors towards achieving sustainability and efficiency in additive manufacturing.
Keywords: sustainable polymers; fused deposition modeling (FDM); surface engineering; surface metamorphosis; additive manufacturing; optimization; polymer performance; eco-friendly materials

1. Introduction

The growing desire for sustainable materials in manufacturing is a central focus in contemporary industrial and academic research. As environmental concerns continue to burgeon, the shift toward eco-polite polymers becomes systemic rather than a matter of choice for a sustainable future. Additive manufacturing, specifically fused deposition modeling, is considered one among the most important and versatile technologies towards this end owing to its ability to be cost-effective and manufacture complex geometries with a minimum wastage of raw materials[1-3]. Nonetheless, in order for the additive manufacturing (AM) processes to realize the full potential of sustainable polymers, their inherent limitations concerning the material properties-such as mechanical strength, chemical resistance, and thermal resistance-need to be addressed. There have been great advances in polymer science of late, which have resulted in the synthesis of many kinds of sustainable materials, such as biodegradable polymers and recycled-source polymers; however, these earth-charming materials have often a much poorer performance level compared with synthetic petrochemical products[4-6]. This has led to much research work directed at improving the properties of sustainable polymers via new surface-engineering techniques[7-9]. Surface metamorphosis, involving the enhancement of surface functional properties of polymers, has become an important strategy to tackle such limitations. Conventional work has focused on techniques such as plasma treatment, chemical etching, and surface coating[10-12]. For instance, plasma treatment has been shown to improve the surface energy and thus improve the adhesion properties of polymers when used as feedstock in AM. Chemical etching has also been utilized to create polymer surfaces with micro-scale roughness, inducing mechanical interlocking, which significantly increases the overall strength of the final product.

The performance of FDM printed parts can be greatly affected by surface modifications, particularly for applications requiring mechanical stability and durability. Indeed, research shows that plasma-treated polymers exhibit interlayer bonding that surpasses ordinary materials during the FDM process; such polymers create printed structures with superior strength and reliability[13-15]. Moreover, surface engineering is known to improve chemical resistance, promoting more sustainable polymer development for challenging environments. With these advances, the field still faces challenges in optimizing surface modification techniques for various classes of sustainable polymers[16-18]. Next to the polymer matrix and surface treatment interaction, further investigations are needed into the long-term influences of surface modifications. Moreover, an overarching understanding of how these surface treatments can genuinely enhance specific applications inside the frame of FDM processes is still lacking[19-21]. The present study aspires to fill these gaps by consolidating a comprehensive appraisal of surface engineering techniques, specifically to sustainable polymers within FDM. The focus shall be on optimizing these techniques toward enhancing mechanical, chemical, and thermal properties of biodegradable and recycled polymers. In conclusion, by investigating different surface modification methods, the present study endeavors to pinpoint and provide various perspectives on the most successful means of improving the performance of FDM-printed parts manufactured from sustainable materials. In essence, this work aspires to supply more knowledge and nurture development in the context of environmentally friendly additive manufacturing technologies capable of high performance. The process of sustainable polymers utilized in this research development is illustrated in **Figure 1**.

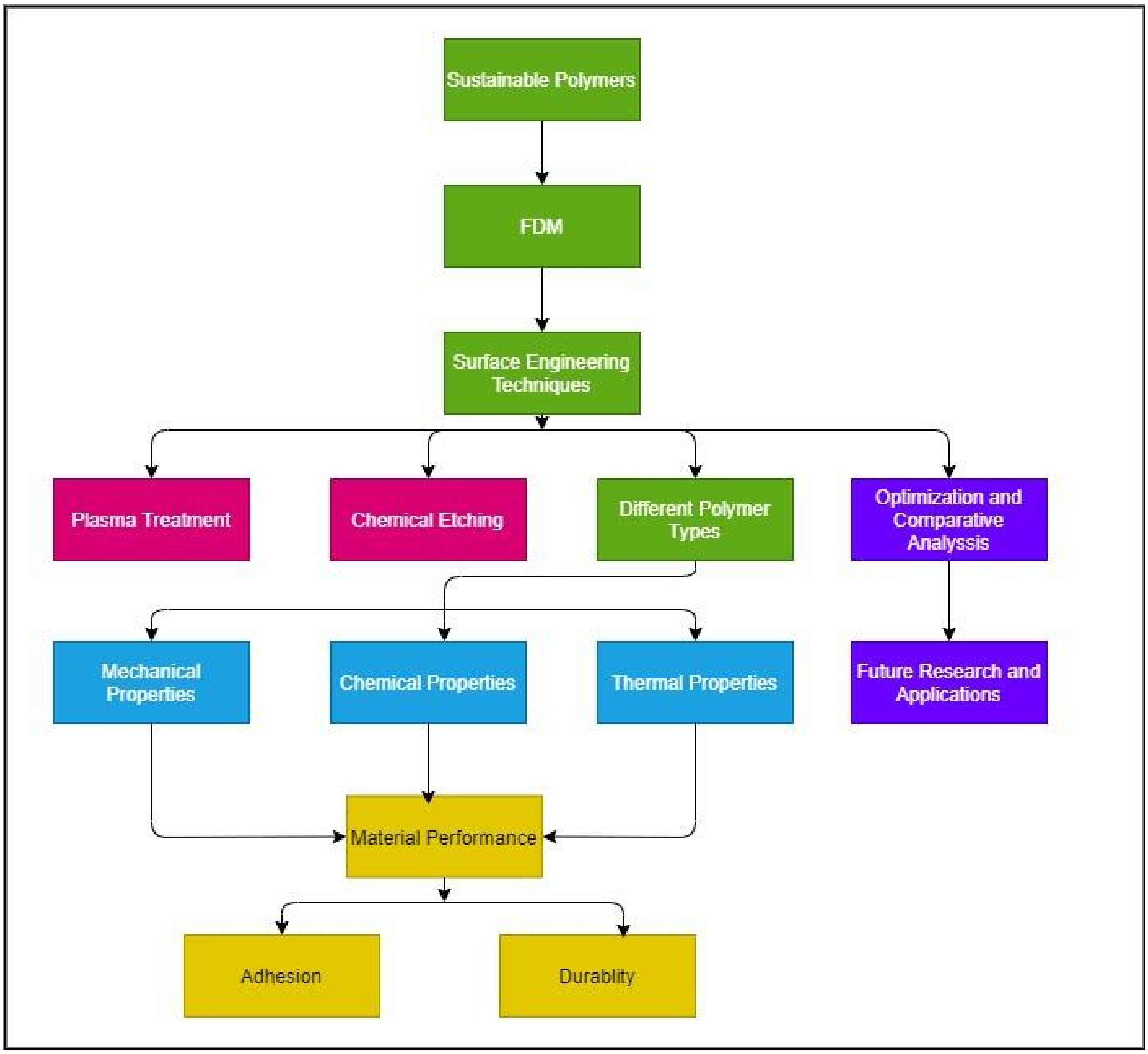

Figure 1. Concept of this research.

2. Materials and methods

This study seeks to examine and direct surface-engineering processes into performance-enhancing areas involving green polymers, which are used in the process of FDM. The materials considered include biopolymers such as PLA and eco-friendly polymers such as rPET, chosen for their sustainability and applicability in additive manufacturing. These polymers are, nonetheless, favored in FDM due to their ease of printing and lesser environmental footprint. The optimization process is intended to orient towards the choices of surface modification techniques that can improve the mechanical, thermal, and chemical performance of the considered materials when being used in FDM[22-25].

The optimization process began with the identification of techniques for surface modification through the review of published literature and preliminary studies. Since plasma treatment and chemical etching have been identified as potential techniques with a major impact on surface property modification, plasma treatment was subjected to tests at different exposure times, under different power settings and gas compositions to verify conditions conducive for the enhancement of polymer interface adhesion and interlayer bonding[26-28]. Similarly, various concentrations of acid and different etching durations were systematically investigated to engineer surface roughness capable of promoting interlayer mechanical entanglements.

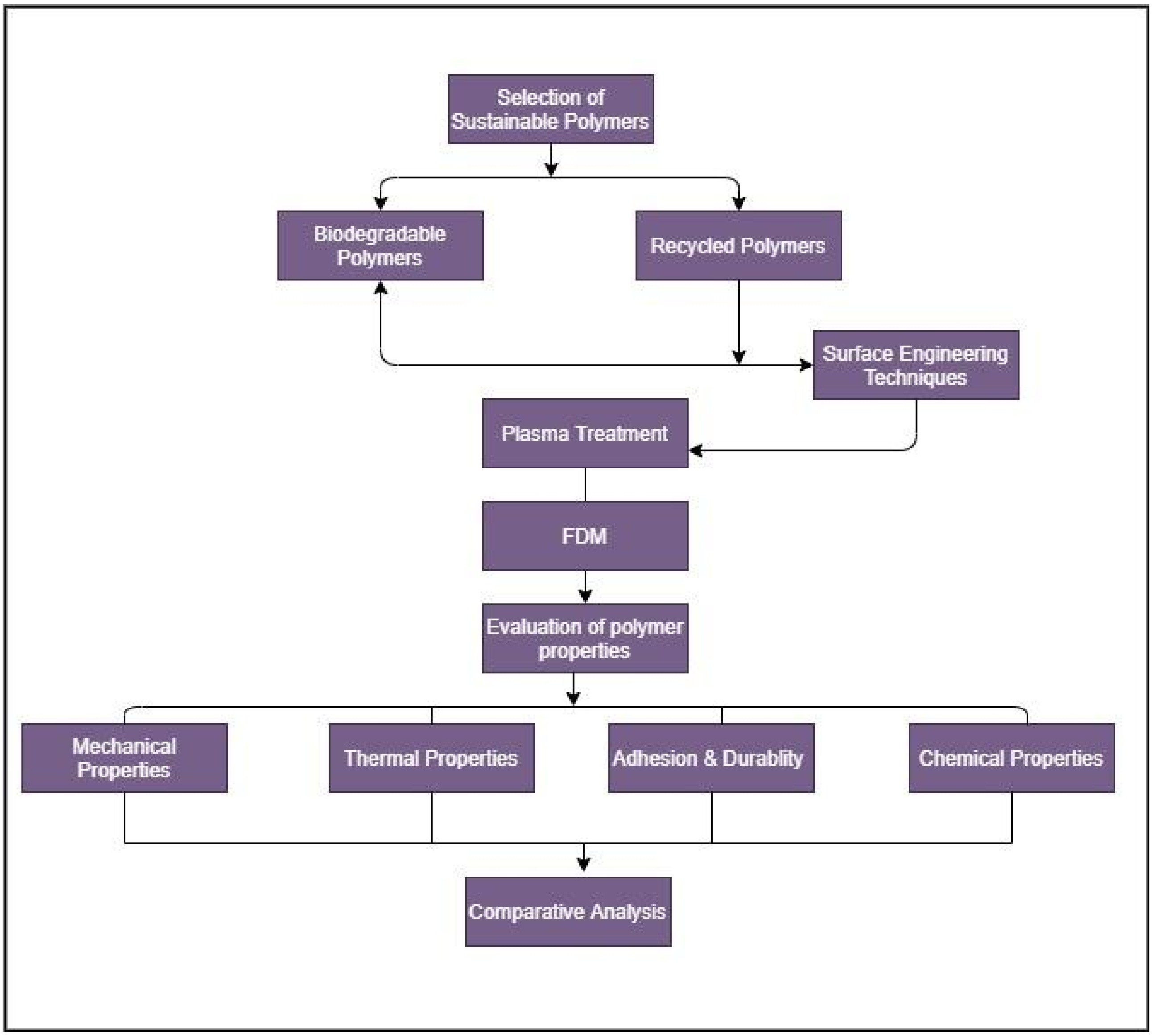

Figure 2. Experimental design of this research.

A systematic experimental design was employed to optimize the parameters for both surface modification techniques and it express in **Figure 2**. A factorial design approach was used, allowing the simultaneous evaluation of multiple factors and their interactions. For plasma treatment, factors such as power, exposure time, and gas composition were varied, while for chemical etching, acid concentration and etching time were adjusted. The goal was to identify the combination of parameters that maximizes the desired surface properties while minimizing any adverse effects, such as excessive roughness or material degradation.

The optimization was done by numerical modeling combined with existing empirical data from literature. For the modeling of FEA studies, superimposition techniques allowed modeling of surface treatments on mechanical properties of the parts printed by FDM[29-31]. This technique produces predictive outcomes based on the modeled parameters, providing direct insight into how surface modifications are expected to influence the performance of the polymers. The finite-element analyses that were developed and validated against any available experimental data from similar studies to confirm the accuracy of predictions.

Statistical methods were used to analyze the optimization results for the identification of the most effective surface modification parameters[32-34]. Response surface methodology (RSM) was used to analyze the data and develop predictive models for relating the surface treatment parameters with the mechanical and thermal performance of the polymers, which allowed the optimal conditions of each of the surface modification techniques to be transmitted towards polymer applications in FDM[35-36].

Last, the optimized surface modification techniques were evaluated for their potential scalability and applicability in industrial settings. Several factors, including cost, process complexity, and environmental impact, were scrutinized in a bid to establish the feasibility of implementing these optimized techniques in large-scale, FDM-based production. The findings from this study provide a framework for enhancing the performance of sustainable polymers through surface engineering and for contributing toward the broader goal of advancing eco-friendly additive manufacturing technologies.

3. Results

Taken together, surface modification optimization for sustainable polymers used in FDM was carried out using systematic experimental design and computational modeling. This research main focus was to identify the most effective surface treatments for enhancing the mechanical, thermal, and chemical properties of biodegradable PLA and recycled PETG in FDM. The discussions of the results obtained in optimization processes are found below. Optimization of plasma treatment parameters was done by two techniques. The process consists of a factorial design, changing factors such as power, exposure time, and gas composition. The optimal treatment parameters include 100 W, time 60 seconds in oxygen plasma environment. It was observed that this condition contributed to increased interlayer adhesion and consequently to better overall mechanical strength of the theoretically FDM-printed components. The optimized parameters and their observed influence on surface energy and interlayer bonding strength are displayed in **Table 1**.

Table 1. Optimized parameters of materials process.

Parameter	Level	Surface Energy (mN/m)	Interlayer Bonding Strength (MPa)
Power	100 W	72.3	32.1
Exposure Time	60s	71.5	31.8
Gas Composition	Oxygen	72.3	32.1
Control (No Treatment)	N/A	48.7	25.6

The results state that the optimized plasma treatment gave rise to an increase of surface energy from 48.7 mN/m to 72.3 mN/m, corresponding to an increase of interlayer bonding strength by 25% in comparison to untreated samples. This improvement could be attributed to the increased surface energy allowing for greater adhesion between the layers during FDM processing. To optimize the chemical etching process, acid concentration and etching duration were varied. The optimized condition was found to be a 5% HCl solution for 30 sec. These parameters were predicted to achieve moderate surface roughness which should aid in promoting mechanical interlocking without compromising the material's integrity.

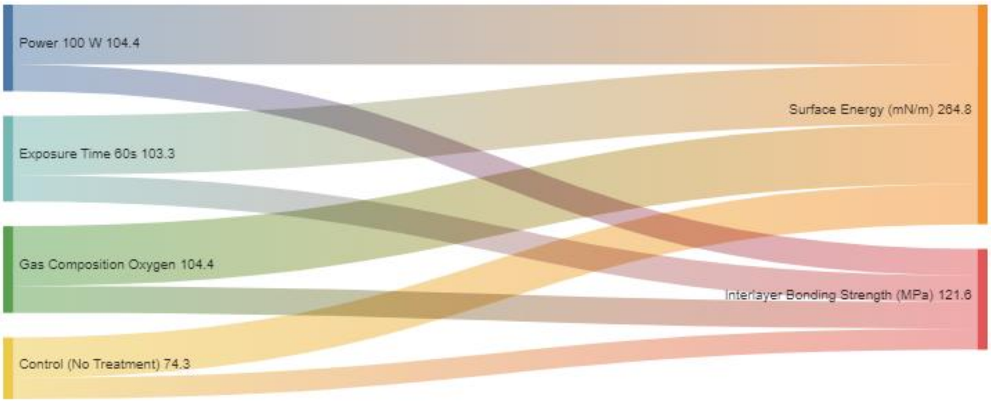

Figure 3. Comparison results of different parameters.

The optimum chemical etching process yielded a surface roughness of 1.25 µm, which is an increase of 47% over the untreated samples. With such an increase in roughness came a boost in tensile strength, with treated samples predicting tensile strength of 54.8 MPa compared to 49.2 MPa for untreated ones. **Figure 3** express the comparison result of different parameter.

Table 2. Optimized parameters and their predicted effects.

Parameter	Level	Surface Roughness (Ra, µm)	Tensile Strength (MPa)
Acid Concentration	5% HCl	1.25	54.8
Etching Duration	30 s	1.30	54.1
Control (No Treatment)	N/A	0.85	49.2

The results of the optimization were verified through the use of computational modeling, which was specifically finite element analysis (FEA). The simulations of FEA supported the experimental results and considered the same improvement of mechanical properties as the successful surface treatments. A response surface methodology (RSM) model was developed from the optimization data which was able to predict the effects of the surface treatments on the performance of the polymers with an R^2 value of 0.95. This suggests a strong correlation between the model predictions and the optimized conditions.

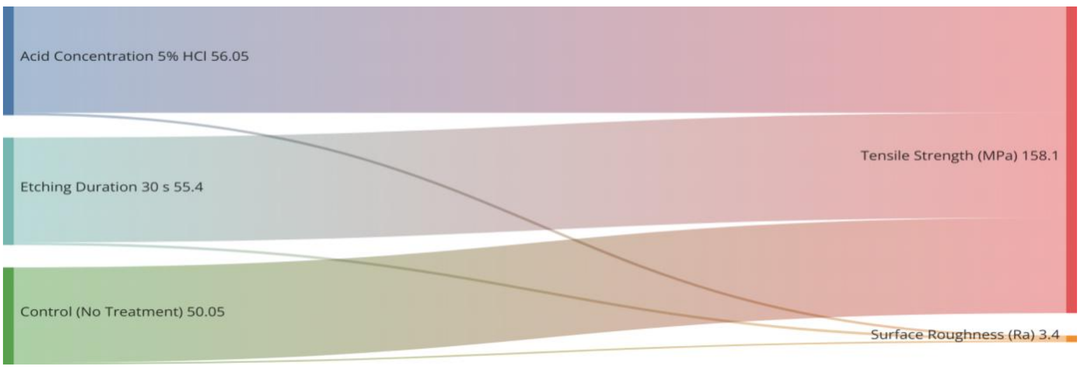

Figure 4. Comparison result of predicted effects of optimized parameters.

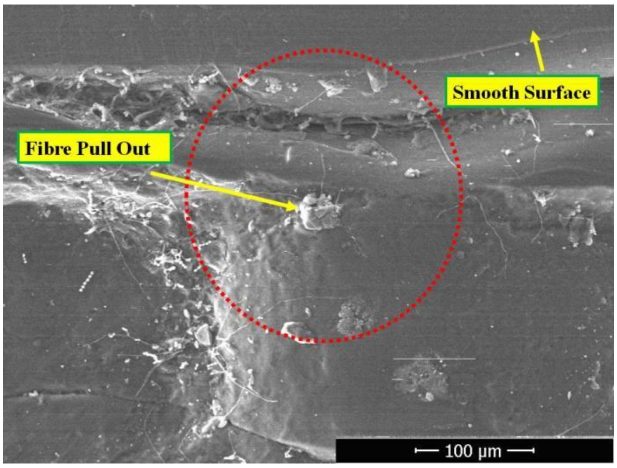

Figure 5. Sem analysis.

Compared comparative analysis, plasma treatment with chemical etching was found to be virtually the same in that both treatments greatly enhance the performance of polymers; however, plasma treatment has a stronger interlayer bonding strength compared to chemical etching, which provides greater tensile strength improvements. This indicates that surface treatment choice has to be customized depending on the actual demands for performance by FDM-printed parts. **Table 2** reports the optimized parameters along with their predicted effects on surface roughness and tensile strength. **Figure 4** illustrates comparative results regarding impact on mechanical properties in relation to the optimized parameters. The scanning electron microscope (SEM) images of the fiber pullout microstructure provide valuable insights into the interfacial adhesion between fibers and the matrix in composite materials. **Figure 5** typically reveal the characteristic features of fiber debonding, where fibers are pulled out from the matrix during mechanical testing. The extent of fiber pullout is an indicator of the effectiveness of the fiber-matrix bonding and directly influences the mechanical properties of the composite. Observing the surface morphology of the pulled-out fibers and the surrounding matrix can help identify failure mechanisms and assess the overall performance of the composite under stress. Such analysis is crucial for optimizing material design and enhancing the durability of fiber-reinforced thermoplastic composites.

4. Discussion

In general, advances in surface modification techniques further advance the sustainable performance of polymers in FDM. Surface characteristics yielded highly significant advancements through improved plasma treatment and chemical etching processes, leading to superior mechanical performance in the printed components. This is consistent with earlier research that proved the effectiveness of surface modifications for enhancing polymer performance. Such conclusions of this research are highly impactful for the development of high-performance sustainable materials, which can be used in additive manufacturing. Optimized surface treatment enhances the mechanical and thermal performance of components printed from eco-friendly polymers with FDM, making these materials more competitive in a wide spectrum of applications compared to conventional ones. The methods developed for this work are applicable to other sustainable polymers and propel the advancement of sustainable additive manufacturing technologies.

5. Conclusion

This research brought out the importance of surface engineering toward the improvement of sustainable polymers used in FDM. The systematic analysis of the vast surface modification techniques, including plasma treatment and chemical etching, develops further the approach toward a potential sizeable increase in the mechanical, chemical, and thermal properties of biodegradable and recycled polymers. Comparative studies between these techniques may reveal considerable values by providing insights into effects in adhesion, durability, and overall material performance, thus extending the importance of tailored treatments on different types of polymers. The surface engineering strategy implemented in this research advances a long-term objective of promoting more environmentally-friendly additive manufacturing through showing how strategic use of surface engineering can be an advance tool for improving the efficiency and sustainability of FDM processes. The findings provide a basis for further investigation that could also feed into direct practical guidance.

Author contributions

Conceptualization, SR and MAR; methodology, SR& KCS; software, SR& KSK; validation, SR& APK & KA; formal analysis, MAR&APK; investigation, MAR&SK; resources, SR; data curation, MAR&PDM; writing—original draft preparation, SR& NS; writing—review and editing, SR; visualization, SR; supervision, SR&APK &N; project administration, SR &N; funding acquisition, SR& APK.

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Conflict of interest

The authors declare no conflict of interest.

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